

METALLOCENE CATALYST COMPOUNDS FOR PRODUCING POLYOLEFINS

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5 **CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of and priority to US Provisional Application No. 63/604966 filed December 1, 2023, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

10 [0002] The present disclosure relates to *ansa*-metallocene catalyst compounds, catalyst systems comprising such compounds, and uses thereof.

BACKGROUND OF THE INVENTION

15 [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.

[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 systems that provide polymers having specific properties, including tunable molecular weights, high activity, and good mechanical properties (*e.g.*, provided by melting point).

20 [0005] In particular, polypropylene (PP) is a polymer that has a large variety of uses. Processes for the manufacture of polypropylene have evolved with improvement in catalyst technology, from complex slurry processes using an inert hydrocarbon diluent, to simpler bulk processes using liquid propylene diluent, to simplified gas phase processes.

25 [0006] However, metallocene catalysts show high sensitivity to exothermic deactivation caused by heat generation within the polymer particle that is formed during such polymerizations. Deactivation is particularly prevalent under conditions with high hydrogen concentrations, erratic heat generation, and insufficient removal of polymer from the reactor, which often leads to loss of particle integrity, leading to fines, and potentially reactor fouling. Often times, highly active catalyst systems can be used with lower reactor loadings of a catalyst system, however, this makes a catalyst more susceptible to impurities and consequent deactivation.

[0007] In addition, regarding end uses of polymers, polymer products used for non-woven fibers should have narrow polydispersity (*e.g.*, to reduce or eliminate fractions of low molecular weight tails to provide improved tensile strength of polypropylene for fiber applications and eliminate volatile organic compounds (VOCs)) and have high isotacticity (again to provide desired stiffness of polypropylene), but with broad melt flow rate (MFR) capability to provide tailored/improved mechanical properties in the area of both meltblown and spunbound fibers, such as those used in medical applications. In addition to fiber application, additional uses of materials with high and tunable stiffness, narrow polydispersities, low volatile organic compounds and xylene solubles, and broad melt flow rate (MFR) lie in injection molding, blown and cast film where such properties are desired.

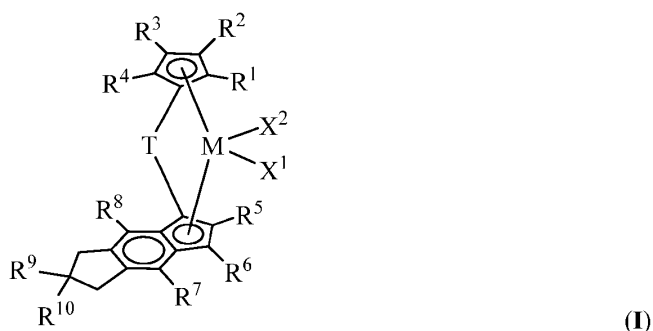
[0008] There is a need for new metallocene catalyst compounds having high activity and low sensitivity to exothermic deactivation and capable of providing polymer products used for medical materials, the polymer products have narrow polydispersity and isotacticity, but with broad melt flow rate (MFR) capability.

[0009] References for citing in an Information Disclosure Statement (37 C.F.R. 1.97(h)): US 9,266,910; US 11,352,386; US 2021/0317239; EP 4017887; JP 6840464; JP 7069284; KR 181114; KR 10-2444573B1; KR 2021056830; WO 2020/184887; WO 2020/251264A; WO 2023/034889.

SUMMARY OF THE INVENTION

[0010] The present disclosure relates to *ansa*-metallocene catalyst compounds, catalyst systems comprising such compounds, and uses thereof.

[0011] In some embodiments, a compound is represented by Formula (I):



wherein:

- 25 M is a group 3 metal, group 4 metal, or group 5 metal;
 T is a bridging group;
 each of X¹ and X² is independently a univalent anionic ligand, or X¹ and X² are joined

to form a metallocycle ring;

R¹, R², R³, and R⁴ are each independently a hydrogen atom or substituted or unsubstituted C₁ to C₆ hydrocarbyl group and, optionally, any adjacent R¹, R², R³ and R⁴ can be joined to form a cyclic structure;

5 R⁵ is a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group;

R⁶ and R⁸ are each independently a hydrogen atom or a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group;

R⁷ is a substituted aryl group, unsubstituted naphthyl, unsubstituted anthracenyl, or substituted or unsubstituted heteroaryl group; and

10 R⁹ and R¹⁰ are each independently a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group.

[0012] In some embodiments, a process for producing olefin homopolymer or copolymer includes polymerizing one or more olefins, selected from one or more C₂-C₂₀ alpha-olefins, by introducing the one or more C₂-C₂₀ alpha olefins and optionally hydrogen with a catalyst system of the present disclosure, in solution, gas phase or slurry reactor, in series, or in parallel, at a reactor pressure of about 0.05 MPa to about 1,500 MPa, and a reactor temperature of about 30°C to about 230°C to form the alpha olefin homopolymer or copolymer.

BREIF DESCRIPTION OF DRAWINGS

20 [0013] FIG. 1 is graphs illustrating catalyst productivity of inventive catalysts and comparative catalysts, according to some embodiments.

[0014] FIG. 2 is histogram illustrating catalyst productivity as a function of example type (top chart) and as a function of hydrogen in reactor (bottom), according to some embodiments.

[0015] FIG. 3 is a graph illustrating average polymer melting points taken across the hydrogen gradient in reactor. Error bars represent the range of melting points obtained at two 25 hydrogen extremes (2 mmol and 15 mmol).

[0016] FIG. 4 is a graph illustrating polymer Mw as a function of hydrogen loading in the reactor, according to some embodiments.

[0017] FIG. 5 is a graph illustrating molecular weight distribution (MWD) dependence on hydrogen loading in the reactor, according to some embodiments.

30 [0018] FIG. 6 is a graph illustrating flexural modulus of iPP produced as a function of mmol H₂ in reactor, according to some embodiments.

[0019] FIG. 7 is a graph illustrating Young's modulus of iPP produced as a function of mmol H₂ in reactor, according to some embodiments.

[0020] FIG. 8 is a graph illustrating tensile strength at yield of iPP produced as a function

of mmol H₂ in reactor, according to some embodiments.

DETAILED DESCRIPTION

[0021] The present disclosure relates to *ansa*-metallocene catalyst compounds, catalyst systems comprising such compounds, and uses thereof. Catalyst compounds of the present disclosure can have high activity and low sensitivity to exothermic deactivation. Catalyst compounds can be capable of providing polymers suitable for use in medical materials.

[0022] Catalyst compounds of the present disclosure can have 2,6,6-substituted-indacenyl moieties in combination with a substituted aryl moiety at the 4-position of the indacenyl ring. It has been discovered that these catalysts exhibit excellent activities, provide high melting points, and have broad molecular weight capabilities particularly for propylene polymerization. Relative to other tetrahydroindacene catalyst systems, catalyst compounds of the present disclosure show significant improvement in supported catalyst activities in preparation of isotactic polypropylene, while also demonstrating excellent reactor operability and granule morphology. For example, granules can be obtained that are not substantially powdery, as powdery material can cause static, stickiness, and ultimately fouling and reactor shutdowns.

