

**Title: METALLOCENE CATALYST COMPOUNDS FOR PRODUCING
POLYOLEFINS**

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CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of and priority to both US Provisional Application No. 63/590,019 filed October 13, 2023, and US Provisional Application No. 63/604,959 filed December 1, 2023, the disclosures of which are incorporated herein by
10 reference.

FIELD OF THE INVENTION

[0002] The present disclosure relates to *ansa*-metallocene catalyst compounds, catalyst systems comprising such compounds, and uses thereof.

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BACKGROUND OF THE INVENTION

[0003] Polyolefins are widely used commercially because of their robust physical properties. For example, various types of polyethylenes, including high density, low density, and linear low density polyethylenes, are some of the most commercially useful. Polyolefins are typically prepared with a catalyst that polymerizes olefin monomers.

20 [0004] Catalysts for olefin polymerization typically have transition metals. For example, some catalysts are *ansa*-metallocenes (also referred to as “bridged” metallocenes), which can be activated by alumoxane or an activator containing a non-coordinating anion. Using these catalysts and catalyst systems, polymerization conditions can be adjusted to provide polyolefins having desired properties. There is interest in finding new metallocene catalysts and catalyst
25 systems that provide polymers having specific properties, including tunable molecular weights, high activity, and good processability (*e.g.*, provided by comonomer incorporation and melting point).

[0005] In particular, polypropylene (PP) is a desired polymer that has a large variety of uses. Processes for the manufacture of polypropylene have evolved with improvement in
30 catalyst technology, from complex slurry processes using an inert hydrocarbon diluent, to simpler bulk processes using liquid propylene diluent, to simplified gas phase processes.

[0006] However, due to their high activity, metallocene catalysts can be difficult to utilize directly in conventional polymerization processes, and particularly in gas phase processes where the catalyst system will be dispersed in a hydrocarbon or in monomer and metered into
35 the reactor through feed lines. For example, supported metallocene catalysts are optimally

active when preactivated, *e.g.*, combined with an activator prior to being introduced into the reactor. Dispersing such catalysts in the olefin monomer stream for direct feed to the reactor system can result in polymer formation which can cause severe plugging of the feedlines. Moreover, polymerization proceeds before the catalyst system is dispersed fully and uniformly through the polymer bed in the reactor, resulting in highly active hot spots that promote the formation of lumps and plating out of polymer/catalyst. Accordingly, the reactor can rapidly become fouled, reducing catalyst activities and requiring frequent shutdowns to clean the reactor.

[0007] Inert gases, hydrocarbons and the like have been employed as diluents and as carriers for use with Ziegler-Natta catalysts. These methods have had some success when employed with soluble metallocene catalysts in solution and bulk polymerization systems. In gas phase processes employing continuously stirred tank reactor and fluid bed technologies, the use of such diluents and carriers for feeding supported metallocene catalyst systems to the reactor with the olefin stream has generally not been successful. Although the problem of plugging may be avoided by dispersing the supported catalyst in an inert hydrocarbon such as propane and separately metering the mixture to the reactor, it is difficult to adequately disperse the catalyst through the reactor polymer bed rapidly enough to avoid forming lumps and strings.

[0008] Temporarily reducing the activity of metallocene catalysts has been attempted. For example, adding a dialkylborane or dialkylaluminum to the reactor during a polymerization to temporarily retard the activity of metallocene catalysts has been disclosed as a method for process control. However, catalyst activity is only partially retarded by such treatment. Catalysts directly treated with a dialkylborane or dialkylaluminum retain sufficient activity to initiate polymerization when dispersed in the monomer feed stream. Moreover, the recovery period is very brief, too brief to allow the catalyst system to be adequately dispersed in a stirred reactor gas phase reactor bed before the catalyst recovers and polymerization proceeds.

[0009] Metallocene catalysts can be deactivated by variety of poisons including polar and oxygenated small molecules as well as Lewis and Bronsted acid and bases. Reactivating a Lewis acid-treated catalyst after it is dispersed in the reactor bed requires adding excess MAO, which is difficult to disperse because of its low volatility. Separately adding an alkali metal alkyl or alkaline earth metal alkyl and a fully active, supported metallocene catalyst to a reactor before contacting with monomer has been disclosed to be useful for avoiding lumps and wall formations in the suspension polymerization of ethylene polymers and copolymers. The use of Lewis bases to retard or terminate a metallocene catalyzed polymerization for process control is also disclosed in the art. Restarting the polymerization, accomplished by adding excess

MAO, may require adding as much MAO as was employed in the initial preparation of the catalyst. Due to poor volatility, dispersing the MAO uniformly through the reactor bed is difficult, and the polymerization activity after restart may be substantially reduced. Moreover, many Lewis base compounds are irreversible catalyst poisons. In a continuous process such poisons will accumulate in the reactor over time, requiring that the process be stopped while the reactor is cleaned.

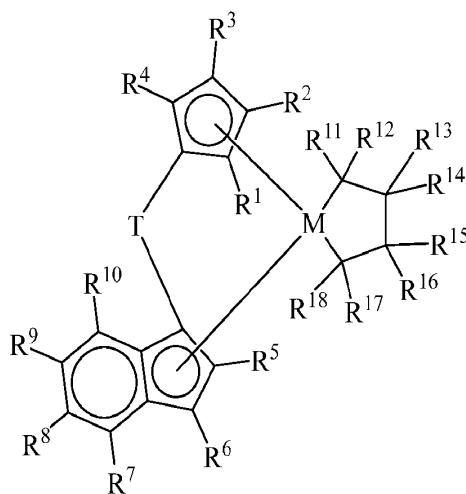
[0010] There is a need for new metallocene catalyst compounds having delayed activation while maintaining a high activity profile and not requiring catalyst reactivation while being able to provide polymers of substantial functional equivalence.

[0011] References for citing in an Information Disclosure Statement (37 C.F.R. 1.97(h)); US 7,041,757; US 7,479,529; US 2015/099856; and WO2021/1242801 A1.

SUMMARY OF THE INVENTION

[0012] The present disclosure relates to *ansa*-metallocene catalyst compounds, catalyst systems comprising such compounds, and uses thereof.

[0013] In some embodiments, a compound is represented by Formula (I):



(I)

wherein:

M is a group 3 metal, group 4 metal, or group 5 metal;

each of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, and R¹⁰ is independently hydrogen, substituted or unsubstituted hydrocarbyl, a substituted or unsubstituted heteroatom, or a substituted or unsubstituted heteroatom-containing group, or one or more of R¹ and R², R² and R³, R³ and R⁴, R⁵ and R⁶, R⁷ and R⁸, R⁸ and R⁹, or R⁹ and R¹⁰ are joined to form a substituted or unsubstituted completely saturated ring or a substituted or unsubstituted aromatic ring;

T represents the formula R^a_2J or $(R^a)_4J_2$ wherein each J is independently C, Si, or Ge, and each R^a is independently hydrogen, halide, a substituted or unsubstituted C_1 to C_{40} hydrocarbyl, or two R^a can form a substituted or unsubstituted completely saturated ring, or a substituted or unsubstituted partially saturated ring; and

5 each of R^{11} , R^{13} , R^{15} , and R^{17} is independently hydrogen or substituted or unsubstituted hydrocarbyl,

wherein each of R^{12} , R^{14} , R^{16} , and R^{18} , if present, is independently hydrogen or substituted or unsubstituted hydrocarbyl, but the 5-membered metallocyclic ring of Formula (I) can optionally have one or two carbon-carbon double bonds such that two or more of R^{12} , R^{14} ,
10 R^{16} , or R^{18} are not present.

[0014] In yet another aspect, embodiments of the present disclosure provide a catalyst system comprising an activator and a catalyst compound of the present disclosure.

[0015] In still another aspect, embodiments of the present disclosure provide a polymerization process comprising a) contacting one or more olefin monomers with a catalyst
15 system comprising: i) an activator and ii) a catalyst compound of the present disclosure.

BREIF DESCRIPTION OF DRAWINGS

[0016] FIG. 1 is a graph illustrating pressure uptake kinetics (psi/s) for propylene polymerization at 70°C, according to some embodiments.

[0017] FIG. 2 is a graph illustrating pressure uptake kinetics (psi/s) for propylene
20 polymerization at 100°C. Data is shown as running average of 3 replicates for clarity, according to some embodiments.

[0018] FIG. 3 is a graph illustrating initial rates after activation induction period for catalysts C1-dichloride, C1-dimethyl and I1, according to some embodiments.

DETAILED DESCRIPTION

25 [0019] The present disclosure relates to metallocene catalyst compounds (such as *ansa*-metallocene catalyst compounds), to catalyst systems comprising such compounds, and to uses thereof. Metallocene catalyst compounds of the present disclosure have 5-membered metallocycle rings (incorporating the catalytic metal as part of the 5-membered metallocycle). Metallocene catalysts of the present disclosure can provide delayed catalyst activation while
30 maintaining a high activity profile and not requiring catalyst reactivation while being able to provide polymers of substantial functional equivalence. In addition to delayed activation kinetics, such catalysts (and catalyst systems thereof) have excellent solubility in a variety of solvents (e.g., alkane solvents), rendering them applicable for toluene free processes both in solution or as supported catalyst systems (slurry or gas phase). The combination of delayed

activation kinetics and excellent solubility reduce or eliminate plugging of feed lines and/or reactor components.

[0020] Without being bound by theory, it is believed that deactivation occurs by 5-membered metallocycle as part of the metallocene complex which provides a bulky group that blocks (at least temporarily) the subsequent insertion of olefin monomer, which is necessary for olefin polymerization to take place. For example, treating a metallocene complex with isoprenyl ligand to form an isoprenyl-functionalized metallocene complex provides delayed activation of the isoprenyl-functionalized metallocene complex that inserts olefin monomer such as propylene at a very slow rate under the process conditions followed by a rapid increase in catalyst activity. As propylene monomer becomes inserted into the complex, the blocking group is displaced from the active metal site, forming an active polymerization catalyst species. The rate that the catalyst becomes activated may be influenced by several factors including monomer concentration and reaction temperature. If the rate that catalyst activation process occurs is impracticably slow, an activator, for example, a compound capable of reducing or alkylating the blocking group such as, for example, hydrogen, an aluminum alkyl or the like, may be utilized to remove the blocking group and regenerate the active metallocene catalyst complex. Hydrogen appears to be particularly effective in this regard, removing the blocking group by hydrogenolysis and forming an inert hydrocarbon species as a byproduct.

[0021] The following abbreviations may be used herein: Me is methyl, Ph is phenyl, PDI is polydispersity index, MAO is methylalumoxane, SMAO is supported methylalumoxane, NMR is nuclear magnetic resonance, ppm is part per million, THF is tetrahydrofuran.

[0022] As used herein, "reactivation" refers to reactivating a catalyst by scavenging a catalyst poison that would otherwise deactivate or has deactivated the catalyst compound. For example, if the catalyst poison is a Lewis base, then adding additional Lewis acid scavenger can be used to reactivate the catalyst compound.

[0023] As used herein, olefin polymerization catalyst(s) refer to any catalyst, such as an organometallic complex or compound that is capable of coordination polymerization addition where successive monomers are added in a monomer chain at the organometallic active center.

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

[0025] 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, when a polymer or copolymer is referred to as including 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. "Different" is used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers. An "ethylene polymer" or "ethylene copolymer" (both of which are examples of a "polyethylene") is a polymer or copolymer including at least 50 mol% ethylene derived units. A "propylene polymer" or "propylene copolymer" (both of which are examples of a "polypropylene") is a polymer or copolymer including at least 50 mol% propylene derived units, and so on. An "ethylene polymer" or "ethylene copolymer" is a polymer or copolymer including at least 50 mol% ethylene derived units, a "propylene polymer" or "propylene copolymer" is a polymer or copolymer including at least 50 mol% propylene derived units, and so on.

[0026] As used herein, "polyethylene" can include "ethylene homopolymer", "ethylene copolymer", or combinations thereof. "Polypropylene" can include "propylene homopolymer", "propylene copolymer", or combinations thereof.

[0027] The term "alpha-olefin" refers to an olefin having a terminal carbon-to-carbon double bond in the structure thereof $((R''R''')-C=CH_2$, where R'' and R''' can be independently hydrogen or any hydrocarbyl group; such as R'' is hydrogen and R''' is an alkyl group). A "linear alpha-olefin" is an alpha-olefin defined in this paragraph wherein R'' is hydrogen, and R''' is hydrogen or a linear alkyl group.

[0028] For the purposes of the present disclosure, ethylene shall be considered an alpha-olefin.

[0029] As used herein, and unless otherwise specified, the term " C_n " means hydrocarbon(s) having n carbon atom(s) per molecule, wherein n is a positive integer. 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 including carbon atoms at a total number thereof from m to y. Thus, a C_1-C_{50} alkyl group refers to an alkyl group including carbon atoms at a total number thereof of

about 1 to about 50.

[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 saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring or chain.

[0031] The terms "hydrocarbyl radical," "hydrocarbyl group," or "hydrocarbyl" may be used interchangeably and are defined to mean a group including hydrogen and carbon atoms only. For example, a hydrocarbyl can be a C₁-C₁₀₀ radical that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such radicals may 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 aryl groups, such as phenyl, benzyl, naphthyl.

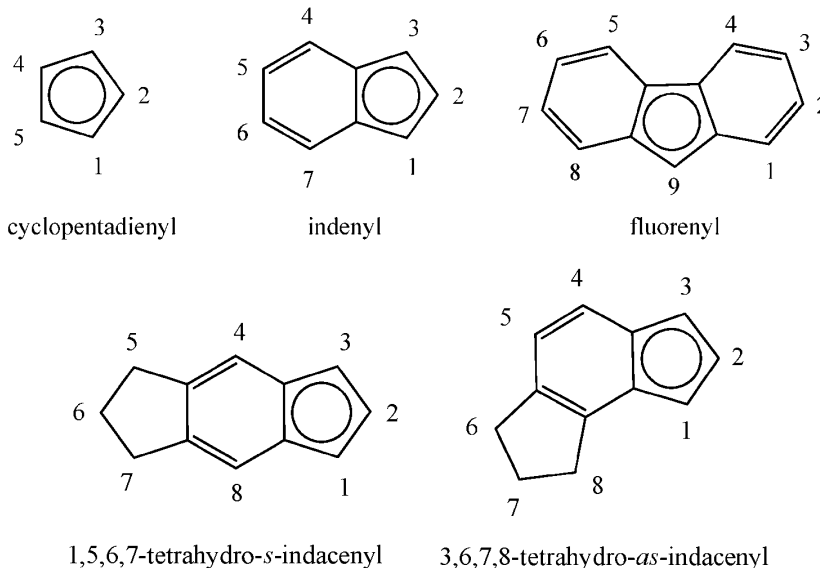
[0032] The terms "alkoxy" and "alkoxide" mean an alkyl or aryl group bound to an oxygen atom, such as an alkyl ether or aryl ether group/radical connected to an oxygen atom and can include those where the alkyl/aryl group is a C₁ to C₁₀ hydrocarbyl. The alkyl group may be straight chain, branched, or cyclic. The alkyl group may be saturated or unsaturated. Examples of suitable alkoxy radicals can include methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, or phenoxy.

[0033] The term "alkenyl" means a straight-chain, branched-chain, or cyclic hydrocarbon radical having one or more double bonds. These alkenyl radicals may be optionally substituted. Examples of suitable alkenyl radicals can include ethenyl, propenyl, allyl, 1,4-butadienyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cycloctenyl, including their substituted analogues.

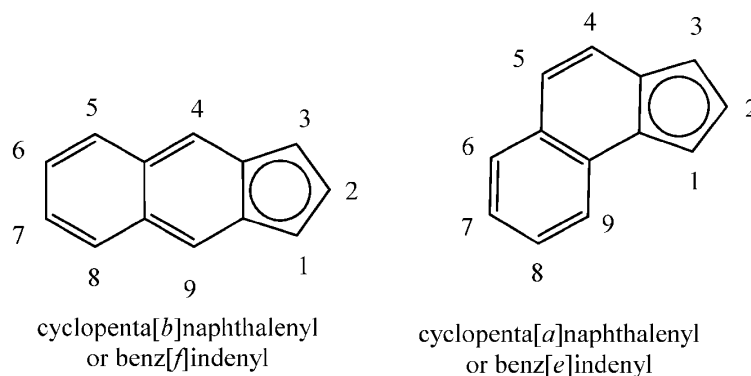
[0034] The terms "alkyl radical," "alkyl group," and "alkyl" are used interchangeably throughout this disclosure. For purposes of this disclosure, "alkyl radical" is defined to be C₁-C₁₀₀ alkyls that may be linear, branched, or cyclic. Examples of such radicals can include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, including their substituted analogues. Some examples of alkyl may include 1-methylethyl, 1-methylpropyl,

1-methylbutyl, 1-ethylbutyl, 1,3-dimethylbutyl, 1-methyl-1-ethylbutyl, 1,1-diethylbutyl, 1-propylpentyl, 1-phenylethyl, i-propyl, 2-butyl, sec-pentyl, sec-hexyl, and the like.