[0023] In addition to improved operability, it has been discovered that broad polymer product capability can be achieved. For example, polymers of the present disclosure can have narrow polydispersity, robust isotacticity, and broad melt flow rate (MFR) capability. High MFR can be provided by high hydrogen loading in the reactor, which catalysts of the present disclosure are amenable to.

[0024] Higher activity achieved while maintaining relatively comparable molecular weight capability and narrow polydispersities (PDI) represents a clear advantage of using catalyst systems based on 6,6-dimethylindacenes. Such molecular weight capability range corresponds to a broad MFR range (1 – 1000 MFR), thus significantly extending the applicability of *ansa*-metallocene catalysts. In addition to above mentioned benefits, catalysts tested were able to maintain narrow MWD while eliminating higher fractions of low molecular weight tails. Such benefit allows for preparation of resins for fiber spinning (spunbound and meltblown) and injection molding articles used in medical applications, all which involve cleanliness, narrow polydispersities, low volatile organic compounds (VOCs) and low odor. In addition, high melting points of polypropylene provided by catalyst compounds of the present disclosure allows for improved stiffness for rigid parts, allowing application of polypropylene for impact copolymers commonly used in automotive industry. Polypropylenes of the present disclosure can have improved stiffness (*e.g.*, provided by 2,6,6-trimethylsubstitution of catalyst compounds). In addition to improved stiffness, polypropylenes can have significantly improved

tensile properties, especially at higher hydrogen loadings (and thus polymer MFR).

[0025] The following abbreviations may be used herein: Me is methyl, iPr is isopropyl, tBu is *tert*-butyl, Ph is phenyl, OMe is methoxy, PDI is polydispersity index, MWD is molecular weight distribution, MAO is methylalumoxane, SMAO is supported methylalumoxane, NMR is nuclear magnetic resonance, ppm is part per million, THF is tetrahydrofuran.

[0026] 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.

[0027] The terms "substituent," "radical," "group," and "moiety" may be used interchangeably.

[0028] 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.

[0029] As used herein, "polyethylene" can include "ethylene homopolymer", "ethylene copolymer", or combinations thereof. "Polypropylene" can include "propylene homopolymer", "propylene copolymer", or combinations thereof.

[0030] The term "alpha-olefin" refers to an olefin having a terminal carbon-to-carbon

double bond in the structure thereof ((R''R''')-C=CH₂, 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.

5 [0031] For the purposes of the present disclosure, ethylene shall be considered an alpha-olefin.

[0032] 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) 10 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 C₁-C₅₀ alkyl group refers to an alkyl group including carbon atoms at a total number thereof of 15 about 1 to about 50.

[0033] Unless otherwise indicated, 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, 20 -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.

[0034] The terms "hydrocarbyl radical," "hydrocarbyl group," or "hydrocarbyl" may be 25 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, 30 cyclohexyl, cyclooctyl, and aryl groups, such as phenyl, benzyl, naphthyl.

[0035] 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.

[0036] 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.

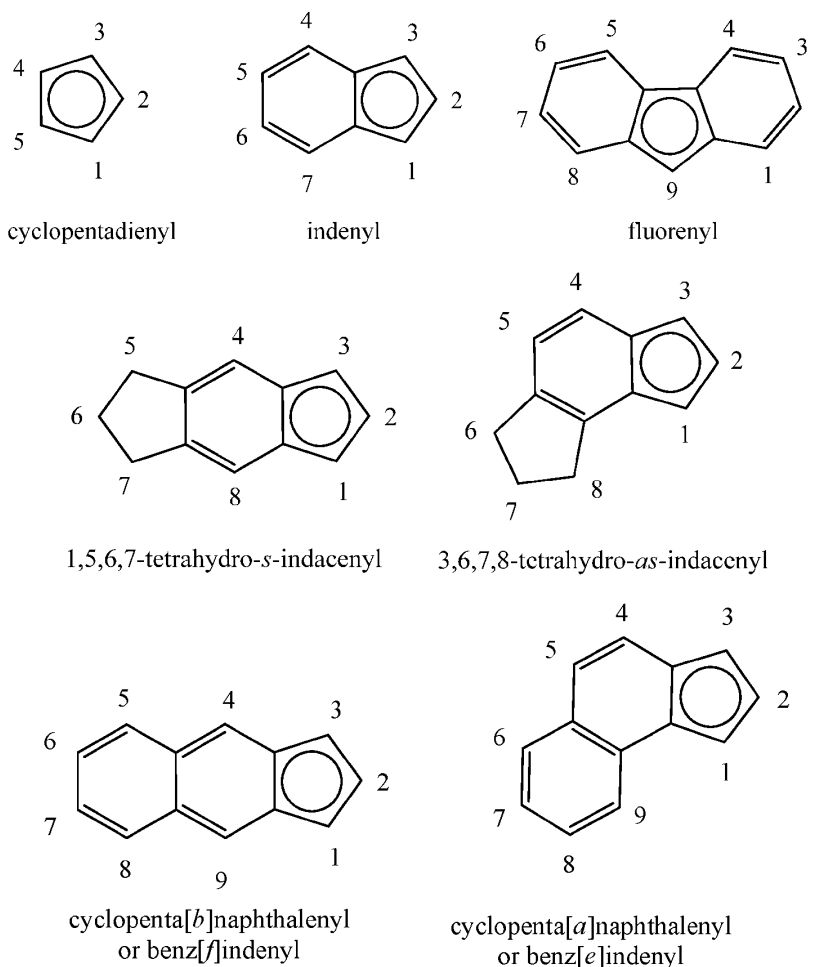
- 5 Examples of suitable alkenyl radicals can include ethenyl, propenyl, allyl, 1,4-butadienyl, cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cycloctenyl, including their substituted analogues.

[0037] 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

- 10 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, 15 1-propylpentyl, 1-phenylethyl, i-propyl, 2-butyl, sec-pentyl, sec-hexyl, and the like.

[0038] 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
20 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.

[0039] For nomenclature purposes, the following numbering schemes are used for cyclopentadienyl, indenyl, fluorenyl, cyclopenta[*b*]naphthalenyl (also termed benz[*e*]indenyl),
25 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,
30 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.



[0040] 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.

[0041] 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.

[0042] 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).

[0043] 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.

[0044] 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).

[0045] 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.

[0046] 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.

[0047] 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.

[0048] The terms "catalyst compound", "catalyst complex", "transition metal complex", "transition metal compound", "precatalyst compound", and "precatalyst complex" are used interchangeably.

[0049] 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.

5 [0050] 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
10 heterocycles. Examples of heterocyclic Lewis bases include pyridine, imidazole, thiazole, and furan.