- [0035] The term "aryl" or "aryl group" means an aromatic ring and the substituted variants thereof, such as phenyl, 2-methyl-phenyl, xylyl, 4-bromo-xylyl. Likewise, "heteroaryl" means an aryl group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, such as N, O, or S. As used herein, the term "aromatic" also refers to pseudoaromatic heterocycles which are heterocyclic substituents that have similar properties and structures (nearly planar) to aromatic heterocyclic ligands, but are not by definition aromatic; likewise, the term aromatic also refers to substituted aromatics.
- 10 [0036] For nomenclature purposes, the following numbering schemes are used for cyclopentadienyl, indenyl, fluorenyl, cyclopenta[*b*]naphthalenyl (also termed benz[*e*]indenyl), cyclopenta[*a*]naphthalenyl (also termed benz[*f*]indenyl), tetrahydro-*s*-indacenyl and tetrahydro-*as*-indacenyl. The numbering schemes indicate the positions along the ring(s) to which a moiety can be connected. As an example, a moiety such as a phenanthridinyl moiety, can be coupled to the 4-position of an indenyl or a 1,5,6,7-tetrahydro-*s*-indacenyl. It should be noted that indenyl can be considered a cyclopentadienyl with a fused benzene ring. Analogously, fluorenyl can be considered a cyclopentadienyl with two fused benzene rings fused to the cyclopentadienyl ring. Each structure below is drawn and named as an anion.



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[0037] Partially hydrogenated polycyclic arenyl ligands retain the numbering scheme of the parent polycyclic arenyl ligand, namely the numbering schemes defined for indenyl, fluorenyl, cyclopenta[b]naphthalenyl, cyclopenta[a]naphthalenyl tetrahydro-s-indenyl, and tetrahydro-as-indacenyl ligands.

[0038] The term “arenyl” ligand is used herein to mean an unsaturated cyclic hydrocarbyl ligand that can consist of one ring, or two or more fused or catenated rings.

[0039] As used herein, the term “monocyclic arenyl ligand” is used herein to mean a substituted or unsubstituted monoanionic C₅ to C₁₀₀ hydrocarbyl ligand that contains an aromatic five-membered single hydrocarbyl ring structure (also referred to as a cyclopentadienyl ring).

[0040] As used herein, the term “polycyclic arenyl ligand” is used herein to mean a substituted or unsubstituted monoanionic C₉ to C₁₀₃ hydrocarbyl ligand that contains an aromatic five-membered hydrocarbyl ring (also referred to as a cyclopentadienyl ring) that is fused to one or two partially unsaturated, or aromatic hydrocarbyl ring structures which may be fused to additional saturated, partially unsaturated, or aromatic hydrocarbyl rings. Polycyclic arenyl ligands include, but are not limited to indenyl, fluorenyl, cyclopenta[b]naphthalenyl, cyclopenta[a]naphthalenyl tetrahydro-s-indenyl, and tetrahydro-as-indacenyl ligands.

[0041] Where isomers of a named alkyl, alkenyl, alkoxide, or aryl group exist (*e.g.*, n-butyl, iso-butyl, sec-butyl, and tert-butyl), reference to an alkyl, alkenyl, alkoxide, or aryl group without specifying a particular isomer (*e.g.*, butyl) expressly discloses all isomers (*e.g.*, n-butyl, iso-butyl, sec-butyl, and tert-butyl).

[0042] The term “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 five ring atoms.

[0043] A heterocyclic ring is a ring having a heteroatom in the ring structure as opposed to a heteroatom substituted ring where a hydrogen on a ring atom is replaced with a heteroatom.

For example, tetrahydrofuran is a heterocyclic ring and 4-N,N-dimethylamino-phenyl is a heteroatom-substituted ring. Other examples of heterocycles may include pyridine, imidazole, and thiazole.

[0044] As used herein, M_n is number average molecular weight, M_w is weight average molecular weight, and M_z is z average molecular weight, wt% is weight percent, and mol% is mole percent. Molecular weight distribution (MWD), also referred to as polydispersity (PDI), is defined to be M_w divided by M_n . Unless otherwise noted, all molecular weight units (*e.g.*, M_w , M_n , M_z) are g/mol.

[0045] The terms “catalyst compound”, “catalyst complex”, “transition metal complex”, “transition metal compound”, “precatalyst compound”, and “precatalyst complex” are used interchangeably.

[0046] A “catalyst system” is a combination of at least one catalyst compound, at least one 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 represented by formulae herein are intended to embrace both neutral and ionic forms of the catalyst compounds and activators.

[0047] An “anionic ligand” is a negatively charged ligand which donates one or more pairs of electrons to a metal ion. A “Lewis base” or “neutral donor ligand” is a neutrally charged ligand which donates one or more pairs of electrons to a metal ion. Examples of Lewis bases include ethylether, trimethylamine, pyridine, tetrahydrofuran, dimethylsulfide, and triphenylphosphine. The term “heterocyclic Lewis base” refers to Lewis bases that are also heterocycles. Examples of heterocyclic Lewis bases include pyridine, imidazole, thiazole, and furan.

[0048] A scavenger is a compound that can be added to facilitate polymerization by scavenging impurities. Some scavengers may also act as activators and may be referred to as coactivators. A coactivator, that is not a scavenger, may also be used in conjunction with an

activator in order to form an active catalyst. In at least one embodiment, a coactivator can be pre-mixed with the transition metal compound to form an alkylated transition metal compound.

[0049] The term "continuous" means a system that operates without interruption or cessation for an extended period of time. For example, a continuous process to produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually withdrawn.

[0050] A solution polymerization means 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 can be homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Suitable systems may be not turbid as described in J. Vladimir Oliveira, *et al.* (2000), *Ind. Eng. Chem. Res.*, vol. 29, p. 4627.

[0051] A bulk polymerization means a polymerization process in which the monomers and or comonomers being polymerized are used as a solvent or diluent using little or no inert solvent as a solvent or diluent. A small fraction of inert solvent might be used as a carrier for catalyst and scavenger. A bulk polymerization system contains less than 25 wt% of inert solvent or diluent, such as less than 10 wt%, such as less than 1 wt%, such as 0 wt%.

[0052] The term "single catalyst compound" refers to a catalyst compound corresponding to a single structural formula, although such a catalyst compound may comprise and be used as a mixture of isomers, *e.g.*, stereoisomers.

[0053] A catalyst system that utilizes a single catalyst compound means a catalyst system that is prepared using only a single catalyst compound in the preparation of the catalyst system. Thus, such a catalyst system is distinguished from, for example, "dual" catalyst systems, which are prepared using two catalyst compounds having different structural formulas, *e.g.*, the connectivity between the atoms, the number of atoms, and/or the type of atoms in the two catalyst compounds is different. Thus, one catalyst compound is considered different from another if it differs by at least one atom, either by number, type, or connection. For example, bisindenyl zirconium dichloride is different from (indenyl)(2-methylindenyl) zirconium dichloride which is different from (indenyl)(2-methylindenyl) hafnium dichloride. Catalyst compounds that differ only in that they are stereoisomers of each other are not considered to be different catalyst compounds. For example, *rac*-dimethylsilylbis(2-methyl 4-phenyl)hafnium dimethyl and *meso*-dimethylsilylbis(2-methyl 4-phenyl)hafnium dimethyl are considered to be not different.

[0054] The terms "cocatalyst" and "activator" are used herein interchangeably and are

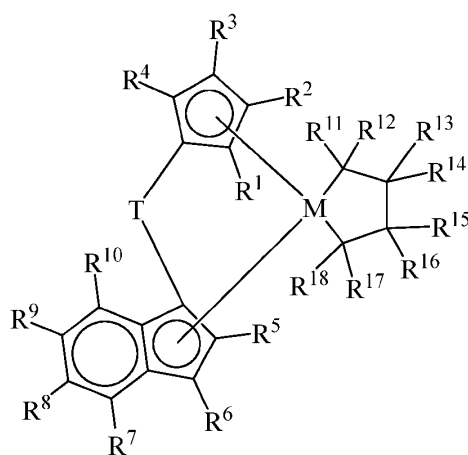
defined to be any compound which can activate any one of the catalyst compounds described above by converting the neutral catalyst compound to a catalytically active catalyst compound cation.

- [0055] Noncoordinating anion (NCA) means an anion either that does not coordinate to the catalyst metal cation or that does coordinate to the metal cation, but only weakly. The term NCA is also defined to include multicomponent NCA-containing activators, such as N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, that contain an acidic cationic group and the non-coordinating anion. The term NCA is also defined to include neutral Lewis acids, such as tris(pentafluorophenyl)boron, that can react with a catalyst to form an activated species by abstraction of an anionic group. An NCA coordinates weakly enough that a neutral Lewis base, such as an olefinically or acetylenically unsaturated monomer can displace it from the catalyst center. Any metal or metalloid that can form a compatible, weakly coordinating complex may be used or contained in the noncoordinating anion. Suitable metals include, but are not limited to, aluminum, gold, and platinum. Suitable metalloids include, but are not limited to, boron, aluminum, phosphorus, and silicon. The term non-coordinating anion activator includes neutral activators, ionic activators, and Lewis acid activators. The terms “non-coordinating anion activator” and “ionizing activator” are used interchangeably herein.

[0056] The terms “process” and “method” are used interchangeably.

Catalyst Compounds

- [0057] This disclosure relates to metallocene catalyst compounds represented by Formula (I):



(I)

wherein:

M is a group 3 metal (*e.g.*, scandium or yttrium), group 4 metal (*e.g.*, titanium, zirconium, or hafnium), or group 5 metal (*e.g.*, vanadium, niobium, or tantalum);

each of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is independently hydrogen, substituted or unsubstituted hydrocarbyl, a substituted or unsubstituted heteroatom, or a substituted or unsubstituted heteroatom-containing group, or one or more of R^1 and R^2 , R^2 and R^3 , R^3 and R^4 , R^5 and R^6 , R^7 and R^8 , R^8 and R^9 , and R^9 and R^{10} are joined to form a substituted or unsubstituted completely saturated ring or a substituted or unsubstituted aromatic ring (fused to the indenyl ring shown in Formula (I));

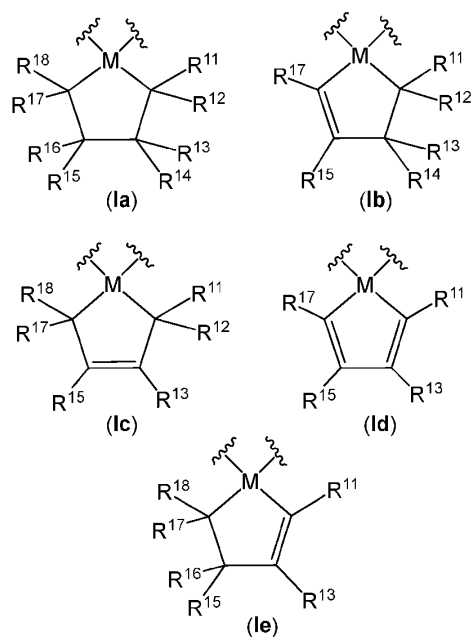
T represents the formula R^a_2J or $(R^a)_4J_2$ wherein each J is independently C, Si, or Ge, and each R^a is independently hydrogen, halide, a substituted or unsubstituted C_1 to C_{40} hydrocarbyl, or two R^a can form a substituted or unsubstituted completely saturated ring or a substituted or unsubstituted partially saturated ring; and

each of R^{11} , R^{13} , R^{15} , and R^{17} is independently hydrogen or substituted or unsubstituted hydrocarbyl,

wherein each of R^{12} , R^{14} , R^{16} , and R^{18} , if present, is independently hydrogen or substituted or unsubstituted hydrocarbyl, but the 5-membered metallocyclic ring of Formula (I) can optionally have one or two carbon-carbon double bonds such that two or more of R^{12} , R^{14} , R^{16} , or R^{18} are not present.

[0058] In some embodiments, each of R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , and R^{18} is independently hydrogen or C_1 - C_{10} alkyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl). In some embodiments, each of R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , and R^{18} is hydrogen. In some embodiments, each of R^{11} , R^{12} , R^{15} , R^{16} , R^{17} , and R^{18} is hydrogen and at least one of R^{13} or R^{14} is C_1 - C_{10} alkyl and at least one of R^{13} or R^{14} is hydrogen. In some embodiments, each of R^{11} , R^{12} , R^{13} , R^{14} , R^{17} , and R^{18} is hydrogen and at least one of R^{15} or R^{16} is C_1 - C_{10} alkyl and at least one of R^{15} or R^{16} is hydrogen.

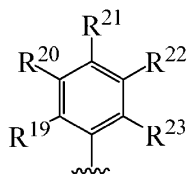
[0059] In some embodiments, the 5-membered metallocycle ring of Formula (I) has one of the following structures:



where each of M, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, and R¹⁸ is as described above.

[0060] In some embodiments, R⁷ is a substituted or unsubstituted aryl group or a substituted or unsubstituted heteroaryl group. R⁷ can be selected from the group substituted or unsubstituted phenyl and substituted or unsubstituted phenyl.

[0061] In some embodiments, R⁷ is an aryl group represented by the formula:



wherein each of R¹⁹, R²⁰, R²¹, R²², and R²³ is independently hydrogen, hydrocarbyl, a heteroatom, or heteroatom-containing group, or one or more of R¹⁹ and R²⁰, R²⁰ and R²¹, R²¹ and R²², or R²² and R²³ are joined to form a completely saturated, partially saturated, or aromatic ring. In some embodiments, each of R¹⁹, R²⁰, R²¹, R²², and R²³ is independently hydrogen or C₁-C₁₀ alkyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl). In some embodiments, each of R¹¹, R¹², R¹³, R¹⁴, and R¹⁵ is hydrogen.

[0062] In some embodiments, R⁷ is selected from phenyl, 1-naphthyl, 2-naphthyl, 9-anthracenyl, 2-biphenyl, 3-biphenyl, 4-biphenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2,4,5-trimethylphenyl,

3,4,5-trimethylphenyl, 2,3,4,5,6-pentamethylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 2,3-diethylphenyl, 2,4-diethylphenyl, 2,5-diethylphenyl, 2,6-diethylphenyl, 3,4-diethylphenyl, 3,5-diethylphenyl, 2-isopropylphenyl, 3-isopropylphenyl, 4-isopropylphenyl, 3,5-di-isopropylphenyl, 2,5-di-isopropylphenyl, 2-tert-butylphenyl, 3-tert-butylphenyl, 4-tert-butylphenyl, 3,5-di-tert-butylphenyl, 3,5-di-tert-butyl-4-methoxyphenyl, 3,5-di-tert-butyl-4-dimethylamino-phenyl, 2,5-di-tert-butylphenyl, ortho-biphenyl, meta-biphenyl, para-biphenyl, 2-trimethylsilylphenyl, 3-trimethylsilylphenyl, 4-trimethylsilylphenyl, 3,5-bis(trimethylsilyl)phenyl, 2-trifluoromethylphenyl, 3-trifluoromethylphenyl, 4-trifluoromethylphenyl, 3,5-bis(trifluoromethyl)phenyl, cyclopropyl, carbazolyl, indolyl, pyrrolyl, or 2-furanyl, 3-furanyl, 5-methyl-2-furanyl, 5-ethyl-2-furanyl, 4,5-dimethyl-2-furanyl, 2-methyl-3-furanyl, 5-methyl-3-furanyl, 2-thiophenyl, 3-thiophenyl, 5-methyl-2-thiophenyl, 2-methyl-3-thiophenyl, or 5-methyl-3-thiophenyl.

[0063] In some embodiments, each of R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} of Formula (I) is independently hydrogen or C_1 - C_{10} alkyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl). In some embodiments, each of R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is hydrogen. In some embodiments, R^5 is C_1 - C_{10} alkyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl).

[0064] In some embodiments, at least one of (1) R^5 and R^6 , (2) R^7 and R^8 , (3) R^8 and R^9 , or (4) R^9 and R^{10} are joined to form an unsubstituted completely saturated C_5 ring, an unsubstituted completely saturated C_6 ring, or an unsubstituted completely saturated C_7 ring. In some embodiments, R^8 and R^9 are joined to form an unsubstituted completely saturated C_5 ring, an unsubstituted completely saturated C_6 ring, or an unsubstituted completely saturated C_7 ring. For example, R^8 and R^9 can be joined to form an unsubstituted completely saturated C_5 ring. In some embodiments, R^9 and R^{10} are joined to form an unsubstituted completely saturated C_5 ring, an unsubstituted completely saturated C_6 ring, or an unsubstituted completely saturated C_7 ring. For example, R^9 and R^{10} can be joined to form an unsubstituted completely saturated C_5 ring.

[0065] In some embodiments, each of R^1 , R^2 , R^3 , and R^4 of Formula (I) is independently hydrogen or C_1 - C_{10} alkyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl). In some embodiments, each of R^1 , R^2 , R^3 , and R^4 is independently methyl, ethyl, or propyl. In some embodiments, each of R^1 , R^2 , R^3 , and R^4 is methyl.

[0066] In some embodiments of Formula (I), T is represented by the formula R^a_2J , $(R^a)_4J_2$, or $(R^a)_6J_3$ where J is C, Si, or Ge, and each R^a is independently hydrogen or C_1 to C_{20} hydrocarbyl. In some embodiments, two R^a can form a cyclic structure including unsubstituted

completely saturated, partially saturated, or aromatic ring. In some embodiments, T is selected from CH_2 , CH_2CH_2 , $\text{C}(\text{CH}_3)_2$, CPh_2 , $\text{Si}(\text{CH}_3)_2$, $\text{Si}(\text{CH}_2\text{CH}_3)_2$, $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$, SiPh_2 , $\text{Si}(\text{CH}_3)\text{Ph}$, $\text{Si}(\text{CH}_2)_3$, $\text{Si}(\text{CH}_2)_4$, or $\text{Si}(\text{CH}_2)_5$. In some embodiments, T is SiMe_2 , $\text{Si}(\text{CH}_2\text{CH}_3)_2$, or $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$.

- 5 [0067] In some embodiments, each of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} (and R^{19} , R^{20} , R^{21} , R^{22} , and R^{23}) of Formula (I) is independently hydrogen, hydrocarbyl, silylcarbyl, alkoxy, halide, or siloxyl.

[0068] In some embodiments of Formula (I), M is a group 4 metal, such as titanium (Ti), zirconium (Zr), or hafnium (Hf). In some embodiments, M is Zr or Hf.

- 10 [0069] In some embodiments of Formula (I), (1) M is Zr or Hf, (2) T is SiMe_2 , $\text{Si}(\text{CH}_2\text{CH}_3)_2$, or $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$, (3) each of R^6 , R^8 , R^9 , and R^{10} is independently hydrogen or substituted or unsubstituted C_1 - C_{10} alkyl, (4) each of R^1 , R^2 , R^3 , and R^4 is independently methyl, ethyl, or propyl, (5) R^5 is C_1 - C_{10} alkyl, (6) R^7 is substituted or unsubstituted aryl or substituted or unsubstituted heteroaryl, and (7) each of R^{11} , R^{12} , R^{15} , R^{16} , R^{17} , and R^{18} is
15 hydrogen and at least one of R^{13} or R^{14} is C_1 - C_{10} alkyl and at least one of R^{13} or R^{14} is hydrogen.

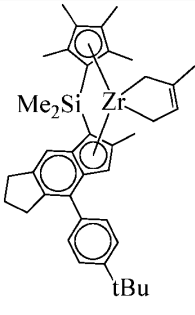
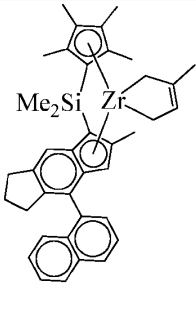
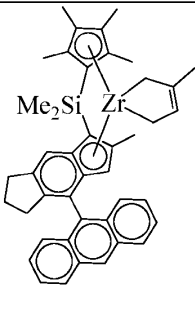
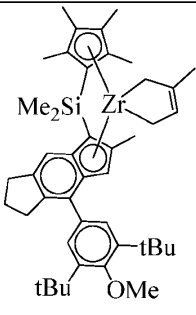
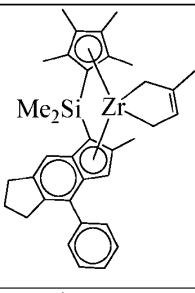
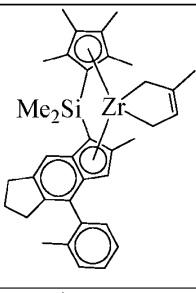
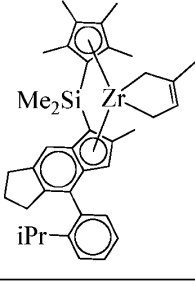
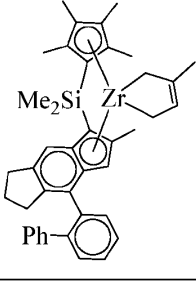
[0070] In some embodiments of Formula (I), (1) M is Zr or Hf, (2) T is SiMe_2 , $\text{Si}(\text{CH}_2\text{CH}_3)_2$, or $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$, (3) each of R^6 , R^8 , R^9 , and R^{10} is independently hydrogen or substituted or unsubstituted C_1 - C_{10} alkyl, (4) each of R^1 , R^2 , R^3 , and R^4 is independently methyl, ethyl, or propyl, (5) R^5 is C_1 - C_{10} alkyl, (6) R^7 is substituted or unsubstituted aryl or substituted or unsubstituted heteroaryl, and (7) each of R^{11} , R^{12} , R^{13} , R^{14} , R^{17} , and R^{18} is
20 hydrogen and at least one of R^{15} or R^{16} is C_1 - C_{10} alkyl and at least one of R^{15} or R^{16} is hydrogen.

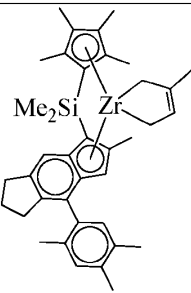
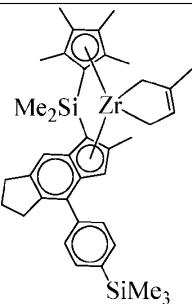
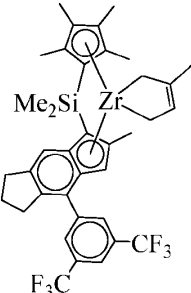
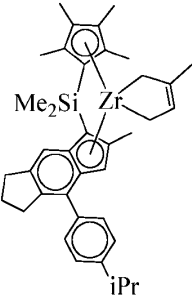
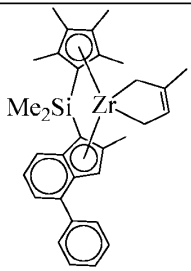
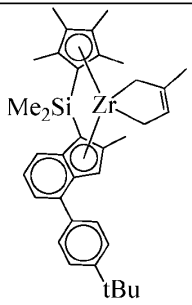
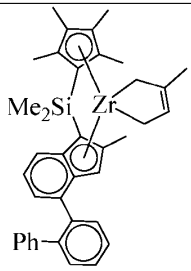
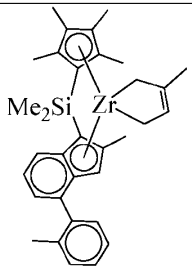
[0071] In some embodiments of Formula (I), (1) M is Zr or Hf, (2) T is SiMe_2 , $\text{Si}(\text{CH}_2\text{CH}_3)_2$, or $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$, (3) each of R^6 and R^{10} is independently hydrogen or substituted or unsubstituted C_1 - C_{10} alkyl, (4) each of R^8 and R^9 are joined to form an
25 unsubstituted completely saturated C_5 ring, (5) each of R^1 , R^2 , R^3 , and R^4 is independently methyl, ethyl, or propyl, (6) R^5 is C_1 - C_{10} alkyl, (7) R^7 is substituted or unsubstituted aryl or substituted or unsubstituted heteroaryl, and (8) each of R^{11} , R^{12} , R^{15} , R^{16} , R^{17} , and R^{18} is hydrogen and at least one of R^{13} or R^{14} is C_1 - C_{10} alkyl and at least one of R^{13} or R^{14} is hydrogen.

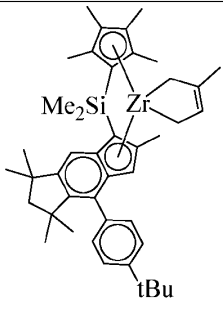
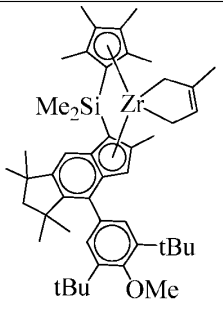
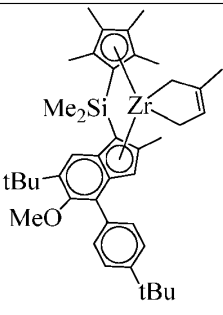
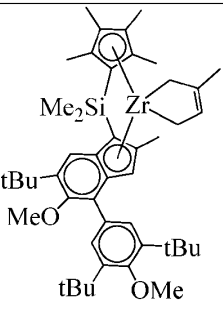
[0072] In some embodiments of Formula (I), (1) M is Zr or Hf, (2) T is SiMe_2 , $\text{Si}(\text{CH}_2\text{CH}_3)_2$, or $\text{Si}(\text{CH}_2\text{CH}_2\text{CH}_3)_2$, (3) each of R^6 and R^{10} is independently hydrogen or substituted or unsubstituted C_1 - C_{10} alkyl, (4) each of R^8 and R^9 are joined to form an
30 unsubstituted completely saturated C_5 ring, (5) each of R^1 , R^2 , R^3 , and R^4 is independently methyl, ethyl, or propyl, (6) R^5 is C_1 - C_{10} alkyl, (7) R^7 is substituted or unsubstituted aryl or substituted or unsubstituted heteroaryl, and (8) each of R^{11} , R^{12} , R^{13} , R^{14} , R^{17} , and R^{18} is

hydrogen and at least one of R^{15} or R^{16} is C_1 - C_{10} alkyl and at least one of R^{15} or R^{16} is hydrogen.

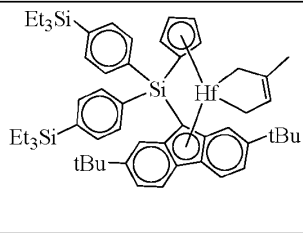
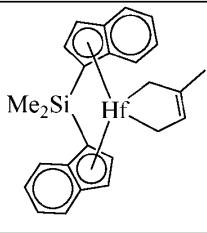
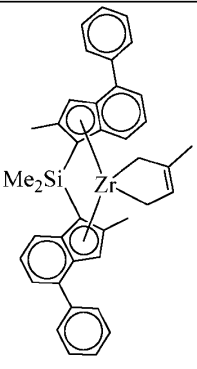
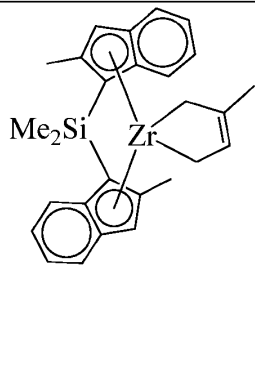
[0073] In some embodiments of Formula (I), the catalyst is selected from:

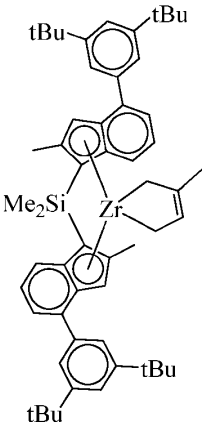
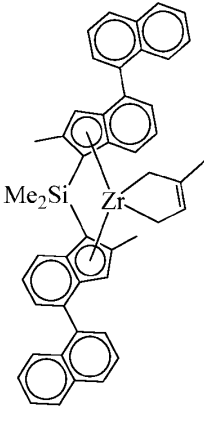
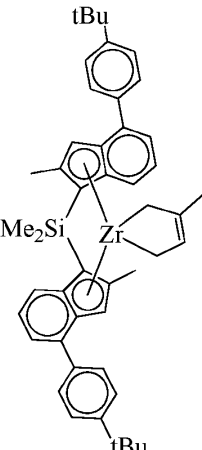
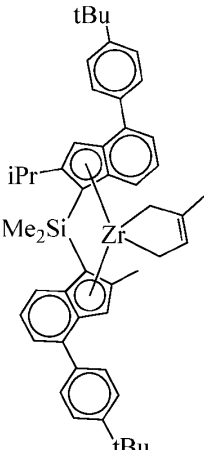
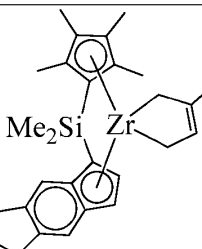
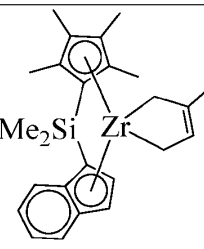
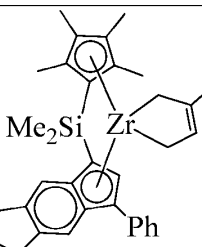
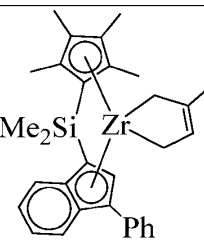
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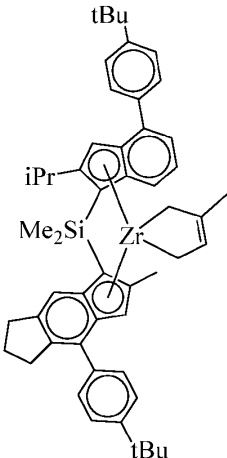
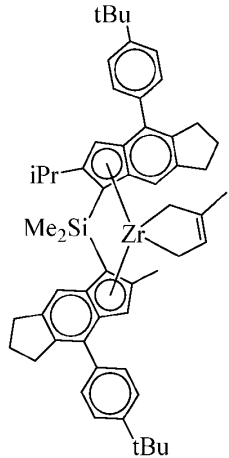
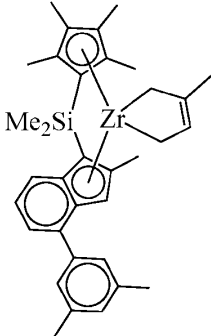
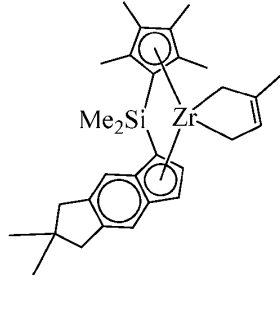
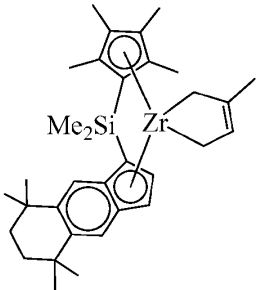
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[0074] In some embodiments of Formula (I), the catalyst is selected from:

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[0075] In one or more embodiments, a mixture of an unsupported catalyst compound in n-hexane, isohexane, cyclohexane, methylcyclohexane, or a combination thereof, forms a clear homogeneous solution at 25°C, such as about 1 mM to about 25 mM mixture of the catalyst compound in n-hexane, isohexane, cyclohexane, methylcyclohexane, or a combination thereof, forms a clear homogeneous solution at 25°C.

[0076] In some embodiments, an unsupported catalyst compound has a solubility of greater than 3 mM (or greater than 5 mM, or greater than 15 mM) to about 20 mM at 25°C (stirred 2

hours) in isohexane.

[0077] In one or more embodiments, a mixture of a supported catalyst compound in n-hexane, isohexane, cyclohexane, methylcyclohexane, or a combination thereof, forms a clear homogeneous solution at 25°C, such as about 1 mM to about 25 mM mixture of the catalyst compound in n-hexane, isohexane, cyclohexane, methylcyclohexane, or a combination thereof, forms a clear homogeneous solution at 25°C.

[0078] In some embodiments, a supported catalyst compound has a solubility of greater than 3 mM (or greater than 5 mM, or greater than 15 mM) to about 20 mM at 25°C (stirred 2 hours) in isohexane.

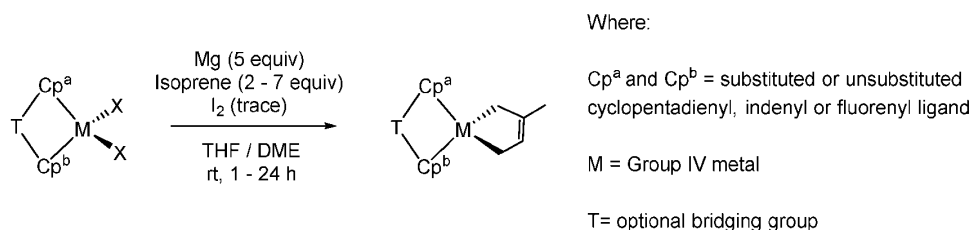
[0079] In at least one embodiment, two or more different catalyst compounds are present in a catalyst system. In at least one embodiment, two or more different catalyst compounds are present in the reaction zone of a reactor where the polymerization process(es) of the present disclosure occur. When two catalyst compounds are used in one reactor as a mixed catalyst system, the two catalyst compounds can be chosen such that the two are compatible. A simple screening method, such as by ^1H or ^{13}C NMR, known to those of ordinary skill in the art, can be used to determine which catalyst compounds are compatible. The same activator can be used for both catalyst compounds, however, two different activators, such as a non-coordinating anion activator and an alumoxane, can be used in combination. If one or more catalyst compounds contain an X^1 or X^2 ligand which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the alumoxane may be contacted with the catalyst compound(s) prior to addition of the non-coordinating anion activator.

[0080] The two catalyst compounds may be used in any suitable ratio. Molar ratios of (A) transition metal compound to (B) transition metal compound can be (A:B) of 1:1000 to 1000:1, alternatively 1:100 to 500:1, alternatively 1:10 to 200:1, alternatively 1:1 to 100:1, alternatively 1:1 to 75:1, and alternatively 5:1 to 50:1. The suitable ratio chosen will depend on the exact catalyst compounds chosen, the method of activation, and the end product desired. In at least one embodiment, when using the two catalyst compounds, where both are activated with the same activator, mole percentages, based upon the molecular weight of the catalyst compounds, can be about 10% to about 99.9% A to about 0.1% to about 90% B, alternatively about 25% to about 99% A to about 0.5% to about 75% B, alternatively about 50% to about 99% A to about 1% to about 50% B, and alternatively about 75% to about 99% A to about 1% to about 10% B.