[0051] 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
15 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.

[0052] 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
20 and polymer product is continually withdrawn.

[0053] 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
25 may be not turbid as described in J. Vladimir Oliveira, C. Dariva and J. C. Pinto, *Ind. Eng. Chem. Res.*, 2000, v,29, p. 4627.

[0054] 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
30 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%.

[0055] 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.

[0056] 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.

[0057] 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.

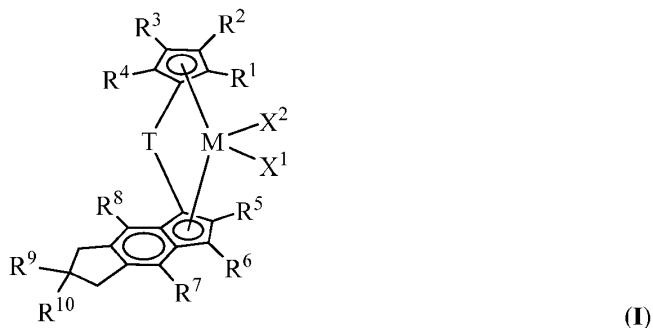
[0058] Noncoordinating anion (NCA) means an anion either that does not coordinate to the catalyst metal cation or that does coordinate to the metal cation, but only weakly. The term NCA is also defined to include multicomponent NCA-containing activators, such as N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, 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.

[0059] The terms “process” and “method” are used interchangeably.

Catalyst Compounds

[0060] This disclosure relates to metallocene catalyst compounds represented by

Formula (I):



where:

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);

T is a bridging group;

each of X¹ and X² is independently a univalent anionic ligand, or X¹ and X² are joined to form a metallocycle ring;

R¹, R², R³, and R⁴ are each independently a hydrogen atom or substituted or unsubstituted C₁ to C₆ hydrocarbyl group and, optionally, any adjacent R¹, R², R³ and R⁴ can be joined to form a cyclic structure;

R⁵ is a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group;

R⁶ and R⁸ are each independently a hydrogen atom or a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group;

R⁷ is a substituted aryl group, unsubstituted naphthyl, unsubstituted anthracenyl, or substituted or unsubstituted heteroaryl group; and

R⁹ and R¹⁰ are each independently a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group.

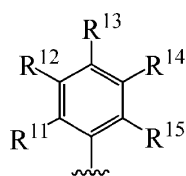
[0061] In some embodiments, R¹, R², R³, and R⁴ are each independently substituted or unsubstituted C₁ to C₆ hydrocarbyl group. In some embodiments, R¹, R², R³, and R⁴ are each independently selected from methyl, ethyl, propyl, butyl, pentyl, and hexyl. In some embodiments, each of R¹, R², R³, and R⁴ is independently methyl, ethyl, or propyl. In some embodiments, R¹, R², R³, and R⁴ are each methyl.

[0062] In some embodiments, R⁵ is an unsubstituted C₁ to C₂₀ hydrocarbyl group. In some embodiments, R⁵ is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl. In some embodiments, R⁵ is a primary substituted or unsubstituted C₁-C₁₂ alkyl group, such as methyl, ethyl, propyl, isopropyl, butyl, iso-butyl, sec-butyl, pentyl,

isopentyl, neopentyl. In some embodiments, R^5 is C_1 - C_{10} alkyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl). In some embodiments, R^5 is methyl.

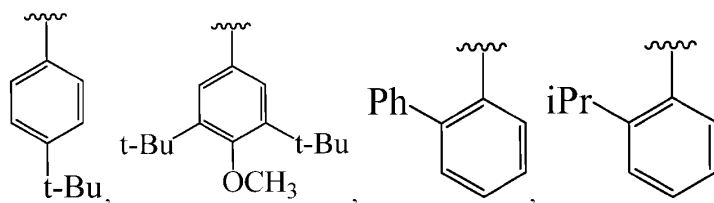
[0063] In some embodiments, R^6 and R^8 are each independently hydrogen or substituted or unsubstituted C_1 to C_6 hydrocarbyl group. In some embodiments, R^6 and R^8 are each independently selected from hydrogen, methyl, ethyl, propyl, butyl, pentyl, and hexyl. In some embodiments, R^6 and R^8 are each hydrogen.

[0064] In some embodiments, R^7 is a substituted aryl group represented by the formula:

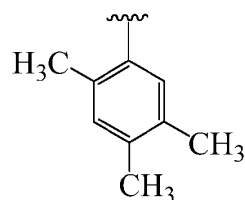


, wherein each of R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} is independently hydrogen, hydrocarbyl, a heteroatom, or heteroatom-containing group, where at least one of R^{11} , R^{12} , R^{13} , R^{14} , or R^{15} is not hydrogen, or one or more of R^{11} and R^{12} , R^{12} and R^{13} , R^{13} and R^{14} , or R^{14} and R^{15} are joined to form a completely saturated, partially saturated, or aromatic ring. In some embodiments, each of R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} is independently hydrogen or C_1 - C_{10} alkyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, or decyl), where at least one of R^{11} , R^{12} , R^{13} , R^{14} , or R^{15} is not hydrogen. In some embodiments, each of R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} is independently hydrogen, methyl, ethyl, isopropyl, tert-butyl, C_1 - C_6 alkoxy, or phenyl, where at least one of R^{11} , R^{12} , R^{13} , R^{14} , or R^{15} is not hydrogen. In some embodiments, at least one of R^{11} , R^{12} , R^{13} , R^{14} , or R^{15} is not hydrogen and is an electron donating group.

[0065] In some embodiments, R^7 is selected from:



or



[0066] In some embodiments, R^7 is selected from 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-methoxy-phenyl, 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, and 3,5-bis(trifluoromethyl)phenyl. In some embodiments, R⁷ is selected from 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, and 5-methyl-3-thiophenyl.

[0067] In some embodiments, R⁹ and R¹⁰ are each independently an unsubstituted C₁ to C₆ hydrocarbyl group. In some embodiments, R⁹ and R¹⁰ are each independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl. In some embodiments, R⁹ and R¹⁰ are each independently a primary substituted or unsubstituted C₁-C₆ alkyl group, such as methyl, ethyl, propyl, isopropyl, butyl, iso-butyl, sec-butyl, pentyl, isopentyl, neopentyl. In some embodiments, R⁹ and R¹⁰ are each methyl.