Methods of Preparing the Catalyst Compounds

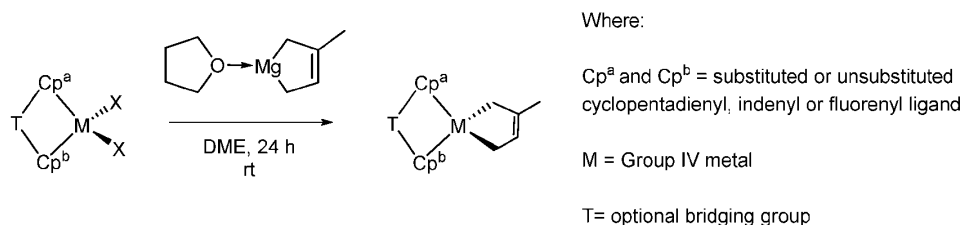
[0081] All air sensitive syntheses are carried out in nitrogen purged dry boxes. All solvents are available from commercial sources. Aluminum alkyls are available as hydrocarbon

solutions from commercial sources. Metallocene isoprenyl complexes can be prepared according to following general scheme:

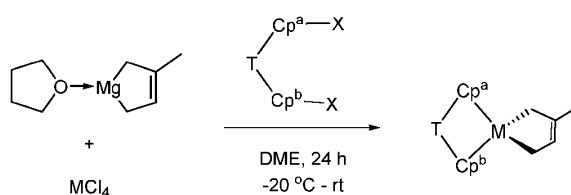


[0082] Typically, a metallocene dihalide complex is suspended in solution of THF or DME (or mixture thereof), along with excess magnesium powder which is in-situ activated with trace amounts of molecular iodine. Isoprene is then added to start the reaction. Upon completion (typically between 1- 24 hours) the pure complexes can be isolated upon extraction and filtration.

[0083] Alternatively, isoprenyl complexes can be isolated by reacting >1 equiv. of Mg(isoprene)(thf) adduct in ethereal solvent, most preferably dimethoxyethane. Typically, desired metallocene is suspended in solvent, and solid magnesium isoprene complex is added. The reaction mixtures were stirred for 1-24 hours at room temperature. Isolated complexes can be obtained upon extraction and filtration according to following general scheme:



[0084] Another alternate method involves *in situ* treatment of MCl₄ (M = Zr, Hf, Ti) with Mg(isoprene)(thf) adduct in ethereal solvent, most preferably dimethoxyethane at reduced temperature. Addition of group I ligand salt X (such as Na, Li, K) to this solution of the general formula X₂(Cp^a)(T)(Cp^b), where Cp^a is the same or different from Cp^b and constitutes substituted or unsubstituted cyclopentadienyl, fluorenyl or indenyl ligand and T is a bridging group, yields desired isoprenyl complexes. The reaction mixtures were then stirred for 1-24 hours at room temperature. Solvent removal in vacuo and extraction with pentane or benzene affords isoprenyl metallocenes analogous to methods 1 and 2.



Where:

Cp^a and Cp^b = substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl ligand

X = Group I alkali metal

M = Group IV metal

T = optional bridging group

Catalyst Systems

- [0085] In one or more embodiments, the catalyst system of the present disclosure comprises an activator and any of the catalyst compounds described above. While the catalyst systems of the present disclosure may utilize any of the catalyst compounds described above in combination with each other or with one or more catalyst compounds not described above, in some embodiments, the catalyst systems utilize a single catalyst compound corresponding to one of the catalyst compounds of the present disclosure. In yet other embodiments, a catalyst system further includes a support material. In some embodiments, a support material is silica.
- 10 In some embodiments, the activator includes one or more of alumoxanes, aluminum alkyls, ionizing activators, or combinations thereof.

- [0086] In another embodiment, the present disclosure relates to a method for preparing a catalyst system by contacting a catalyst compound of the present disclosure with an activator, where the catalyst compound is a single catalyst compound, and the single catalyst compound is the only catalyst compound contacted by an activator in said method. In yet another embodiment, the present disclosure relates to a method of polymerizing olefins comprising contacting at least one olefin with a catalyst system and obtaining a polyolefin. In still another embodiment, the present disclosure relates to a method of polymerizing olefins comprising contacting two or more different olefins with a catalyst system and obtaining a polyolefin. In a further embodiment, the present disclosure relates to a catalyst system comprising the catalyst compound of any of the embodiments described above, where the catalyst system includes a single catalyst compound. In a still further embodiment, the present disclosure relates to a catalyst system including the catalyst compound of any of the embodiments described above, where the catalyst system consists essentially of a single catalyst compound.

Activators

- [0087] The terms “cocatalyst” and “activator” are used herein interchangeably.

- [0088] 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 compounds described herein with activators in any manner known from the literature including combining them with supports, 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 components. 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, σ -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.

[0089] In at least one embodiment, the catalyst system includes an activator, a catalyst compound of Formula (I) and optional support.

Alumoxane Activators

[0090] Alumoxane activators are utilized as activators in the catalyst systems described herein. Alumoxanes are generally oligomeric compounds containing $-Al(R^{a'''})-O-$ sub-units, where $R^{a'''}$ 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, such as 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 patent number US 5,041,584, which is incorporated by reference herein). Another useful alumoxane is solid polymethylaluminum as described in US 8,404,880, US 8,975,209, and US 9,340,630, which are incorporated by reference herein.

[0091] When the activator is an alumoxane (modified or unmodified), in at least one embodiment, an amount of activator at up to a 5,000-fold molar excess Al/M over the catalyst compound (per metal catalytic site) may be used. The minimum activator-to-catalyst-compound may be a 1:1 molar ratio. Alternate ranges may include about

1:1 to about 500:1, alternately about 1:1 to about 200:1, alternately about 1:1 to about 100:1, or alternately about 1:1 to about 50:1, alternatively about 250:1 to about 500:1.

[0092] 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
5 the alumoxane can be present at a molar ratio of aluminum to catalyst compound transition metal less than 500:1, such as less than 300:1, such as less than 100:1, such as less than 1:1.

Ionizing/Non-Coordinating Anion Activators

[0093] 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
10 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 by-product from the anion. Non-coordinating anions useful in accordance with the present disclosure are those that are
15 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. Suitable ionizing activators may include an NCA, such as a compatible NCA.

[0094] It is within the scope of the present disclosure to use an ionizing activator, neutral or ionic. It is also within the scope of the present disclosure to use neutral or ionic activators
20 alone or in combination with alumoxane or modified alumoxane activators.

[0095] For descriptions of some suitable activators please see US 6,211,105 and US 8,658,556 incorporated by reference herein. Additional suitable activators are described in U.S. Patent No. 11,718,635, incorporated by reference herein.

[0096] In some embodiments, an activator can be one or more of N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
25 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.
30

[0097] In at least one embodiment, the activator is selected from one or more of a triaryl carbenium (such as triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,

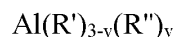
triphenylcarbenium tetrakis(perfluorobiphenyl)borate, or triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

[0098] Suitable activator-to-catalyst ratio, *e.g.*, all NCA activators-to-catalyst ratio may be about a 1:1 molar ratio. Alternate ranges include about 0.1:1 to about 100:1, alternately about 0.5:1 to about 200:1, alternately about 1:1 to about 500:1, alternately about 1:1 to about 1000:1. Suitable ranges can be about 0.5:1 to about 10:1, such as about 1:1 to about 5:1.

[0099] It is also within the scope of the present disclosure that the catalyst compounds can be combined with combinations of alumoxanes and NCA's (see for example, US 5,153,157; US 5,453,410; EP 0573120 B1; WO1994/007928; and WO1995/014044, incorporated herein by reference, which discuss the use of an alumoxane in combination with an ionizing activator).

[0100] Chain transfer agents may be used in polymerization processes of the present disclosure. Useful chain transfer agents can be hydrogen, alkylalumoxanes, a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic radical, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, or an isomer thereof) or a combination thereof, such as diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

[0101] Furthermore, a catalyst system of the present disclosure may include a metal hydrocarbenyl chain transfer agent represented by the formula:



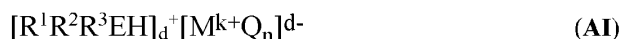
where each R' can be independently a C_1 - C_{30} hydrocarbyl group, and or each R'' , can be independently a C_4 - C_{20} hydrocarbenyl group having an end-vinyl group; and v can be from 0.1 to 3.

Alkane-Soluble Activators

[0102] Activators of the present disclosure may be those designed to have improved solubility in alkane solvents, such as the activators described in US No. 11,414,436, US No. 11,584,707, US Pub. No. 2021/0122844, US Pub. No. 2021/0121863, and WO2021/025903, incorporated herein by reference.

[0103] For example, activators, such as ammonium or phosphonium metallate or metalloid activator compounds, can include (1) ammonium or phosphonium groups and long-chain aliphatic hydrocarbyl groups and (2) metallate or metalloid anions, such as borates or aluminates.

[0104] In some embodiments, an activator compound is represented by Formula (AI):



wherein:

E is nitrogen or phosphorus, such as nitrogen;

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

5 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_5 - 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_5 - C_{50} aryl, C_6 - C_{35} arylalkyl, C_6 - C_{35} alkylaryl and, in the case of the C_5 - C_{50} -aryl, C_1 - C_{50} alkyl); wherein R^1 , R^2 , and R^3 together comprise 15 or more carbon atoms,

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

each Q is independently selected from the group consisting of a hydrogen, bridged or unbridged dialkylamido, halide, alkoxy, substituted alkoxy, aryloxy, substituted aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-
15 hydrocarbyl radical, such as a fluorinated aryl group, such fluoro-phenyl or fluoro-naphthyl, such as perfluorophenyl or perfluoronaphthyl.

[0105] In some embodiments of activator compounds represented by Formula (AI), at least one of R^1 , R^2 , and R^3 is a linear or branched C_3 - C_{40} alkyl group (alternately such as a linear or branched C_7 to C_{40} alkyl group).

20 [0106] The present disclosure also provides activator compounds represented by Formula (AI), described above where R^1 is a C_1 - C_{30} alkyl group (such as a C_1 - C_{10} alkyl group, such as C_1 to C_2 alkyl, such as methyl), wherein R^1 is optionally substituted, and each of R^2 and R^3 is independently an optionally substituted branched or linear C_1 - C_{40} alkyl group or meta and/or para-substituted phenyl group, where the meta and para substituents are, independently,
25 an optionally substituted C_1 to C_{40} hydrocarbyl group, an optionally substituted alkoxy group, an optionally substituted silyl group, a halide, or a halide containing group, 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 40 or more carbon atoms)
30 and at least one of R^1 , R^2 , and R^3 is a linear or branched alkyl (such as a C_3 - C_{40} branched alkyl, alternately C_7 - C_{40} branched alkyl).

[0107] The present disclosure further provides catalyst systems including activator compounds represented by Formula (AI), as described above where R^1 is methyl; and each of R^2 and R^3 is independently C_1 - C_{40} branched or linear alkyl or C_5 - C_{50} -aryl, wherein each of R^1 ,

- R², and R³ is independently unsubstituted or substituted with at least one of halide, C₅-C₅₀ aryl, C₆-C₃₅ arylalkyl, C₆-C₃₅ alkylaryl and, in the case of the C₅-C₅₀-aryl, C₁-C₅₀ alkyl; wherein R¹, R², and R³ together comprise 15 or more carbon atoms (such as 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 40 or more carbon atoms).

[0108] Activator compounds can include one or more of:

- N,N-di(hydrogenated tallow)methylammonium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-nonadecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 10 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],
 15 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],
 20 N-methyl-4-nonadecyl-N-hexadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-ethyl-4-nonadecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-N,N-di-octadecylammonium [tetrakis(perfluorophenyl)borate],
 N-methyl-N,N-di-hexadecylammonium [tetrakis(perfluorophenyl)borate],
 N-methyl-N,N-di-tetradecylammonium [tetrakis(perfluorophenyl)borate],
 25 N-methyl-N,N-di-dodecylammonium [tetrakis(perfluorophenyl)borate],
 N-methyl-N,N-di-decylammonium [tetrakis(perfluorophenyl)borate],
 N-methyl-N,N-di-octylammonium [tetrakis(perfluorophenyl)borate],
 N-ethyl-N,N-di-octadecylammonium [tetrakis(perfluorophenyl)borate],
 N,N-di(octadecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
 30 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],
 5 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],
 10 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
 15 N-methyl-N-octylanilinium [tetrakis(perfluorophenyl)borate].

Optional Support Materials

- [0109] In embodiments herein, the catalyst system may include an inert support material. The supported material can be a porous support material, for example, talc, and inorganic oxides. Other support materials include zeolites, clays, organoclays, or another organic or
 20 inorganic support material, or mixtures thereof.

- [0110] The support material can be an inorganic oxide. The inorganic oxide can be in a finely divided form. Suitable inorganic oxide materials for use in catalyst systems herein may include groups 2, 4, 13, and 14 metal oxides, such as silica, alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or
 25 alumina can be magnesia, titania, zirconia. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins, such as finely divided polyethylene. Examples of suitable supports may include magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania. In at least
 30 one embodiment, the support material is selected from Al_2O_3 , ZrO_2 , SiO_2 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{TiO}_2$, silica clay, silicon oxide/clay, or mixtures thereof.

- [0111] The support material, such as an inorganic oxide, can have a surface area of about $10 \text{ m}^2/\text{g}$ to about $700 \text{ m}^2/\text{g}$, pore volume of about $0.1 \text{ cm}^3/\text{g}$ to about $4.0 \text{ cm}^3/\text{g}$ and average particle size of about $5 \text{ }\mu\text{m}$ to about $500 \text{ }\mu\text{m}$. The surface area of the support material can be of

about 50 m²/g to about 500 m²/g, pore volume of about 0.5 cm³/g to about 3.5 cm³/g and average particle size of about 10 μm to about 200 μm. For example, the surface area of the support material can be about 100 m²/g to about 400 m²/g, pore volume of about 0.8 cm³/g to about 3.0 cm³/g and average particle size can be about 5 μm to about 100 μm. The average pore size of the support material useful in the present disclosure can be 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 (surface area=300 m²/gm; pore volume of 1.65 cm³/gm). For example, suitable silicas can be the silicas marketed under the tradenames of DAVISON™ 952 or DAVISON™ 955 by the Davison Chemical Division of W.R. Grace and Company. In other embodiments, DAVISON™ 948 is used. Alternatively, a silica can be ES-70™ silica (PQ Corporation, Malvern, Pennsylvania) that has been calcined, for example (such as at 875°C).

[0112] The support material should be dry, that is, free or substantially free of absorbed water. Drying of the support material can be effected by heating or calcining at about 100°C to about 1000°C, such as at least about 600°C. When the support material is silica, it is heated to at least 200°C, such as about 200°C to about 850°C, and such as at about 600°C; and for a time of about 1 minute to about 100 hours, about 12 hours to about 72 hours, or 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 of the present disclosure. The calcined support material is then contacted with at least one polymerization catalyst including at least one catalyst compound and an activator.

[0113] The support material, having reactive surface groups, such as hydroxyl groups, is slurried in a non-polar solvent and the resulting slurry is contacted with a solution of a catalyst compound and an activator. In at least one embodiment, the slurry of the support material is first contacted with the activator for a period of time of about 0.5 hour to about 24 hours, about 2 hours to about 16 hours, or 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 alternate embodiments, the slurry of the support material is first contacted with the catalyst compound for a period of time of about 0.5 hour to about 24 hours, about 2 hours to about 16 hours, or about 4 hours to about 8 hours. The slurry of the supported catalyst compound is then contacted with the activator solution.

[0114] The mixture of the catalyst(s), activator(s) and support is heated about 0°C to about 70°C, such as about 23°C to about 60°C, such as at room temperature. Contact times can be

about 0.5 hours to about 24 hours, such as about 2 hours to about 16 hours, or about 4 hours to about 8 hours.

[0115] 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 polymerization 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.

[0116] In at least one embodiment, the support material is a supported methylalumoxane (SMAO), which is an MAO activator treated with silica (*e.g.*, ES-70-875 silica).

Polymerization Processes

[0117] The present disclosure also relates to polymerization processes where monomer (*e.g.*, ethylene; propylene), and optionally a comonomer, are contacted with a catalyst system including an activator and at least one catalyst compound of the present disclosure. The catalyst compound and activator may be combined in any suitable 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 the catalyst compound and activator subsequently react to form the active catalyst.

[0118] Monomers may include substituted or unsubstituted C₂ to C₄₀ alpha olefins, such as C₂ to C₂₀ alpha olefins, such as C₂ to C₁₂ alpha olefins, such as ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In at least one embodiment, the monomer includes ethylene and an optional comonomer including one or more C₃ to C₄₀ olefins, such as C₄ to C₂₀ olefins, such as C₆ to C₁₂ olefins. The C₃ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₃ to C₄₀ cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and or one or more functional groups. In another embodiment, the monomer includes propylene and an optional comonomer including one or more ethylene or C₄ to C₄₀ olefins, such as C₄ to C₂₀ olefins, such as C₆ to C₁₂ olefins. The C₄ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₄ to C₄₀ cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and or one or more functional groups.

[0119] Exemplary C₂ to C₄₀ olefin monomers and optional comonomers may include ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, ethylenenorbornene, vinylnorbornene, norbornadiene,

dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof, such as hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, 5 dicyclopentadiene, norbornene, norbornadiene, and their respective homologs and derivatives, such as norbornene, norbornadiene, or dicyclopentadiene.

[0120] In some embodiments, a comonomer is selected from ethylene, propylene 1-butene, 1-pentene, 1-hexene, 2-methyl-1-pentene, vinylcyclobutane, 1-heptene, 1-octene, 1-decene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, norbornene, vinylnorbornene, or ethylidene 10 norbornene.

[0121] Polymerization processes of the present disclosure can be carried out in any suitable manner. Any suitable suspension, homogeneous, bulk, solution, slurry, or gas phase polymerization process can be used. Such processes can be run in a batch, semi-batch, or continuous mode. Homogeneous polymerization processes and slurry processes can be used. 15 A bulk homogeneous process can be used. Alternately, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst system or other additives, or amounts found with the monomer; *e.g.*, propane in propylene). In another embodiment, the process is a slurry process. As used herein, the term "slurry polymerization process" means a polymerization process where a supported catalyst is employed, and 20 monomers are polymerized on the supported catalyst particles. At least 95 wt% of polymer products derived from the supported catalyst are in granular form as solid particles (not dissolved in the diluent).

[0122] Suitable diluents/solvents for polymerization may include non-coordinating, inert liquids. Examples of diluents/solvents for polymerization may include straight and branched-chain hydrocarbons, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, 25 heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof, such as can be found commercially (*e.g.*, Isopar™); perhalogenated hydrocarbons, such as perfluorinated C₄ to C₁₀ alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic 30 compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents may also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In at least one embodiment, 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 0 wt% based upon the weight of the solvents.

- 5 [0123] In at least one embodiment, a feedstream to the reactor has a 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.

- [0124] Polymerizations can be run at any temperature and or pressure suitable to obtain the
10 desired polymers. Suitable temperatures and or pressures include a temperature of about 0°C to about 300°C, such as about 20°C to about 200°C, such as about 35°C to about 160°C, such as about 80°C to about 160°C, such as about 85°C to about 140°C. Polymerizations can be run at a pressure 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.

- 15 [0125] In a suitable polymerization, the run time of the reaction can be up to about 300 minutes, such as about 5 minutes to about 250 minutes, such as about 10 minutes to about 120 minutes, such as about 20 minutes to about 90 minutes, such as about 30 minutes to about 60 minutes. In a continuous process the run time may be the average residence time of the reactor. In at least one embodiment, the run time of the reaction is up to about 45 minutes. In a
20 continuous process the run time may be the average residence time of the reactor.

[0126] 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 (0.007 kPa to 345 kPa), such as about 0.01 psig to about 25 psig (0.07 kPa to 172 kPa), such as about 0.1 psig to about 10 psig (0.7 kPa to 70 kPa).

- 25 [0127] In at least one embodiment, the hydrogen content is about 0.0001 ppm to about 2,000 ppm, such as about 0.0001 ppm to about 1,500 ppm, such as about 0.0001 ppm to about 1,000 ppm, such as about 0.0001 ppm to about 500 ppm. Alternately, hydrogen can be present at zero ppm.

- [0128] In at least one embodiment, little or no alumoxane is used in the process to produce
30 the polymers. For example, alumoxane can be present at zero mol%, alternately the alumoxane can be present at a molar ratio of aluminum to transition metal less than 500:1, such as less than 300:1, such as less than 100:1, such as less than 1:1.

[0129] Unless otherwise indicated, “catalyst productivity” is a measure of how many grams of polymer (P) are produced using a polymerization catalyst comprising W g of catalyst (cat),

over a period of time of T hours; and may be expressed by the following formula: $P/(T \times W)$ and expressed in units of $\text{gP/gcat} \cdot \text{hr}^{-1}$. Unless otherwise indicated, “catalyst activity” is a measure of how active the catalyst is and is reported as the mass of product polymer (P) produced per mole of catalyst (cat) used (kgP/molcat) or as the mass of product polymer (P) produced per mass of catalyst (cat) used (gP/gcat). Catalyst activity may also be expressed over a period of time T of hours and reported as the mass of product polymer (P) produced per mole or millimole of catalyst (cat) used and expressed in units of $\text{gPmmolcat}^{-1} \cdot \text{hr}^{-1}$.

[0130] In at least one embodiment, according to the present disclosure, a catalyst system has a catalyst activity of greater than $10,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as greater than $100,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as greater than $500,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as about $50,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $1,200,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as about $200,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $1,000,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as about $200,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $500,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, alternatively about $500,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $950,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as about $800,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $950,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$.

[0131] In at least one embodiment, the polymerization: 1) is conducted at temperatures of about 0°C to about 300°C (such as about 25°C to about 250°C , such as about 50°C to about 160°C , such as about 80°C to about 140°C); 2) is conducted at a pressure of 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 about 4 MPa); 3) is conducted in an aliphatic hydrocarbon solvent (such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; such as where aromatics are present in the solvent at less than 1 wt%, such as less than 0.5 wt%, such as at 0 wt% based upon the weight of the solvents); 4) wherein the catalyst system used in the polymerization comprises less than 0.5 mol%, such as about 0 mol% alumoxane, alternately the alumoxane is present at a molar ratio of aluminum to transition metal less than 500:1, such as less than 300:1, such as less than 100:1, such as less than 1:1; 5) the polymerization occurs in one reaction zone; 6) optionally scavengers (such as trialkyl aluminum compounds) are absent (*e.g.*, present at zero mol%, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, such as less than 50:1, such as less than 15:1, such as less than 10:1); and 7) optionally hydrogen is present in the polymerization reactor at a partial pressure of about 0.001 psig to about 50 psig (0.007 kPa to 345 kPa) (such as about 0.01 psig to about 25 psig (0.07 kPa to 172 kPa), such as about 0.1 psig to about 10 psig (0.7 kPa to 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. Room temperature is 23°C unless otherwise noted.

[0132] Other additives may also be used in the polymerization, as desired, such as one or more scavengers, hydrogen, aluminum alkyls, or chain transfer agents such as alkylalumoxanes, a compound represented by the formula AlR_3 or ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic radical, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

Polyolefin Products

[0133] The present disclosure also relates to compositions of matter produced by the methods described herein.

[0134] In at least one embodiment, a process described herein produces C_2 to C_{20} olefin homopolymers (*e.g.*, ethylene homopolymer; propylene homopolymer), or C_2 to C_{20} olefin copolymers (*e.g.*, ethylene-octene, ethylene-propylene) and or propylene- α -olefin copolymers, such as C_3 to C_{20} copolymers (such as propylene-ethylene, propylene-hexene, or propylene-octene).

[0135] A process of the present disclosure produces olefin polymers, such as polyethylene and propylene homopolymers and copolymers. In at least one embodiment, the polymers produced herein are homopolymers of ethylene or copolymers of ethylene having, for example, about 0.1 wt% to about 40 wt% (alternately about 5 wt% to about 40 wt%, such as about 10 wt% to about 35 wt%, such as about 10 wt% to about 20 wt%, alternatively about 20 wt% to about 30 wt%, such as about 25 wt% to about 30 wt%, of one or more C_3 to C_{20} olefin comonomer (such as C_3 to C_{12} α -olefin, such as propylene, butene, hexene, octene, decene, dodecene, such as propylene, butene, hexene, octene). For example, it has been discovered that catalyst compounds of the present disclosure can provide ethylene copolymers having high comonomer content, which can provide improved processability and/or toughness. In at least one embodiment, the monomer is ethylene and the comonomer is hexene or octene, such as about 5 wt% to about 40 wt% hexene or octene, such as about 10 wt% to about 35 wt% hexene or octene, such as about 15 wt% to about 25 wt% hexene or octene, alternatively about 25 wt% to

about 33 wt%, based on the weight of the polymer.

[0136] In at least one embodiment, the polymers produced herein are homopolymers of propylene or are copolymers of propylene having, for example, about 0.1 wt% to about 22 wt% (alternately about 0.5 wt% to about 20 wt%, such as about 1 wt% to about 18 wt%, such as about 1 wt% to about 16 wt%) of one or more of C₂ or C₄ to C₂₀ olefin comonomer (such as ethylene or C₄ to C₁₂ alpha-olefin, such as ethylene, butene, hexene, octene, decene, dodecene, such as ethylene, butene, hexene, octene). In at least one embodiment, the monomer is propylene and the comonomer is ethylene, such as about 0.1 wt% to about 22 wt% ethylene, such as about 0.5 wt% to about 20 wt% ethylene, such as about 1 wt% to about 18 wt% ethylene, alternatively about 10 wt% to about 30 wt% ethylene, alternatively about 3 wt% to about 10 wt%, based on the weight of the polymer.

[0137] In at least one embodiment, a polymer produced herein has a unimodal or multimodal molecular weight distribution as determined by Gel Permeation Chromatography (GPC). By "unimodal" is meant that the GPC trace has one peak or inflection point. By "multimodal" is meant that the GPC trace has at least two peaks or inflection points. An inflection point is that point where the second derivative of the curve changes in sign (*e.g.*, from negative to positive or vice versa).

[0138] In at least one embodiment, a propylene homopolymer or propylene copolymer of the present disclosure has an Mw about 10,000 g/mol to about 1,000,000 g/mol, such as about 10,000 g/mol to about 500,000 g/mol, such as about 10,000 g/mol to about 300,000 g/mol, such as about 10,000 g/mol to about 150,000 g/mol, such as about 10,000 g/mol to about 100,000 g/mol, such as about 10,000 g/mol to about 50,000 g/mol, alternatively about 50,000 g/mol to about 100,000 g/mol, such as about 75,000 g/mol to about 95,000 g/mol, alternatively about 100,000 g/mol to about 150,000 g/mol.

[0139] In at least one embodiment, a propylene homopolymer or propylene copolymer of the present disclosure has an Mn about 5,000 g/mol to about 100,000 g/mol, such as about 25,000 g/mol to about 100,000 g/mol, such as about 25,000 g/mol to about 50,000 g/mol, alternatively about 5,000 g/mol to about 25,000 g/mol, such as about 5,000 g/mol to about 15,000 g/mol.

[0140] In at least one embodiment, a propylene homopolymer or propylene copolymer of the present disclosure has an Mw/Mn (PDI) value about 1 to about 8, such as about 1.5 to about 8, such as about 1.5 to about 3, such as about 1.5 to about 2.5, alternatively about 1.75 to about 2.25.

[0141] In at least one embodiment, a propylene homopolymer or propylene copolymer of

the present disclosure can have a T_m (°C) of about 120°C to about 165°C, such as about 125°C to about 164°C, about 135°C to about 160°C, such as about 140°C to about 155°C, alternatively about 145°C to about 155°C.

[0142] The stereoregularity of isotactic propylene homopolymers can be determined by the catalyst, total monomer concentrations, and reactor temperature. It is believed that isotactic propylene homopolymers (or copolymers) made according to processes of the present disclosure may comprise up to 99.99% m-dyads based on the total number of dyads present in the polymer, such as a meso dyad (m-dyad) content (m%) of about 85% to about 99.99%, such as about 95% to about 99.95%, such as about 99% to about 99.9%, such as about 98% to about 99%, as determined by ^{13}C NMR, the remainder balance being r-dyad content (r%).

[0143] In some embodiments, an isotactic propylene homopolymer has an [mmmm] pentad content of about 95.0% to about 99.5%, such as about 96.0% to about 99.0%, such as about 96.2% to about 98.5%, as determined by ^{13}C NMR. In some embodiments, an isotactic propylene homopolymer has an [rrrr] pentad content of about 0% to about 0.5%, such as about 0.0% to about 0.2%, such as about 0.01% to about 0.1%, as determined by ^{13}C NMR. In some embodiments, an isotactic propylene homopolymer has an [mmmr] pentad content of about 0.1% to about 1%, such as about 0.2% to about 0.9%, such as about 0.3% to about 0.9%, as determined by ^{13}C NMR. In some embodiments, an isotactic propylene homopolymer has an [rmmr] pentad content of about 0.1% to about 1%, such as about 0.2% to about 0.8%, such as about 0.2% to about 0.7%, as determined by ^{13}C NMR. In some embodiments, an isotactic propylene homopolymer has an [mmrr] pentad content of about 0.1% to about 1%, such as about 0.2% to about 0.8%, such as about 0.3% to about 0.7%, as determined by ^{13}C NMR. In some embodiments, an isotactic propylene homopolymer has an [mmrm+rmrr] pentad content of about 0.1% to about 1%, such as about 0.2% to about 0.8%, such as about 0.2% to about 0.7%, as determined by ^{13}C NMR. In some embodiments, an isotactic propylene homopolymer has an [rmm] pentad content of about 0.1% to about 1%, such as about 0.1% to about 0.5%, such as about 0.1% to about 0.4%, as determined by ^{13}C NMR. In some embodiments, an isotactic propylene homopolymer has an [mrrr] pentad content of about 0% to about 0.1%, such as about 0%, as determined by ^{13}C NMR. In some embodiments, an isotactic propylene homopolymer has an [mrrm] pentad content of about 0.1% to about 1%, such as about 0.1% to about 0.5%, such as about 0.1% to about 0.3%, as determined by ^{13}C NMR.

[0144] Regio Defect Concentrations by ^{13}C Carbon (^{13}C NMR): ^{13}C NMR spectroscopy is used to measure stereo and regio defect concentrations of polypropylene. ^{13}C NMR spectra are acquired as described in more detail below.

[0145] The regio defects each give rise to multiple peaks in the ¹³Carbon NMR spectrum, and these are all integrated and averaged (to the extent that they are resolved from other peaks in the spectrum), to improve the measurement accuracy. The chemical shift offsets of the resolvable resonances used in the analysis are tabulated below. The precise peak positions may shift as a function of NMR solvent choice.

Regio defect	Chemical shift range (ppm)
2,1-erythro	42.3, 38.6, 36.0, 35.9, 31.5, 30.6, 17.6, 17.2
2,1-threo	43.4, 38.9, 35.6, 34.7, 32.5, 31.2, 15.4, 15.0
3,1 insertion	37.6, 30.9, 27.7

[0146] The stereo defects measured as “stereo defects/10,000 monomer units” are calculated from the sum of the intensities of mmrr, mmrm+rrmr, and rrmr resonance peaks times 5,000. The intensities used in the calculations are normalized to the total number of monomers in the sample polymer. Methods for measuring 2,1 regio defects/10,000 monomers and 1,3 regio defects/10,000 monomers follow standard methods. Additional references include Grassi, A. et. al. (1988) *Macromolecules*, v.21, pp. 617-622 and Busico et.al. (1994) *Macromolecules*, v.27, pp. 7538-7543. The average meso run length = 10000/[(stereo defects/10000 C) + (2,1-regio defects/10000 C) + (1,3-regio-defects/10000 C)].

[0147] A low amount of regio defects provides a low or eliminated amount of haze of isotactic polypropylene films. It has been discovered that isotactic polypropylenes of the present disclosure can have a low amount of regio defects. In some embodiments, a polypropylene (or copolymer thereof) advantageously has less than 200 regio defects (defined as the sum of 2,1-erythro and 2,1-threo insertions, and 3,1-isomerizations) per 10,000 propylene units, alternatively greater than 5, 10 or 15 and less than 200, 150, or 100 regio defects per 10,000 propylene units.

[0148] In some embodiments, a propylene homopolymer or propylene copolymer advantageously has less than 100 2,1-regio defects (defined as the sum of 2,1-erythro and 2,1-threo insertions) per 10,000 propylene units, such as greater than 5, 15 or 25 and less than 100, 75, or 65 2,1-regio defects per 10,000 propylene units. In some embodiments, a propylene homopolymer or propylene copolymer advantageously has less than 100 1,3-regio defects (defined as 3,1 insertions/isomerizations) per 10,000 propylene units, such as greater than 5, 7 or 15 and less than 75, 55, or 40 1,3-regio defects per 10,000 propylene units. In some embodiments, a propylene homopolymer or propylene copolymer advantageously has less than 150 total regio defects (defined as the sum of 3,1 insertions/isomerizations, 2,1-erythro insertions and 2,1-threo insertions) per 10,000 propylene units, such as greater than 20, 30 or

40 and less than 150, 100, or 90 total regio defects per 10,000 propylene units.

[0149] In some embodiments, a propylene homopolymer or propylene copolymer has less than 100 stereo defects per 10,000 propylene units, alternatively greater than 5, 15 or 30 and less than 100 or 85 stereo defects per 10,000 propylene units. In some embodiments, a propylene homopolymer has an average meso run length of about 20 to about 130, such as about 50 to about 120, such as about 60 to about 110. In some embodiments, the propylene homopolymer has a meso run length of greater than 50, alternatively greater than 60, alternatively greater than 70.