[0068] In some embodiments, T is represented by the formula R^a₂J or (R^a)₄J₂ wherein each J is independently C, Si, or Ge, and each R^a is independently hydrogen, halide, a substituted or unsubstituted C₁ to C₄₀ hydrocarbyl, or two R^a can form a substituted or unsubstituted completely saturated ring or a substituted or unsubstituted partially saturated ring. In some embodiments, T is represented by the formula R^a₂J, (R^a)₄J₂, or (R^a)₆J₃ where J is C, Si, or Ge, and each R^a is independently hydrogen or C₁ to C₂₀ 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 CH₂, CH₂CH₂, C(CH₃)₂, CPh₂, Si(CH₃)₂, Si(CH₂CH₃)₂, Si(CH₂CH₂CH₃)₂, SiPh₂, Si(CH₃)Ph, Si(CH₂)₃, Si(CH₂)₄, or Si(CH₂)₅. In some embodiments, T is SiMe₂, Si(CH₂CH₃)₂, or Si(CH₂CH₂CH₃)₂. Some examples of suitable bridging groups include P(=S)R*, P(=Se)R*, P(=O)R*, R*₂C, R*₂Si, R*₂Ge, R*₂CCR*₂, R*₂CCR*₂CR*₂, R*₂CCR*₂CR*₂CR*₂, R*C=CR*, R*C=CR*CR*₂, R*₂CCR*=CR*CR*₂, R*C=CR*CR*=CR*, R*C=CR*CR*₂CR*₂, R*₂CSiR*₂, R*₂SiSiR*₂,

$R^*_2SiOSiR^*_2$, $R^*_2CSiR^*_2CR^*_2$, $R^*_2SiCR^*_2SiR^*_2$, $R^*C=CR^*SiR^*_2$, $R^*_2CGeR^*_2$,
 $R^*_2GeGeR^*_2$, $R^*_2CGeR^*_2CR^*_2$, $R^*_2GeCR^*_2GeR^*_2$, $R^*_2SiGeR^*_2$, $R^*C=CR^*GeR^*_2$, R^*B ,
 $R^*_2C-BR^*$, $R^*_2C-BR^*-CR^*_2$, $R^*_2C-O-CR^*_2$, $R^*_2CR^*_2C-O-CR^*_2CR^*_2$, R^*_2C-O-
 $CR^*_2CR^*_2$, $R^*_2C-O-CR^*=CR^*$, $R^*_2C-S-CR^*_2$, $R^*_2CR^*_2C-S-CR^*_2CR^*_2$, R^*_2C-S-
5 $CR^*_2CR^*_2$, $R^*_2C-S-CR^*=CR^*$, $R^*_2C-Se-CR^*_2$, $R^*_2CR^*_2C-Se-CR^*_2CR^*_2$, R^*_2C-Se-
 $CR^*_2CR^*_2$, $R^*_2C-Se-CR^*=CR^*$, $R^*_2C-N=CR^*$, $R^*_2C-NR^*-CR^*_2$, $R^*_2C-NR^*-CR^*_2CR^*_2$,
 $R^*_2C-NR^*-CR^*=CR^*$, $R^*_2CR^*_2C-NR^*-CR^*_2CR^*_2$, $R^*_2C-P=CR^*$, $R^*_2C-PR^*-CR^*_2$, O, S,
Se, Te, NR^* , PR^* , AsR^* , SbR^* , O-O, S-S, R^*N-NR^* , R^*P-PR^* , O-S, O- NR^* , O- PR^* , S-
10 NR^* , S- PR^* , and R^*N-PR^* where R^* is hydrogen or a C_1 - C_{20} containing hydrocarbyl,
halocarbyl, silylcarbyl or germlylcarbyl substituent and optionally two or more adjacent R^* may
join to form a saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent.
Some examples of the bridging group T include CH_2 , CH_2CH_2 , $SiMe_2$, $SiPh_2$, $SiMePh$,
 $Si(CH_2)_3$, $Si(CH_2)_4$, O, S, NPh, PPh, NMe, PMe, NEt, NPr, NBu, PEt, PPr, $Me_2SiOSiMe_2$, and
PBu.

15 [0069] 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.

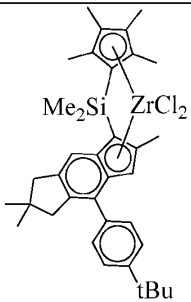
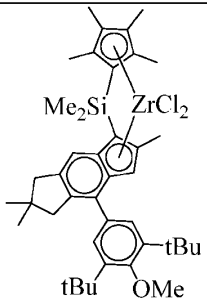
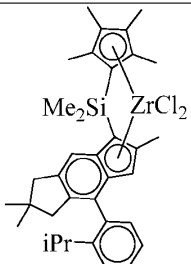
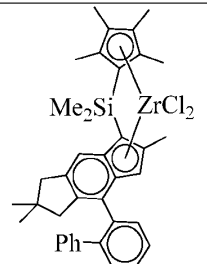
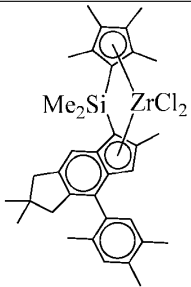
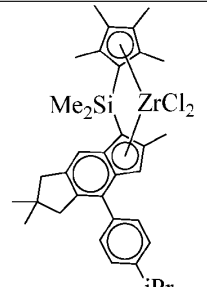
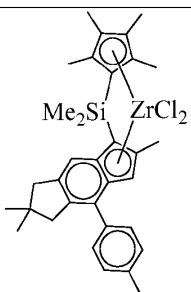
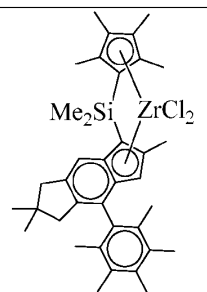
[0070] In some embodiments, X^1 and X^2 of Formula (I) are independently selected from a
halide or C_1 - C_{50} hydrocarbyl, hydride, amide, alkoxide, sulfide, phosphide, or two of X are
joined together to form a metallocycle ring, or X^1 and X^2 are joined to form a chelating ligand,
20 a diene ligand, or an alkylidene. In some embodiments, X^1 and X^2 can be independently
selected from hydrocarbyl, substituted hydrocarbyl, a heteroatom or heteroatom-containing
group such as for example methyl, benzyl, trimethylsilyl, methyl(trimethylsilyl), neopentyl,
ethyl, propyl, butyl, phenyl, hydrido, chloro, fluoro, bromo, iodo, trifluoromethanesulfonate,
dimethylamido, diethylamido, dipropylamido, and diisopropylamido. In at least one
25 embodiment, X^1 and X^2 are each chloro.