GPC 4-D

[0150] Unless otherwise indicated, for purposes of the Claims, the distribution and the moments of molecular weight (M_w , M_n , M_z , M_w/M_n , etc.), the comonomer content are determined by using a high temperature Gel Permeation Chromatography (Polymer Char GPC-IR) equipped with a multiple-channel band-filter based Infrared detector IR5 with a multiple-channel band filter based infrared detector ensemble IR5 with band region covering about 2700 cm^{-1} to about 3000 cm^{-1} (representing saturated C-H stretching vibration), an 18-angle light scattering detector and a viscometer. Three Agilent PLgel 10- μm Mixed-B LS columns are used to provide polymer separation. Reagent grade 1,2,4-trichlorobenzene (TCB) (from Sigma-Aldrich) comprising ~ 300 ppm antioxidant BHT can be used as the mobile phase at a nominal flow rate of $\sim 1.0\text{ mL/min}$ and a nominal injection volume of $\sim 200\text{ }\mu\text{L}$. The whole system including transfer lines, columns, and detectors can be contained in an oven maintained at $\sim 145^\circ\text{C}$. A given amount of sample can be weighed and sealed in a standard vial with $\sim 10\text{ }\mu\text{L}$ flow marker (heptane) added thereto. After loading the vial in the auto-sampler, the oligomer or polymer may automatically be dissolved in the instrument with $\sim 8\text{ mL}$ added TCB solvent at $\sim 160^\circ\text{C}$ with continuous shaking. The sample solution concentration can be from ~ 0.2 to $\sim 2.0\text{ mg/mL}$, with lower concentrations used for higher molecular weight samples. The concentration, c , at each point in the chromatogram can be calculated from the baseline-subtracted IR5 broadband signal, I , using the equation: $c = \alpha I$, where α is the mass constant determined with polyethylene or polypropylene standards. The mass recovery can be calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume. The conventional molecular weight (IR MW) is determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards ranging from 700 to 10M gm/mole. The MW at each elution volume is calculated with following equation:

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

where the variables with subscript “PS” stand for polystyrene while those without a subscript are for the test samples. In this method, $\alpha_{PS} = 0.67$ and $K_{PS} = 0.000175$, α and K for other materials are as calculated by GPC ONE™ software (Polymer Characterization, S.A., Valencia, Spain). Concentrations are expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity (hence K in the Mark-Houwink equation) is expressed in dL/g unless otherwise noted.

[0151] The comonomer composition is determined by the ratio of the IR5 detector intensity corresponding to CH₂ and CH₃ channel calibrated with a series of PE and PP homo/copolymer standards whose nominal value are predetermined by NMR or FTIR. In particular, this provides the methyls per 1000 total carbons (CH₃/1000TC) as a function of molecular weight. The short-chain branch (SCB) content per 1000TC (SCB/1000TC) is then computed as a function of molecular weight by applying a chain-end correction to the CH₃/1000TC function, assuming each chain to be linear and terminated by a methyl group at each end. The weight % comonomer is then obtained from the following expression in which f is 0.3, 0.4, 0.6, 0.8, and so on for C₃, C₄, C₆, C₈, and so on co-monomers, respectively:

$$w2 = f * SCB/1000TC.$$

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

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

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

$$w2b = f * \text{bulk CH}_3/1000TC$$

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

and bulk SCB/1000TC is converted to bulk $w2$ in the same manner as described above.

[0152] The LS detector is the 18-angle Wyatt Technology High Temperature DAWN HELEOSII. The LS molecular weight (M) at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (*Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press, 1972.):

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

Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , c is the polymer concentration determined from the IR5 analysis, A_2 is the second virial coefficient, $P(\theta)$ is the form factor for a monodisperse random coil, and K_o is the optical constant for the system:

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

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system, $n = 1.500$ for TCB at 145°C and $\lambda = 665$ nm. For analyzing polyethylene homopolymers, ethylene-hexene copolymers, and ethylene-octene copolymers, $dn/dc = 0.1048$ ml/mg and $A_2 = 0.0015$; for analyzing ethylene-butene copolymers, $dn/dc = 0.1048*(1 - 0.00126*w_2)$ ml/mg and $A_2 = 0.0015$ where w_2 is weight percent butene comonomer.

[0153] A high temperature Agilent (or Viscotek Corporation) viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the equation $[\eta] = \eta_s/c$, where c is concentration and is determined from the IR5 broadband channel output. The viscosity MW at each point is calculated as

20 $M = K_{ps} M^{\alpha_{ps}+1} / [\eta]$, where α_{ps} is 0.67 and K_{ps} is 0.000175.

Blends

[0154] In some embodiments, the polymer (such as the polyethylene, polypropylene, or copolymers thereof) 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

25 polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and or butene, and or hexene, polybutene, ethylene vinyl acetate, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers

30 polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, ethylene-

propylene-diene monomer (EPDM) polymers, block copolymers, styrenic block copolymers, polyamides, polycarbonates, polyethylene terephthalate (PET) resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-l esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and or polyisobutylene.

[0155] In at least one embodiment, the polymer (such as the polyethylene, polypropylene) is present in the above blends, at about 10 wt% to about 99 wt%, based upon the weight of the polymers in the blend, such as about 20 wt% to about 95 wt%, such as at least about 30 wt% to about 90 wt%, such as at least about 40 wt% to about 90 wt%, such as at least about 50 wt% to about 90 wt%, such as at least about 60 wt% to about 90 wt%, such as at least about 70 wt% to about 90 wt%.

[0156] 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

[0157] Any of the foregoing polymers, 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 suitable 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, an ethylene 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. However, in another embodiment the film is oriented to the same extent in both the MD and TD directions.

- 5 [0158] The films may vary in thickness depending on the intended application; however, films of a thickness of about 1 μm to about 50 μm can be suitable. Films intended for packaging can be about 10 μm to about 50 μm thick. The thickness of the sealing layer can be about 0.2 μm to about 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.

10 EXPERIMENTAL

[0159] The experimental methods and analytical techniques utilized in Examples below are described in this section.

[0160] General procedure for preparing metallocene isoprenyl complexes I1-I11. Corresponding method used in preparation is also disclosed.

15 **Catalyst I1 (preparation method 1)**

- [0161] Mg powder (38 mg, 1.56 mmol) and I_2 (2.2 mg) were combined in 3 mL of diethyl ether. While stirring a THF solution (ca 3 mL) of dichloride complex C_1 (200 mg, 0.312 mmol) was added. Following the addition of metallocene, isoprene (0.156 mL, 1.56 mmol) was added as neat liquid. The reaction mixture was stirred for 1 hour at room temperature. After 1 hour, solvent was removed *in vacuo* and the residue was extracted with pentane (3 x 5 mL) and filtered through celite. Solvent removal afforded the title compound as a red solid in 83% yield. ^1H NMR (400 MHz, C_6D_6) δ 7.74 (s, 1H), 7.51 (d, 2H), 7.37 (d, 2H), 5.90 (s, 1H), 4.82 (m, 1H), 3.07 (m, 1H), 2.86 (m, 2H), 2.68 (m, 2H), 2.42 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H), 1.88 (m, 3H), 1.69 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.29 (s, 9H), 1.12 (s, 3H), 0.95 (s, 3H), -0.94 (m, 1H), -1.28 (m, 1H).
- 25

Catalyst I2 (preparation method 1)

- [0162] Mg powder (38 mg, 1.56 mmol) and I_2 (3.2 mg) were combined in 3 mL of diethyl ether. While stirring, a THF solution of complex C_2 (200 mg, 0.315 mmol) was added. Following the addition of metallocene, isoprene (0.189 mL, 1.89 mmol) was added as neat liquid. The reaction mixture was stirred for 1 hour at room temperature. After 1 hour, solvent was removed *in vacuo* and the residue was extracted with pentane (3 x 5 mL) and filtered through celite. Solvent removal afforded the 100 mg of a bright red solid which was spectroscopically pure. The compound exists as a mixture of two isomers in ca 3:2 ratio due to hindered rotation around naphthyl group. ^1H NMR (400 MHz, C_6D_6) δ 8.13 (d, ^1H , isomer 1)
- 30

7.87 (s, ¹H, isomer 1) 7.84 (s, ¹H, isomer 2) 7.76 (d, ¹H, isomer 1) 7.70 (overlapping m, ²H isomer 1 and 2) 7.48 (m, ²H, isomer 2) 7.46 (m, ²H, isomer 1) 7.31 (m, ³H, isomer 2) 6.99 (m, ¹H isomer 2) 5.76 (s, ¹H, isomer 1) 5.22 (s, ¹H, isomer 2) 5.01 (m, ¹H, isomer 2) 4.51 (m, ¹H, isomer 1) 2.44 (bs, ⁶H, isomer 1) 2.28 (s, ⁶H, isomer 1) 2.22 (s, ³H, isomer 2) 2.16 (s, ³H, isomer 1) 2.02 (s, ³H, isomer 2) 1.64 (s, ³H, isomer 2) 1.61 (s, ³H, isomer 2) 1.50 (s, ³H, isomer 2) 1.48 (s, ³H, isomer 1) 1.43 (s, ³H, isomer 1) 1.41 (s, ³H, isomer 2) 1.29 (s, ³H, isomer 2) 1.24 (s, ³H, isomer 1) 1.16 (s, ³H isomer 1) 0.95 (s, ³H, isomer 1) 0.91 (s, ³H, isomer 2) -0.87 (m, ¹H, isomer 2) -1.14 (m, ¹H, isomer 1) -1.24 (m, ¹H, isomer 2), -1.26 (m, ¹H, isomer 1).

Catalyst I3 (preparation method 1)

10 [0163] Mg powder (41 mg, 1.66 mmol) and I₂ (4.0 mg) were combined in 3 mL of diethyl ether. While stirring, a THF solution of C₃ (200 mg, 0.333 mmol) was added. Following the addition of metallocene, isoprene (0.166 mL, 1.66 mmol) was added as neat liquid. The reaction mixture was stirred for 1 hour at room temperature. After 1 hour, solvent was removed *in vacuo* and the residue was extracted with pentane (3 x 5 mL) and filtered through celite. Solvent
15 removal afforded the 113 mg of a bright red solid in 60% yield. ¹H NMR (400 MHz, C₆D₆) δ 7.78 (d, ¹H), 7.56 (d, ²H), 7.34 (d, ²H), 7.09 (d, ¹H), 6.99 (m, ¹H), 6.06 (s, ¹H), 4.66 (m, ¹H), 2.75 (s, ¹H), 2.34 (s, ³H), 2.27 (two s, ⁶H), 1.69 (s, ³H), 1.64 (^dH), 1.33 (s, ³H), 1.38 (m, ¹H), 1.28 (s, ⁹H), 1.04 (s, ³H), 0.93 (s, ³H), -0.97 (m, ¹H), -1.41 (m, ¹H).

Catalyst I4 (preparation method 1)

20 [0164] To a stirring suspension of magnesium powder (550 mg, 22.6 mmol, 4.8 equiv.) in diethyl ether (20mL), minimal iodine was added. The mixture was stirred until the suspension lost its red-brown color. Then, bis((4-triethylsilyl)phenyl)methylene(cyclopentadienyl)(3,7-di-tert-butyl-fluoren-9-yl)hafnium dichloride (4.645 g, 4.69 mmol) in tetrahydrofuran (30 mL) was added. Then, isoprene (3.3 mL, 33 mmol, 7 equiv.). The reaction was stirred at room
25 temperature for 4 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with pentane (3 × 20mL) and filtered over Celite. The combined pentane extracts were concentrated under a stream of nitrogen and then under high vacuum. The resulting solid was stirred in pentane (10mL) overnight. The resulting suspension was filtered over a plastic, fritted funnel. The filtered solid was collected and
30 concentrated under high vacuum to afford the product as an orange solid (0.808g, 17% yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 8.11 (dt, 2H, *J* = 7.6, 2.0 Hz), 7.73 (dd, 1H, *J* = 8.6, 0.7 Hz), 7.70 (dd, 1H, *J* = 8.6, 0.7 Hz), 7.65-7.57 (m, 4H), 7.40 (td, 2H, *J* = 7.8, 1.3 Hz), 7.26 (dd, 1H, *J* = 8.6, 1.7 Hz), 7.19 (dd, 1H, *J* = 8.7, 1.7 Hz), 6.46 (dd, 1H, *J* = 1.7, 0.8 Hz), 6.35 (d, 1H, *J* = 1.0 Hz), 6.07 (dt, 1H, *J* = 3.1, 2.3 Hz), 5.94 (q, 1H, *J* = 2.5 Hz), 5.27 (td, 1H, *J* = 3.3, 2.0 Hz),

5.18 (td, 1H, $J = 3.3, 2.1$ Hz), 3.79-3.70 (m, 1H), 1.67 (s, 3H), 1.093 (s, 9H), 1.091 (s, 9H), 1.04-0.97 (m, 18H), 0.85-0.76 (m, 13H), 0.46 (t, 1H, $J = 10.7$ Hz), -0.96--1.07 (m, 1H), -1.67 (d, 1H, $J = 10.5$ Hz).

5 Catalyst I5-rac and I5-meso. (preparation method 2)

[0165] Solid rac-dimethylsilyl(bis-2-methyl-indenyl) zirconium dichloride (100 mg, 0.21 mmol) was suspended in 5 mL of DME. While stirring, solid (THF)Mg(isoprene) complex (0.038 g, 1.1 equiv.) was added. Almost instantly the reaction mixture changed color to dark red. The reaction was stirred overnight at room temperature. After 18 hours, solvent was removed *in vacuo* to give a foamy dark residue. The residue was extracted with pentane (3 x 4 mL) and minimal benzene and filtered over celite. Solvent removal afforded red solid. ¹H NMR appears to show isoprene complex as the mixture of essentially 1:1 rac/meso material. This reaction leads to isomerization ¹H NMR (400 MHz, Benzene-d₆) δ 8.04 (m, 3H), 7.72 (m, 1H), 6.87 (s, 4H), 6.70 (s, 6H), 6.69 – 6.59 (m, 2H), 5.38 (s, 1H), 5.13 (s, 2H), 5.07 (s, 1H), 4.22 (s, 1H), 3.97 (s, 1H), 2.36 (s, 3H), 2.29 (s, 3H), 2.09 (s, 3H), 1.80 (s, 3H), 1.34 (s, 1H), 1.17 (s, 3H), 1.02 (s, 3H), 0.94 (s, 3H), 0.87 (s, 4H), 0.81 (d, $J = 9.9$ Hz, 1H), -0.66 (s, 1H).

Catalyst I6. (preparation method 1)

[0166] To a stirring suspension of magnesium powder (29 mg, 1.2 mmol, 5.4 equiv.) in diethyl ether (2mL), minimal iodine was added. The mixture was stirred until the suspension lost its red-brown color. Then, dimethylsilylbis(tetrahydro)indenylzirconium dichloride (101 mg, 0.221 mmol) in tetrahydrofuran (5 mL) was added. Then, isoprene (0.15 mL, 1.5 mmol, 6.8 equiv.). The reaction was stirred at room temperature for 19 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was stirred in pentane (10 mL). The resulting suspension was filtered over Celite, washing further with additional pentane (5 mL). The filtered solid was then extracted with toluene (10 mL, then 5 mL) and filtered over Celite. The combined toluene filtrate was concentrated under a stream of nitrogen at 40°C and then under high vacuum to afford the product as an orange oil, containing toluene (1.2 equiv.), tetrahydrofuran (1.3 equiv.), and minor impurities (114 mg, 85% yield, 5:1 mixture of isomers). ¹H NMR (400 MHz, C₆D₆), major isomer: δ 6.61 (d, 1H, $J = 3.2$ Hz), 6.15 (d, 1H, $J = 3.1$ Hz), 6.02 (d, 1H, $J = 3.2$ Hz), 4.81 (d, 1H, $J = 3.1$ Hz), 4.65 (t, 1H, $J = 9.8$ Hz), 3.47 (t, 1H, $J = 9.1$ Hz), 3.04-2.87 (m, 3H), 2.80-2.68 (m, 3H), 2.64-2.55 (m, 1H), 2.26-2.13 (m, 2H), 1.97 (s, 3H), 1.94 (s, 3H, potential impurity), 1.77-1.48 (m, 8H), 0.77 (s, 3H), 0.69 (s, 3H), 0.13-0.04 (m, 1H), -1.21--1.29 (m, 1H).

Catalyst I7 (preparation method 3)

[0167] Mg(isoprene)(THF) complex (0.55 g, 1.3 equiv.) was added as a solid to a stirring mixture of ZrCl₄ (0.586 g, 2.51 mmol) in dimethoxyethane at -30°C. The mixture became red and was allowed to stir for 30 minutes. After 30 minutes, the reaction mixture was cooled back in the freezer. Once cold, dilithium-dimethylsilyl-tetramethylcyclopentadienyl (2-Me-4-(3,5-Me₂-indenyl) ligand (1.25 g, 2.51 mmol) was added as a solid, and the reaction mixture was allowed to warm up to room temperature and was stirred overnight. After 18 hours, the dark reaction mixture was concentrated *in vacuo*. The resulting residue was extracted with toluene (3 x 30 mL) and filtered over celite and concentrated. The mixture was suspended in minimal pentane, stirred and filtered to afford brick-red powder which was spectroscopically pure (1.01 g, 70.5% yield). ¹H NMR (400 MHz, Benzene-d₆) δ 7.79 (d, 1H), 7.32 (s, 2H), 7.08 (m, 1H), 6.99 (m, 1H), 6.82 (s, 1H), 6.12 (s, 1H), 4.73 (t, 1H), 2.67 (dd, J = 9.6, 2.2 Hz, 1H), 2.34 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H), 2.16 (s, 6H), 1.79 (s, 3H), 1.32 (s, 3H), 1.28 (s, 3H), 1.03 (s, 3H), 0.91 (s, 3H), -0.96 (t, 1H), -1.37 (d, 1H). One Zr-isoprene resonance (1H) is likely obscured by tetramethylcyclopentadienyl signals.

15 **Catalyst 18 (preparation method 3)**

[0168] Mg(isoprene)(THF) complex (0.459 g, 1.3 equiv.) was added as a solid to a stirring mixture of ZrCl₄ (0.500 g, 2.15 mmol) in dimethoxyethane at -30°C. The mixture became red and was allowed to stir for 30 minutes. After 30 minutes, the reaction mixture was cooled back in the freezer. Once cold, dilithium-dimethylsilyl-tetramethylcyclopentadienyl (3-Ph-indenyl) ligand (0.98 g, 2.15 mmol) was added as a solid, and the reaction mixture was allowed to warm up to room temperature and was stirred overnight. After 18 hours, the dark reaction mixture was concentrated *in vacuo*. The resulting residue was extracted with toluene (3 x 30 mL) and filtered over celite and concentrated. The mixture was suspended in minimal pentane, stirred and filtered to afford brick-red powder which was spectroscopically pure (0.45 g, 39.7% yield). ¹H NMR (400 MHz, Benzene-d₆) δ 7.72 (m, 1H), 7.46 (m, 3H), 7.21 (m, 2H), 7.06 (m, 1H), 6.93 (m, 1H), 6.80 (m, 1H), 6.24 (s, 1H), 3.22 (t, 1H), 2.41 (s, 3H), 2.38 (d, 1H), 2.19 (s, 3H), 1.56 (s, 3H), 1.51 (s, 3H), 1.46 (t, 1H), 1.13 (s, 3H), 0.88 (s, 3H), 0.79 (s, 3H), -0.21 (t, 1H), -1.20 (d, 1H).

Catalyst 19 (preparation method 3)

30 [0169] Mg(isoprene)(THF) complex (0.459 g, 1.3 equiv.) was added as a solid to a stirring mixture of ZrCl₄ (0.500 g, 2.15 mmol) in dimethoxyethane at -30°C. The mixture became red and was allowed to stir for 30 minutes. After 30 minutes, the reaction mixture was cooled back in the freezer. Once cold, dilithium-dimethylsilyl-tetramethylcyclopentadienyl-(6,6-dimethyl-indacenyl)etherate ligand (0.963 g, 2.15 mmol) was added as a solid, and the reaction mixture

was allowed to warm up to room temperature and was stirred overnight. After 18 hours, the dark reaction mixture was concentrated *in vacuo*. The resulting residue was extracted with toluene (3 x 30 mL) and filtered over celite and concentrated. The mixture was re-extracted in pentane and concentrated. The resulting brick-red powder was further washed with minimal pentane to afford spectroscopically pure product (0.47 g, 42.1% yield). ¹H NMR (400 MHz, Benzene-d₆) δ 7.50 (s, 1H), 7.09 (s, 1H), 5.85 (d, 1H), 5.79 (dd, 1H), 3.79 (t, 1H), 2.73 (m, 1H), 2.58 (m, 4H), 2.28 (s, 3H), 2.26 (s, 3H), 2.12 (s, 3H), 1.51 (s, 3H), 1.50 (d, 1H), 1.26 (s, 3H), 1.10 (s, 3H), 1.02 (s, 3H), 0.95 (s, 3H), 0.79 (s, 3H), -0.31 (t, 1H), -1.41 (d, 1H).

Catalyst I10 (preparation method 3)

[0170] Mg(isoprene)(THF) complex (0.459 g, 1.3 equiv.) was added as a solid to a stirring mixture of ZrCl₄ (0.500 g, 2.15 mmol) in dimethoxyethane at -30°C. The mixture became red and was allowed to stir for 30 minutes. After 30 minutes, the reaction mixture was cooled back in the freezer. Once cold, dilithium-dimethylsilyl-tetramethylcyclopentadienyl (5,5,8,8-tetramethyl-5,6,7,8-tetrahydrocyclopenta[b]naphthalenyl)etherate ligand (1.05 g, 2.15 mmol) was added as a solid, and the reaction mixture was allowed to warm up to room temperature and was stirred overnight. After 18 hours, the dark reaction mixture was concentrated *in vacuo*. The resulting residue was extracted with toluene (3 x 30 mL) and filtered over celite and concentrated. The mixture was suspended in minimal pentane, stirred and filtered to afford brick-red powder which was spectroscopically pure (0.78 g, 64.7% yield). ¹H NMR (400 MHz, Benzene-d₆) δ 7.64 (s, 1H), 7.31 (s, 1H), 5.86 (d, 1H), 5.77 (dd, 1H), 3.66 (t, 1H), 2.68 (d, 1H), 2.30 (s, 3H), 2.26 (s, 3H), 2.14 (s, 3H), 1.60 (m, 5H), 1.50 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H), 1.22 (s, 3H), 0.98 (s, 3H), 0.80 (s, 3H), -0.31 (t, 1H), -1.47 (d, 1H).

General procedure for solution polymerization

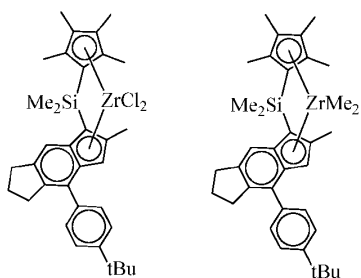
[0171] Unless stated otherwise, propylene homopolymerizations and ethylene-propylene copolymerizations (if any) were carried out in a parallel, pressure reactor, as generally described in US Pat. Nos. 6,306,658; 6,455,316; 6,489,168; WO2000/009255; and Murphy *et al.* (2003) *J. Am. Chem. Soc.*, v.125, pp. 4306-4317, each of which is fully incorporated herein by reference for US purposes. Although the specific quantities, temperatures, solvents, reactants, reactant ratios, pressures, and other variables may have changed from one polymerization run to the next, the following describes a typical polymerization performed in a parallel, pressure reactor.

[0172] **Propylene Polymerization with Metallocene:** A pre-weighed glass vial insert and disposable stirring paddle were fitted to each reaction vessel of the reactor, which contains 48 individual reaction vessels. The reactor was then closed and propylene (typically 1 mL) was

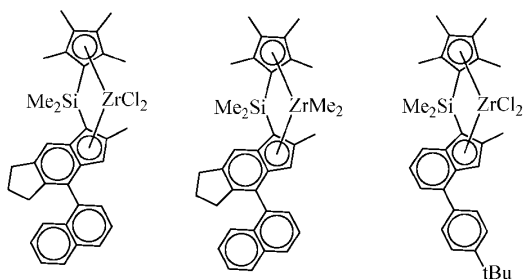
introduced to each vessel as a condensed gas liquid (typically 1 mL) (as shown in examples in Table 1) or gas (as shown in the examples in Table 3). Then solvent (typically the isohexane) was added to bring the total reaction volume, including the subsequent additions, to 5 mL and the reactor vessels were heated to their set temperature (usually from about 50°C to about 110°C). The contents of the vessel were stirred at 800 rpm. An activator solution (typically 100-1,000 molar equivalents of methyl alumoxane (MAO) in toluene) was then injected into the reaction vessel along with 500 microliters of toluene, followed by a toluene solution of catalyst (typically 0.50 mM in toluene, such as 20-40 nanomols of catalyst) and another aliquot of toluene (500 microliters). Equivalence is determined based on the mol equivalents relative to the moles of the transition metal in the catalyst complex. The reaction was then allowed to proceed until a pre-determined amount of pressure had been taken up by the reaction. Alternatively, the reaction may be allowed to proceed for a set amount of time. At this point, the reaction was quenched by pressurizing the vessel with compressed air. After the polymerization reaction, the glass vial insert containing the polymer product and solvent was removed from the pressure cell and the inert atmosphere glove box, and the volatile components were removed using a Genevac HT-12 centrifuge and Genevac VC3000D vacuum evaporator operating at elevated temperature and reduced pressure. The vial was then weighed to determine the yield of the polymer product. The resultant polymer was analyzed by Rapid GPC (see below) to determine the molecular weight and by DSC (see below) to determine melting point.

[0173] One advantage of the approach described in this application is that the catalysts are discrete molecules and do not require modifications to the existing polymerization processes (no additional need to build costly feeding systems for kinetic modifier feeding).

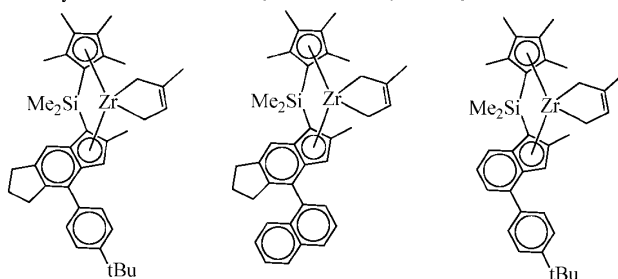
[0174] To demonstrate the advantage of using isoprenyl catalysts, the following complexes were prepared and tested in propylene polymerization using parallel pressure reactors (PPR) using MAO activation at polymerization temperature at both 70°C and 100°C. The top row represents comparative catalysts with chloride and methyl ligands as leaving groups, whereas bottom row shows inventive examples with isoprenyl leaving groups. The list of other isoprenyl catalysts is shown at the bottom.



Catalyst C1 - dichloride Catalyst C1 - dimethyl



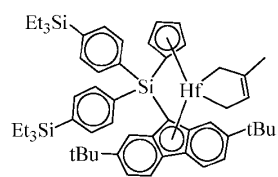
Catalyst C2 - dichloride Catalyst C2 - dimethyl Catalyst C3 - dichloride



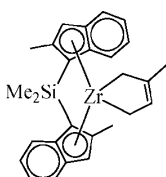
Catalyst I1

Catalyst I2

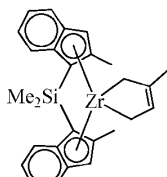
Catalyst I3



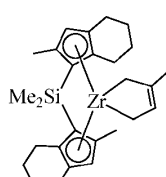
Catalyst I4



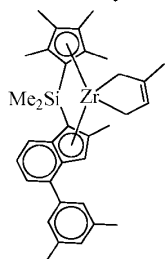
Catalyst I5-rac



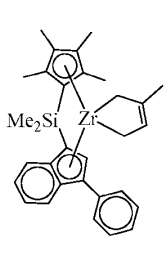
Catalyst I5-meso



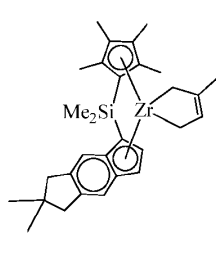
Catalyst I6



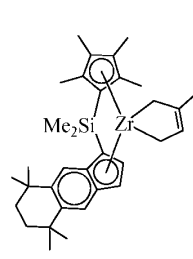
Catalyst I7



Catalyst I8



Catalyst I9



Catalyst I10

[0175] The results from propylene polymerization are shown below. As it can be observed in FIGs. 1 and 2, inventive catalysts bearing isoprenyl moiety demonstrate faster activation kinetics compared to inventive catalysts I1 - I3 bearing identical ligand structure. For example, the activation time was fastest for dimethyl analogs (<50 s), followed by dichlorides (~50 s), whereas the activation time for inventive catalysts I1 – I3 was usually >75 s. In addition to this, initial rates upon activation (excluding the activation induction period) appear similar regardless of the nature of the leaving group (Figure 3). For example, the initial rate of isoprenyl analog I1 was 0.14 psi/s – a value comparable to initial rate of C₁ dichloride (0.17 psi/s) and C₁-dimethyl (0.19 psi/s). The combination of these results indicate that inventive catalysts indeed demonstrate delay in activation, while maintaining high catalyst activity in propylene polymerization. In addition to above mentioned benefits, isoprenyl catalysts also demonstrate slightly improved Mw capability relative to control dichloride and dimethyl analogs especially at 70°C polymerization temperature (Table 1 and Table 2).

Table 1 Polymerization data at T_p = 70°C. Data is represented as average of 3 runs.

Example #	Catalyst	Yield (mg)	Mn (g/mol)	Mw (g/mol)	PDI
1	C1-dichloride	213.8	41,214	90,221	2.19
2	C1-dimethyl	282.6	31,709	74,308	2.34
3	I1	238.6	42,227	93,277	2.21
4	C2-dichloride	276.9	38,519	87,177	2.26
5	C2-dimethyl	259.7	39,644	81,951	2.07
6	I2	278.3	46,740	104,825	2.24
7	C3-dichloride	218.9	38,064	87,337	2.29
8	I3	205.6	51,472	105,996	2.06

Table 2 Polymerization data at T_p = 100°C. Data is represented as average of 3 runs.

Example #	Catalyst	Yield (mg)	Mn (g/mol)	Mw (g/mol)	PDI
9	C1-dichloride	123.5	10,166	20,377	2.00
10	C1-dimethyl	199.4	7,045	18,108	2.57
11	I1	144.7	10,468	20,948	2.00
12	C2-dichloride	157.1	12,049	24,173	2.01
13	C2-dimethyl	152.7	10,090	23,395	2.32
14	I2	173.0	10,679	25,311	2.37
15	C3-dichloride	139.2	10,535	24,543	2.33
16	I3	137.2	12,128	23,646	1.95

[0176] FIG. 1 is a graph illustrating pressure uptake kinetics (psi/s) for propylene polymerization at 70°C. Data is shown as running average of 3 replicates for clarity. FIG. 2 is a graph illustrating pressure uptake kinetics (psi/s) for propylene polymerization at 100°C. Data is shown as running average of 3 replicates for clarity. Linear fit is shown with slopes of each curve corresponding to uptake rates (in psi/s). FIG. 3 is a graph illustrating initial rates after activation induction period for catalysts C1-dichloride, C1-dimethyl and I1.

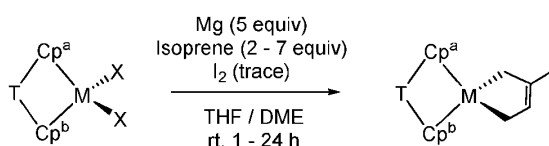
[0177] In addition, inventive catalysts demonstrate significantly increased solubility relative to comparative catalysts. Solubility estimates are described in Table 4. All comparative example catalysts did not fully dissolve at the indicated amounts in 20 mL of isohexane. However, inventive catalysts I1-I3 showed remarkable solubility and were able to prepare more concentrated solutions in isohexane between 4.72 and 18.39 mM. This solubility effect originates from isoprenyl leaving group and the effect can be leveraged for preparation of non-aromatic hydrocarbon soluble catalysts and their implementation in non-aromatic processes.

Table 3 Solubility estimates for prepared catalysts

Catalyst	mmol dry cat used	isohexane (mL)	Final solubility (mM)
C1-dichloride	2.67E-05	20.00	Not fully soluble
C1-dimethyl	3.45E-05	20.00	Not fully soluble
I1	3.48E-05	9.00	6.96
C2-dichloride	2.96E-05	20.00	Not fully soluble
C2-dimethyl	3.97E-05	20.00	Not fully soluble
I2	3.31E-05	13.00	4.72
C3-dichloride	3.68E-05	20.00	Not fully soluble
I3	3.68E-05	3.00	18.39

General synthesis of isoprenyl catalysts I1 – I3 (method 1).

[0178] Unless otherwise noted, all catalysts were isolated using method 1.



Where:

Cp^a and Cp^b = substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl ligand

M = Group IV metal

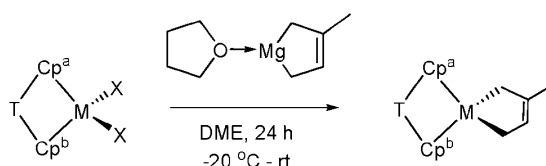
T = optional bridging group

[0179] In general, isoprenyl complexes can be prepared according to scheme above. A

single crystal of I₂ was slowly added to a stirring mixture of Mg powder (5 equiv.) in diethylether. While stirring, a THF solution of metallocene dichloride (1 equiv.) was added, followed by addition of 2-7 equiv. of isoprene. The reaction mixtures were stirred for 1-24 hours at room temperature. Solvent was removed *in vacuo* and the residue was extracted with pentane or benzene (2 x 10 mL) and filtered over celite. Solvent removal afforded title catalysts 11-13.

General synthesis of isoprenyl catalysts (method 2).

[0180] Alternatively, isoprenyl complexes can be isolated by reacting >1 equiv. of Mg(isoprene)(thf) adduct in ethereal solvent, most preferably dimethoxyethane. Typically, desired metallocene is suspended in solvent, and solid magnesium isoprene complex is added. The reaction mixtures were stirred for 1-24 hours at room temperature. Solvent was removed *in vacuo* and the residue was extracted with pentane or benzene (2 x 10 mL) and filtered over celite. Solvent removal affords isoprenyl metallocenes analogous to method 1.



Where:

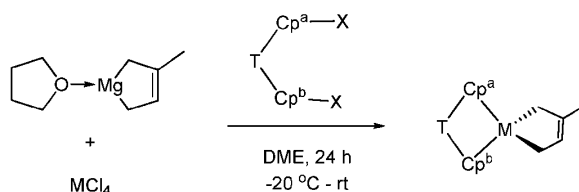
Cp^a and Cp^b = substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl ligand

M = Group IV metal

T = optional bridging group

General synthesis of isoprenyl catalysts (method 3).