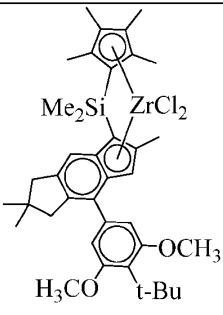
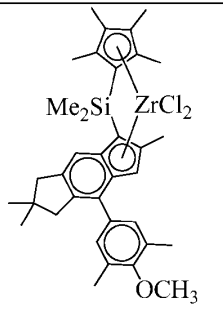
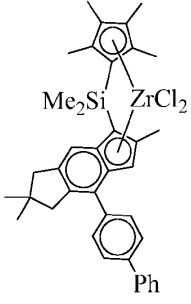
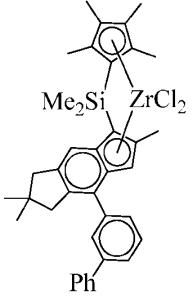
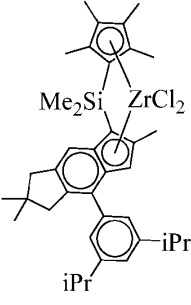
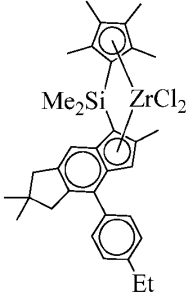
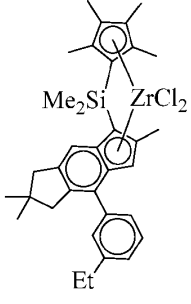
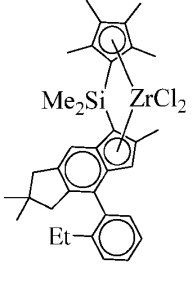
[0071] In some embodiments of Formula (I), (1) M is Zr or Hf, (2) T is $SiMe_2$,
 $Si(CH_2CH_3)_2$, or $Si(CH_2CH_2CH_3)_2$, (3) each of R^6 and R^8 is hydrogen or unsubstituted C_1 - C_{10}
alkyl, (4) each of R^9 and R^{10} is independently unsubstituted C_1 - C_{10} alkyl, (5) each of R^1 , R^2 , R^3 ,
and R^4 is independently methyl, ethyl, or propyl, (6) R^5 is C_1 - C_{10} alkyl, (7) R^7 is substituted
30 aryl, and (8) each of X^1 and X^2 is independently chloro or methyl.

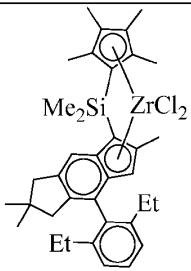
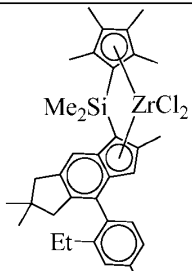
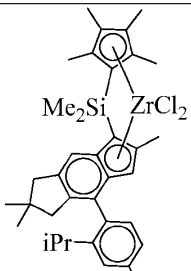
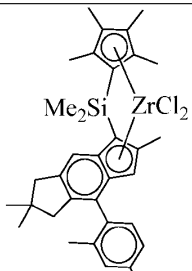
[0072] In some embodiments of Formula (I), (1) M is Zr, (2) T is $SiMe_2$, $Si(CH_2CH_3)_2$, or
 $Si(CH_2CH_2CH_3)_2$, (3) each of R^6 and R^8 is hydrogen, (4) each of R^9 and R^{10} is independently
unsubstituted C_1 - C_5 alkyl, (5) each of R^1 , R^2 , R^3 , and R^4 is independently methyl or ethyl, (6)
 R^5 is C_1 - C_5 alkyl, (7) R^7 is substituted aryl, and (8) each X^1 and X^2 is chloro.

- [0073] In some embodiments of Formula (I), (1) M is Zr, (2) T is SiMe₂, Si(CH₂CH₃)₂, or Si(CH₂CH₂CH₃)₂, (3) each of R⁶ and R⁸ is hydrogen, (4) each of R⁹ and R¹⁰ is methyl, (5) each of R¹, R², R³, and R⁴ is independently methyl or ethyl, (6) R⁵ is methyl or ethyl, (7) R⁷ is phenyl having one or more substitutions independently selected from tert-butyl, methoxy, phenyl, methyl, and isopropyl, and (8) each X¹ and X² is chloro.

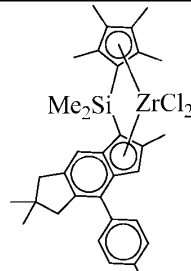
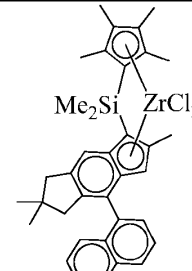
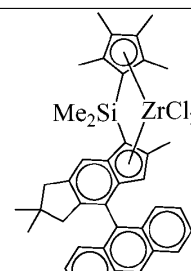
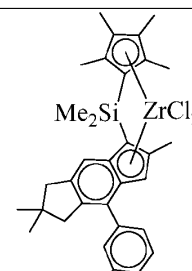
[0074] In some embodiments of Formula (I), the catalyst is selected from:

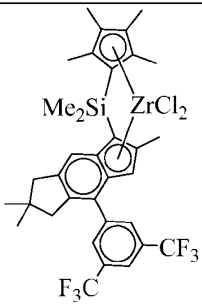
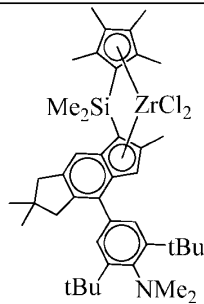
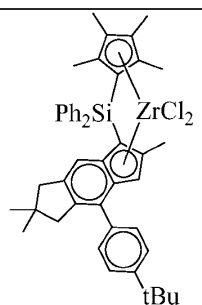
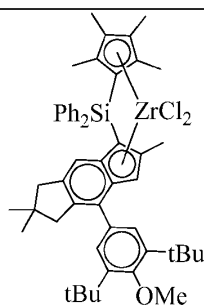
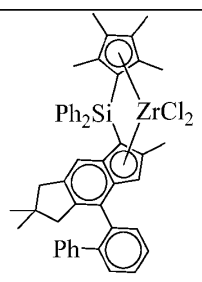
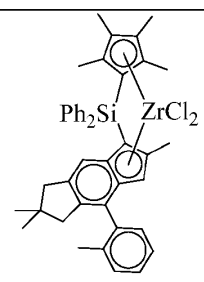
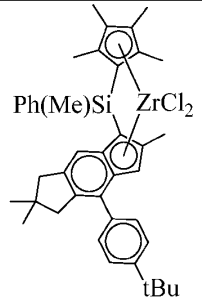
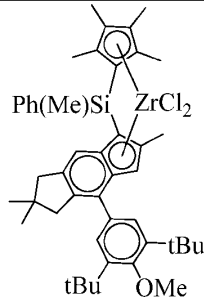
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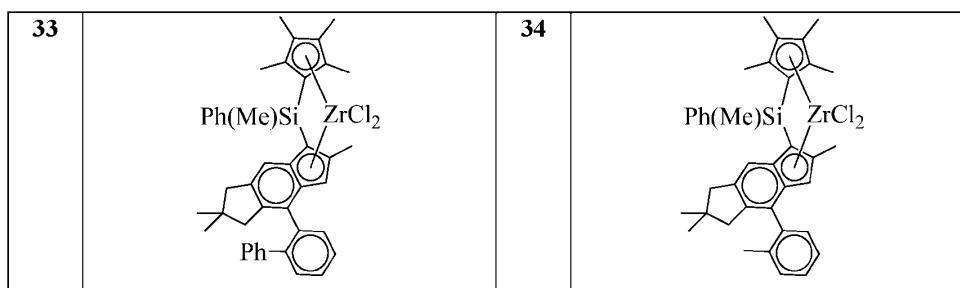
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[0075] In some embodiments of Formula (I), the catalyst is selected from:

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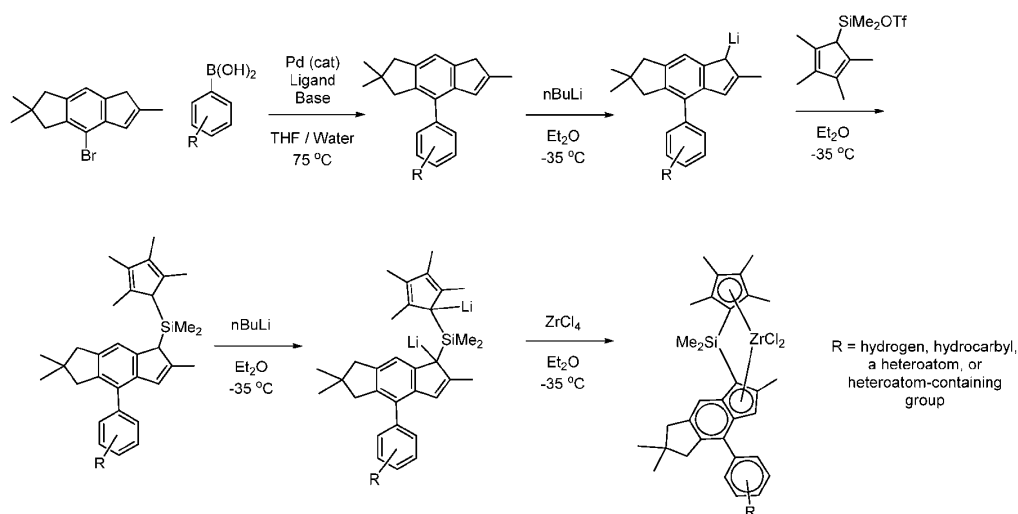


[0076] In at least one embodiment, two or more different catalyst compounds are present in a catalyst system. In at least one embodiment, two or more different catalyst compounds are present in the reaction zone of a reactor where the polymerization process(es) of the present disclosure occur. When two 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.

[0077] 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

[0078] All air sensitive syntheses are carried out in nitrogen purged dry boxes. All solvents are available from commercial sources. Metallocene complexes can be prepared according to the following general Scheme 1. "R" is a substitution on the phenyl ring shown.



Scheme 1

Catalyst Systems

[0079] 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. In some embodiments, the activator includes one or more of alumoxanes, aluminum alkyls, ionizing activators, or combinations thereof.

[0080] 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.

Activators

[0081] The terms “cocatalyst” and “activator” are used herein interchangeably.

[0082] 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.

[0083] In at least one embodiment, the catalyst system includes an activator, a catalyst compound of Formula (I) and optional support.

Alumoxane Activators

[0084] 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.

[0085] 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.

[0086] In an alternate embodiment, little or no alumoxane is used in the polymerization processes described herein. For example, alumoxane can be present at zero mol%, alternately the alumoxane can be present at a molar ratio of aluminum to catalyst compound transition metal less than 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

[0087] The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to a cation or which is only weakly coordinated to a cation thereby remaining sufficiently labile to be displaced by a Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral by-product from the anion. Non-coordinating anions useful in accordance with the present disclosure are those that are compatible, stabilize the transition metal cation in the sense of balancing its ionic charge at +1, and yet retain sufficient lability to permit displacement during polymerization. Suitable ionizing activators may include an NCA, such as a compatible NCA.

[0088] 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 alone or in combination with alumoxane or modified alumoxane activators.

[0089] For descriptions of some suitable activators please see US 8,658,556 and US 6,211,105, incorporated by reference herein. Additional suitable activators are described in US 11,718,635, incorporated by reference herein.

[0090] In some embodiments, an activator can be one or more of N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, dioctadecylmethylammonium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, or triphenylcarbenium tetra(perfluorophenyl)borate.

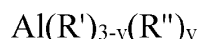
[0091] In at least one embodiment, the activator is selected from one or more of a triaryl carbenium (such as triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, or triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

[0092] 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.

[0093] 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 0 573 120 B1; WO 1994/007928; and WO 1995/014044, incorporated herein by reference, which discuss the use of an alumoxane in combination with an ionizing activator).

[0094] 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.

[0095] Furthermore, a catalyst system of the present disclosure may include a metal hydrocarbenyl chain transfer agent represented by the formula:



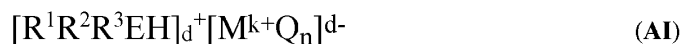
where each R' can be independently a C_1 - C_{30} hydrocarbyl group, and or each R'' , can be independently a C_4 - C_{20} hydrocarbenyl group having an end-vinyl group; and v can be from 0.1 to 3.

Alkane-Soluble Activators

[0096] Activators of the present disclosure may be those designed to have improved solubility in alkane solvents, such as the activators described in US 11,414,436; US 11,584,707; US 2021/0121863; US 2021/0122844; and WO 2021/025903, incorporated herein by reference.

[0097] 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.

[0098] In some embodiments, an activator compound is represented by Formula (AI):



wherein:

E is nitrogen or phosphorus, such as nitrogen;

5 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);

each of R¹, R², and R³ is independently H, optionally substituted C₁-C₄₀ alkyl (such as branched or linear alkyl), or optionally substituted C₅-C₅₀-aryl (alternately each of R¹, 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,

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-hydrocarbyl radical, such as a fluorinated aryl group, such as fluoro-phenyl or fluoro-naphthyl, such as perfluorophenyl or perfluoronaphthyl.

[0099] In some embodiments of activator compounds represented by Formula (AI), at least one of R¹, R², and R³ is a linear or branched C₃-C₄₀ alkyl group (alternately such as a linear or branched C₇ to C₄₀ alkyl group).

[0100] The present disclosure also provides activator compounds represented by Formula (AI), described above where R¹ is a C₁-C₃₀ alkyl group (such as a C₁-C₁₀ alkyl group, such as C₁ to C₂ alkyl, such as methyl), wherein R¹ is optionally substituted, and each of R² and R³ is independently an optionally substituted branched or linear C₁-C₄₀ alkyl group or meta and/or para-substituted phenyl group, where the meta and para substituents are, independently, an optionally substituted C₁ to C₄₀ hydrocarbyl group, an optionally substituted alkoxy group, an optionally substituted silyl group, a halide, or a halide containing group, wherein R¹, R², and R³ together comprise 15 or more carbon atoms (such as 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 40 or more carbon atoms) and at least one of R¹, R², and R³ is a linear or branched alkyl (such as a C₃-C₄₀ branched alkyl, alternately C₇-C₄₀ branched alkyl).