[0181] Another alternate method involves *in situ* treatment of MCl_4 (M = Zr, Hf, Ti) with Mg(isoprene)(thf) adduct in ethereal solvent, most preferably dimethoxyethane at reduced temperature. Addition of group I ligand salt X (such as Na, Li, K) to this solution of the general formula $\text{X}_2(\text{Cp}^a)(\text{T})(\text{Cp}^b)$, where Cp^a is the same or different from Cp^b and constitutes substituted or unsubstituted cyclopentadienyl, fluorenyl or indenyl ligand and T is a bridging group, yields desired isoprenyl complexes. The reaction mixtures were then stirred for 1-24 hours at room temperature. Solvent removal *in vacuo* and extraction with pentane or benzene affords isoprenyl metallocenes analogous to methods 1 and 2.



Where:

Cp^a and Cp^b = substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl ligand

X = Group I alkali metal

M = Group IV metal

T = optional bridging group

Gel Permeation Chromatography

[0182] High temperature size exclusion chromatography was performed using an automated "Rapid GPC" system as described in US Patent Nos. 6,175,409; 6,260,407; 6,294,388; 6,406,632; 6,436,292; 6,454,947; 6,461,515; 6,475,391; 6,491,816; and 6,491,823; 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 index (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 μ L 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 10 μ m 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, 2, and 3 under the headings Mn, Mw and PDI as defined above. PDI values marked with an "^^" indicate that the ELSD was used; no additional marking indicates that the dual wavelength infrared detector was used.

Differential Scanning Calorimetry

[0183] 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 3 under the heading, Tm (°C).

FTIR

[0184] Samples for infrared analysis were prepared by depositing the stabilized polymer solution onto a silanized wafer. By this method, approximately between 0.12 mg 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. For ethylene-1-octene copolymers, the wt% octene in the copolymer was determined via measurement of the methyl deformation band at $\sim 1375\text{ cm}^{-1}$. The peak height of this band was normalized by the combination and overtone band at $\sim 4321\text{ cm}^{-1}$, which corrects for path length differences. The normalized peak height was correlated to individual calibration curves from ^1H NMR data to predict the wt% octene content within a concentration range of ~ 2 to 35 wt% for octene. Typically, R^2 correlations of 0.98 or greater are achieved. These numbers are reported in Table 3 under the heading C8 (wt%).

^{13}C NMR

[0185] ^{13}C NMR spectroscopy was used to characterize some propylene polymer samples produced in experiments collected in Table 2. Unless otherwise indicated the polymer samples for ^{13}C NMR spectroscopy were dissolved in d_2 -1,1,2,2-tetrachloroethane and the samples were recorded at 125°C using a NMR spectrometer with a ^{13}C NMR frequency of 150 MHz. Polymer resonance peaks are referenced to $\text{mmmm}=21.8\text{ ppm}$. Calculations involved in the characterization of polymers by NMR follow the work of F. A. Bovey in "Polymer Conformation and Configuration" Academic Press, New York 1969 and J. Randall in "Polymer Sequence Determination, Carbon-13 NMR Method", Academic Press, New York, 1977.

[0186] The stereodefects measured as "stereo defects/10,000 monomer units" are calculated from the sum of the intensities of mmrr , $\text{mmrm}+\text{rrmr}$, and rmmr resonance peaks times 5000. The intensities used in the calculations are normalized to the total number of monomers in the sample. Methods for measuring 2,1 regio defects/10,000 monomers and 1,3 regio defects/10,000 monomers follow standard methods. Additional references include Grassi, A. et.al., (1988) *Macromolecules*, v.21, pp. 617-622 and Busico et.al., (1994) *Macromolecules*, v. 27, pp. 7538-7543. The average meso run length = $10000/[(\text{stereo defects}/10000\text{ C}) + (2,1\text{-regio defects}/10000\text{ C}) + (1,3\text{-regio-defects}/10000\text{ C})]$.

Differential Scanning Calorimetry (DSC-2):

[0187] Peak melting point, T_m , described for larger scale reactor batches (also referred to as melting point) and peak crystallization temperature, T_c , (also referred to as crystallization temperature) are determined using the following DSC procedure. Differential scanning calorimetric (DSC-2) data can be obtained using a TA Instruments model DSC2500 machine. Samples weighing approximately 5 mg to 10 mg are sealed in an aluminum hermetic sample pan and loaded into the instrument at about room temperature. The DSC data are recorded by

first gradually heating the sample to 220°C at a rate of 10°C/minute in order to erase all thermal history. The sample is kept at 220°C for 5 minutes, then cooled to -10°C at a rate of 10°C/minute, followed by an isothermal for 5 minutes and heating to 220°C at 10°C/minute, holding at 220°C for 5 minutes and then cooling down to 25°C at a rate of 10°C/minute. Both the first and second cycle thermal events were recorded. The melting and crystallization temperatures reported here were obtained during the second heating/cooling cycle unless otherwise noted.

[0188] Overall, metallocene catalyst compounds (such as *ansa*-metallocene catalyst compounds) of the present disclosure provide improved catalysts, catalyst systems, and polymerization methods. It has been discovered that *ansa*-metallocene catalyst compounds having 5-membered metallocycle rings (incorporating the catalytic metal as part of the 5-membered metallocycle) can provide delayed catalyst activation while maintaining a high activity profile and not requiring catalyst reactivation while providing polymers of substantial functional equivalence. In addition to delayed activation kinetics, such catalysts (and catalyst systems thereof) have excellent solubility, rendering them applicable for toluene free processes both in solution or as supported catalyst systems (slurry or gas phase). The combination of delayed activation kinetics and excellent solubility reduce or eliminate plugging of feed lines and/or reactor components and allow polymers made can be used in end use applications such as food packaging or medical applications.

[0189] 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.

[0190] 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.

[0191] 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

5 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,”

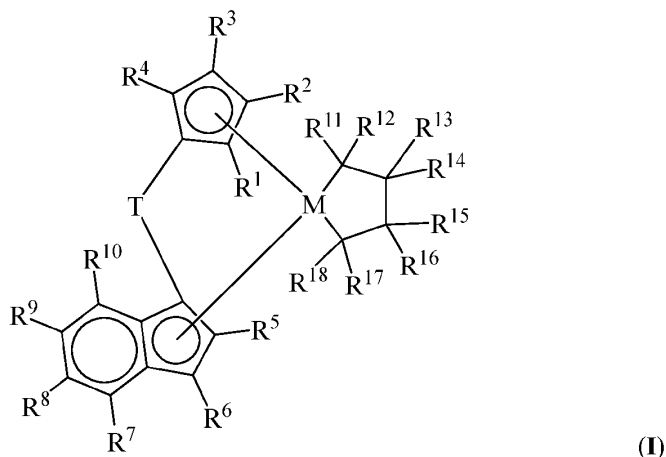
10 “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

[0192] 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

15 of the present disclosure.

CLAIMS:*We claim:*

1. A compound represented by Formula (I):



- 5 wherein:

M is a group 3 metal, group 4 metal, or group 5 metal;

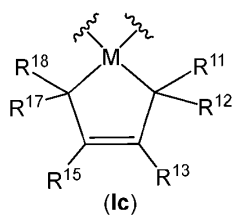
- each of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , and R^{10} is independently hydrogen, substituted or unsubstituted hydrocarbyl, a substituted or unsubstituted heteroatom, or a substituted or unsubstituted heteroatom-containing group, or one or more of R^1 and R^2 , R^2 and R^3 , R^3 and R^4 , R^5 and R^6 , R^7 and R^8 , R^8 and R^9 , are joined to form a substituted or unsubstituted completely saturated ring or a substituted or unsubstituted aromatic ring;

- T represents the bridging group of the formula R^a_2J or $(R^a)_4J_2$ wherein each J is independently C, Si, or Ge, and each R^a is independently hydrogen, halide, a substituted or unsubstituted C_1 to C_{40} hydrocarbyl, or two R^a can form a substituted or unsubstituted completely saturated ring or a substituted or unsubstituted partially saturated ring; and

each of R^{11} , R^{13} , R^{15} , and R^{17} is independently hydrogen or substituted or unsubstituted hydrocarbyl,

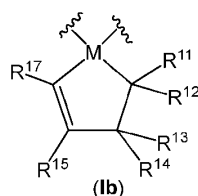
- wherein each of R^{12} , R^{14} , R^{16} , and R^{18} , if present, is independently hydrogen or substituted or unsubstituted hydrocarbyl, but the 5-membered metallocyclic ring of Formula (I) can optionally have one or two carbon-carbon double bonds such that two or more of R^{12} , R^{14} , R^{16} , or R^{18} are not present.

2. The compound of claim 1, wherein the 5-membered metallocycle ring of Formula (I) has the structure of Formula (Ic):



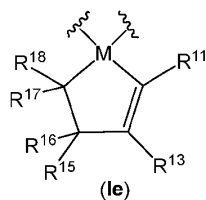
wherein M is a group 4 metal and each of R¹¹, R¹², R¹³, R¹⁵, R¹⁷, and R¹⁸ is independently hydrogen or unsubstituted C₁-C₁₀ alkyl.

- 5 3. The compound of claim 2, wherein R¹⁵ is hydrogen and R¹³ is unsubstituted C₁-C₁₀ alkyl.
4. The compound of claim 1, wherein the 5-membered metallocycle ring of Formula (I) has the structure of Formula (Ib):



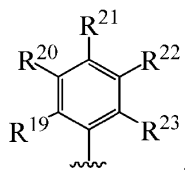
wherein M is a group 4 metal and each of R¹¹, R¹², R¹³, R¹⁴, R¹⁵, and R¹⁷ is independently hydrogen or unsubstituted C₁-C₁₀ alkyl.

5. The compound of claim 1, wherein the 5-membered metallocycle ring of Formula (I) has the structure of Formula (Ie):

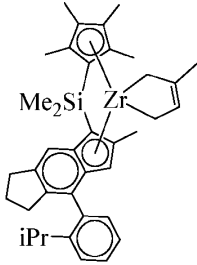
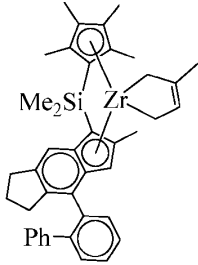
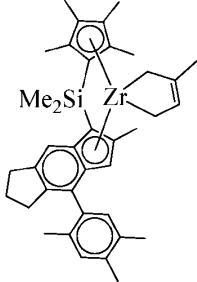
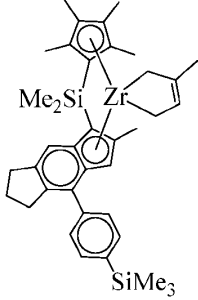
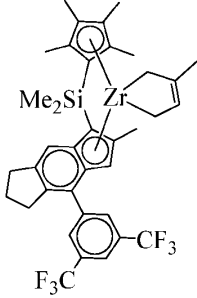
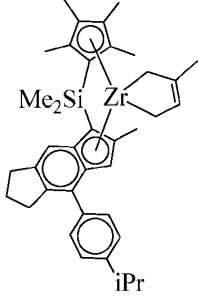
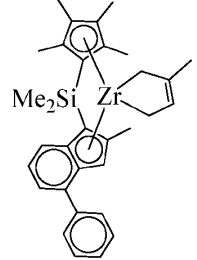
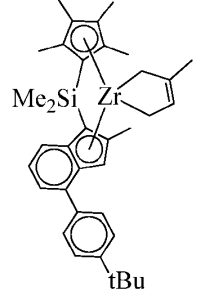


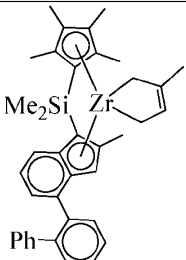
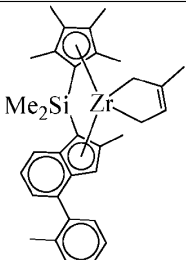
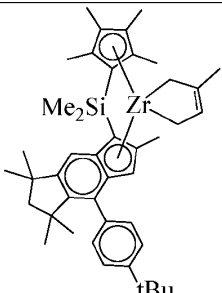
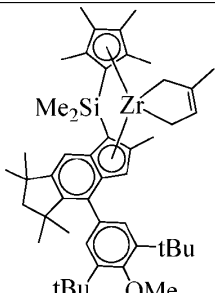
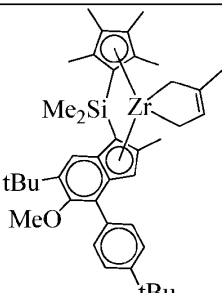
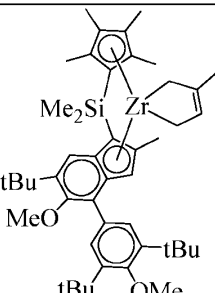
wherein M is a group 4 metal and each of R¹¹, R¹³, R¹⁵, R¹⁶, R¹⁷, and R¹⁸ is independently hydrogen or unsubstituted C₁-C₁₀ alkyl.

- 20 6. The compound of claim 1, wherein R⁷ is a substituted or unsubstituted aryl group.
7. The compound of claim 6, wherein R⁷ is an aryl group represented by the formula:

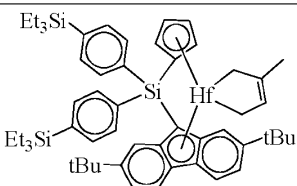
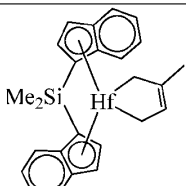


- wherein each of R^{19} , R^{20} , R^{21} , R^{22} , and R^{23} is independently hydrogen, hydrocarbyl, a heteroatom, or heteroatom-containing group, or one or more of R^{19} and R^{20} , R^{20} and R^{21} , R^{21} and R^{22} , or R^{22} and R^{23} are joined to form a completely saturated, partially saturated, or aromatic ring.
8. The compound of claim 7, wherein R^{21} is C_1 - C_{10} alkyl or alkoxide.
 9. The compound of claim 1, wherein R^5 is C_1 - C_{10} alkyl.
 10. The compound of claim 9, wherein R^5 is methyl.
 11. The compound of claim 1, wherein R^8 and R^9 are joined to form a substituted or unsubstituted completely saturated C_5 ring, a substituted or unsubstituted completely saturated C_6 ring, or an aromatic C_6 ring.
 12. The compound of claim 1, wherein each of R^1 , R^2 , R^3 , and R^4 is independently selected from the group consisting of methyl, ethyl, and propyl.
 13. The compound of claim 1, wherein T is selected from the group consisting of $SiMe_2$, $Si(CH_2CH_3)_2$, or $Si(CH_2CH_2CH_3)_2$.
 14. The compound of any of claims 1 to 13, wherein M is Zr or Hf.
 15. The compound of claim 1, wherein the 5-membered metallocyclic ring of Formula (I) has one carbon-carbon double bond.
 16. The compound of claim 1, wherein:
 - M is Zr or Hf;
 - T is $SiMe_2$, $Si(CH_2CH_3)_2$, or $Si(Ph)_2$;
 - each of R^6 , R^8 , R^9 , and R^{10} is independently hydrogen or substituted or unsubstituted C_1 - C_{10} alkyl;
 - each of R^1 , R^2 , R^3 , and R^4 is independently methyl, ethyl, or propyl;

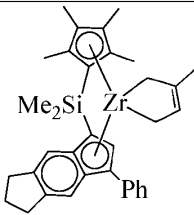
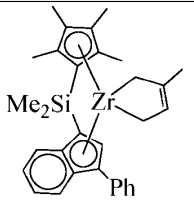
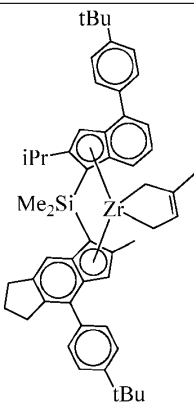
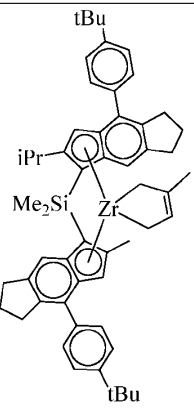
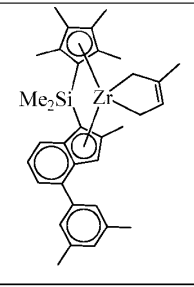
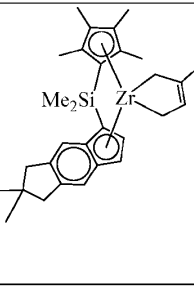
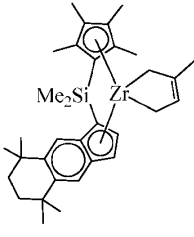
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18. The compound of claim 1, wherein the compound is selected from the group consisting of:

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33		34	
35		36	
37			

19. A catalyst system comprising an activator, the compound of any of claims 1 to 18, and an optional support material.

- 5 20. A process for producing olefin homopolymer or copolymer, the process comprising:
 polymerizing one or more olefins selected from the group consisting of one more C₂-C₂₀ alpha-olefins, by introducing one or more C₂-C₂₀ alpha olefins, optionally hydrogen

with a catalyst system of any of claims 19 to 20, in solution, gas phase or slurry reactor, in series, or in parallel, at a reactor pressure of 0.05 MPa to 1,500 MPa and a reactor temperature of 30°C to 230°C to form the alpha olefin homopolymer or copolymer.