- [0101] The present disclosure further provides catalyst systems including activator compounds represented by Formula (AI), as described above where R¹ is methyl; and each of R² and R³ is independently C₁-C₄₀ branched or linear alkyl or C₅-C₅₀-aryl, wherein each of R¹, 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).
- 10 [0102] 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],
 N-methyl-4-hexadecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-tetradecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 15 N-methyl-4-dodecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-decyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-octyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-hexyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-butyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 20 N-methyl-4-octadecyl-N-decylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-nonadecyl-N-dodecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-nonadecyl-N-tetradecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-4-nonadecyl-N-hexadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-ethyl-4-nonadecyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 25 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],
 N-methyl-N,N-di-dodecylammonium [tetrakis(perfluorophenyl)borate],
 N-methyl-N,N-di-decylammonium [tetrakis(perfluorophenyl)borate],
 30 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],
 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],
 5 N-octadecyl-N-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
 N-octadecyl-N-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
 N-hexadecyl-N-tetradecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
 N-hexadecyl-N-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
 N-hexadecyl-N-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
 10 N-tetradecyl-N-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
 N-tetradecyl-N-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
 N-dodecyl-N-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
 N-methyl-N-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-N-hexadecylanilinium [tetrakis(perfluorophenyl)borate],
 15 N-methyl-N-tetradecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-N-dodecylanilinium [tetrakis(perfluorophenyl)borate],
 N-methyl-N-decylanilinium [tetrakis(perfluorophenyl)borate], and
 N-methyl-N-octylanilinium [tetrakis(perfluorophenyl)borate].

Optional Support Materials

- 20 **[0103]** 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 inorganic support material, or mixtures thereof.
- [0104]** The support material can be an inorganic oxide. The inorganic oxide can be in a
 25 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 alumina can be magnesia, titania, zirconia. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins, such as finely divided
 30 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 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.

[0105] The support material, such as an inorganic oxide, can have a surface area of about 10 m²/g to about 700 m²/g, pore volume of about 0.1 cm³/g to about 4.0 cm³/g and average particle size of about 5 μm to about 500 μm. 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 or PD14024 silica of PQ Corporation or DM-L403 of Asahi Glass Chemical. In other embodiments, PD17062 silica from Ecovyst is used. Alternatively, a silica can be ES-70™ silica (Ecovyst, Malvern, Pennsylvania) that has been calcined, for example (such as at 400°C).

[0106] 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.

[0107] 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 at temperatures from -25°C to about room temperature. The solution of the catalyst compound is then contacted with the isolated support/activator. 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.

[0108] The mixture of the catalyst(s), activator(s) and support is heated about 0°C to about 100°C, such as about 23°C to about 90°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.

[0109] 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.

[0110] 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).

15 Polymerization Processes

[0111] 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.

[0112] 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.

[0113] 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, 5 dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof, such as hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, norbornene, norbornadiene, and their respective homologs and derivatives, 10 such as norbornene, norbornadiene, or dicyclopentadiene.

[0114] 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 norbornene.

[0115] 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. A bulk homogeneous process can be used. Alternately, no solvent or diluent is present or added 15 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 monomers are polymerized on the supported catalyst particles. At least 95 wt% of polymer 20 products derived from the supported catalyst are in granular form as solid particles (not dissolved in the diluent).

[0116] 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, 30 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 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, 5 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.

[0117] In at least one embodiment, a feedstream to the reactor has a feed concentration of 10 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.

[0118] Polymerizations can be run at any temperature and or pressure suitable to obtain the desired polymers. Suitable temperatures and or pressures include a temperature of about 0°C 15 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.

[0119] In a suitable polymerization, the run time of the reaction can be up to about 300 20 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 continuous process the run time may be the average residence time of the reactor.

25 [0120] 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).

[0121] In at least one embodiment, the hydrogen content is about 0.0001 ppm to about 30 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.

[0122] In at least one embodiment, little or no alumoxane is used in the process to produce 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.

[0123] 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 $\text{gPmmolcat}^{-1} \cdot \text{hr}^{-1}$.

[0124] In at least one embodiment, according to the present disclosure, a catalyst system has a catalyst activity of greater than $100,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as greater than $200,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as greater than $300,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as about $50,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $600,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as about $200,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $500,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as about $250,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $300,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, alternatively about $300,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $400,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, such as about $300,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $350,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$, alternatively about $350,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$ to about $400,000 \text{ gPmmolcat}^{-1} \cdot \text{hr}^{-1}$.

[0125] In at least one embodiment, according to the present disclosure, a catalyst system has a catalyst productivity of greater than $10,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$, such as greater than $20,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$, such as greater than $30,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$, such as about $10,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$ to about $80,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$, such as about $20,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$ to about $50,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$, such as about $20,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$ to about $30,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$, alternatively about $30,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$ to about $40,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$, alternatively about $40,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$ to about $50,000 \text{ gP/gcat} \cdot \text{hr}^{-1}$.

[0126] In at least one embodiment, the polymerization can be conducted at temperatures from about 50°C to about 80°C at pressures between 2 MPa and 7 MPa in liquid propylene 1) wherein the catalyst system used in the polymerization comprises alumoxane 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; 2) the polymerization occurs in one reaction zone; 3) 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 to propylene feed is present at 5 to 1000 ppm and 4) 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.

[0127] In an alternate embodiment, the polymerization: 1) can be 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 70°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.

[0128] 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.

10 Polyolefin Products

[0129] The present disclosure also relates to compositions of matter produced by the methods described herein.

[0130] 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).

[0131] 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% hexene or octene, based on the weight of the polymer. In at least one embodiment, the monomer is ethylene and the comonomer is propylene, such as about 1 wt% to about 50 wt% propylene, such as about 2 wt% to about 20 wt% propylene, such as about 3 wt% to about 10 wt% propylene, based on the weight of the polymer.

[0132] 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.

[0133] 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 versus).

[0134] 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 100,000 g/mol to about 300,000 g/mol, such as about 100,000 g/mol to about 200,000 g/mol, alternatively about 200,000 g/mol to about 300,000 g/mol, such as about 250,000 g/mol to about 300,000 g/mol, alternatively about 300,000 g/mol to about 350,000 g/mol, alternatively about 100,000 g/mol to about 200,000 g/mol.

[0135] 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 200,000 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, alternatively about 100,000 g/mol to about 200,000 g/mol.

[0136] 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 4, such as about 2 to about 3.5, such as about 2.5 to about 3.5.

[0137] In at least one embodiment, a propylene homopolymer or propylene copolymer of the present disclosure can have a melting point (T_m) (°C) of about 120°C to about 170°C, such as about 145°C to about 165°C, such as about 150°C to about 160°C, such as about 157°C to

about 162°C, alternatively about 150°C to about 155°C.

[0138] 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%).

[0139] In some embodiments, an isotactic propylene homopolymer has an [mmmm] pentad content of about 95.0% to about 99.5%, such as about 95.0% to about 98.0%, such as about 95.0% to about 97.0%, 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 0.5%, such as about 0.3%, 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.

[0140] 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.

[0141] The regio defects each give rise to multiple peaks in the ^{13}C Carbon 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

5 [0142] The stereodefects measured as “stereo defects/10,000 monomer units” are calculated from the sum of the intensities of mmrr, mrrm+rrmr, and rrrm 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.
 10 et. al. *Macromolecules*, **1988**, v.21, pp. 617-622 and Busico et.al. *Macromolecules*, **1994**, v.27, pp. 7538-7543. The average meso run length = $10000 / [(stereo\ defects/10000\ C) + (2,1-regio\ defects/10000\ C) + (1,3-regio-defects/10000\ C)]$.

[0143] 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
 15 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 less than 100, 50, or 10 regio defects per 10,000 propylene units and most preferably less than 5 regio defects per 10,000 propylene units.

20 [0144] In some embodiments, a propylene homopolymer or propylene copolymer advantageously has less than 200 2,1-regio defects (defined as the sum of 2,1-erythro and 2,1-threo insertions) per 10,000 propylene units, alternatively less than 100, 50, or 10 2,1-regio defects per 10,000 propylene units, such as less than 5 2,1-regio defects per 10,000 propylene units. In some embodiments, a propylene homopolymer or propylene copolymer advantageously has
 25 less than 50 1,3-regio defects (defined as 3,1 insertions/isomerizations) per 10,000 propylene units, such as less than 10, 5 or 2 and such as zero 1,3-regio defects per 10,000 propylene units.

[0145] In some embodiments, a propylene homopolymer or propylene copolymer has less than 500 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
 30 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.

[0146] In some embodiments, a propylene homopolymer or propylene copolymer has a Young's modulus (at 23°C) of about 1700 MPa or more, such as about 1800 MPa or more, such as about 1900 MPa or more, according to ASTM D638. In some embodiments, a propylene homopolymer or propylene copolymer has a Young's modulus (at 23°C) of about 1700 MPa to about 2300 MPa, such as about 1800 MPa to about 2200 MPa, such as about 1900 MPa to about 2200 MPa, such as about 2000 MPa to about 2200 MPa, alternatively about 1700 MPa to about 2000 MPa, such as about 1800 MPa to about 2000 MPa, according to ASTM D638.

[0147] In some embodiments, a propylene homopolymer or propylene copolymer has a tensile stress at yield at 23°C of 30 MPa or more, such as about 34 MPa or more, such as about 35 MPa or more, such as about 36 MPa or more, according to ASTM D638. In some embodiments, a propylene homopolymer or propylene copolymer has a tensile stress at yield at 23°C of about 32 MPa to about 38 MPa, such as about 34 MPa to about 38 MPa, such as about 35 MPa to 38 MPa, such as about 34 MPa to about 36 MPa, according to ASTM D638.

[0148] In some embodiments, a propylene homopolymer or propylene copolymer has a flexural modulus of less than or equal to about 2000 MPa, such as less than or equal to about 1800 MPa, such as less than or equal to about 1600 MPa, when determined according to ASTM D790. In some embodiments, a propylene homopolymer or propylene copolymer has an elongation at break of greater than or equal to about 200%, such as greater than or equal to 300%, such as greater than or equal to 400%, such as greater than or equal to about 500%, when determined according to ASTM D638.

GPC 4-D

[0149] Unless otherwise indicated, the distribution and the moments of molecular weight (M_w , M_n , M_z , M_w/M_n , etc.), the comonomer content, and the branching index (g') are determined by using a high temperature Gel Permeation Chromatography (Polymer Characterization 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 from about 2700 cm^{-1} to about 3000 cm^{-1} (representing saturated C-H stretching vibration), an 18-angle light scattering detector and a viscometer. Three Agilent PLgel 10- μm Mixed-B LS columns are used to provide polymer separation. Reagent grade 1,2,4-trichlorobenzene (TCB) (from Sigma-Aldrich) comprising ~300 ppm antioxidant BHT can be used as the mobile phase at a nominal flow rate of ~1.0 mL/min and a nominal injection volume of ~200 μL . The whole system including transfer lines, columns, and detectors can be contained in an oven maintained at ~145°C. A given amount of sample can be weighed and sealed in a standard vial with ~10 μL flow marker (heptane) added thereto. After loading the vial in the auto-sampler, the oligomer

or polymer may automatically be dissolved in the instrument with ~8 mL added TCB solvent at ~160°C with continuous shaking. The sample solution concentration can be from ~0.2 to ~2.0 mg/ml, with lower concentrations used for higher molecular weight samples. The concentration, c , at each point in the chromatogram can be calculated from the baseline-subtracted IR5 broadband signal, I , using the equation: $c = \alpha I$, where α is the mass constant determined with polyethylene or polypropylene standards. The mass recovery can be calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume. The conventional molecular weight (IR MW) is determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards ranging from 700 to 10M gm/mole. The MW at each elution volume is calculated with following equation:

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

where the variables with subscript “PS” stand for polystyrene while those without a subscript are for the test samples. In this method, $\alpha_{PS} = 0.67$ and $K_{PS} = 0.000175$, α and K for other materials are as calculated and published in literature (Sun, T. *et al.* (2001) *Macromolecules*, v.34, pg. 6812), except that for purposes of this present disclosure and claims thereto, $\alpha = 0.705$ and $K = 0.0000229$ for ethylene-propylene copolymers and ethylene-propylene-diene terpolymers, $\alpha = 0.695$ and $K = 0.000579$ for linear ethylene polymers, $\alpha = 0.705$ and $K = 0.0002288$ for linear propylene polymers, and $\alpha = 0.695$ and $K = 0.000181$ for linear butene polymers. 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.

[0150] 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 is 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:

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

[0151] 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

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

5 [0152] 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

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

10 bulk SCB/1000TC = bulk CH₃/1000TC – bulk CH₃end/1000TC

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

[0153] 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*
15 *Polymer Solutions*; Huglin, M. B., Ed.; Academic Press, 1972.):

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

[0154] Here, Δ*R*(θ) is the measured excess Rayleigh scattering intensity at scattering angle θ, *c* is the polymer concentration determined from the IR5 analysis, *A*₂ is the second virial coefficient, *P*(θ) is the form factor for a monodisperse random coil, and *K*_o is the optical
20 constant for the system:

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

where *N*_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system. The refractive index, *n* = 1.500 for TCB at 145°C and λ = 665 nm. For analyzing polyethylene homopolymers, ethylene-hexene copolymers, and ethylene-octene copolymers, dn/dc =
25 0.1048 ml/mg and *A*₂ = 0.0015; for analyzing ethylene-butene copolymers, dn/dc = 0.1048*(1-0.00126*w₂) ml/mg and *A*₂ = 0.0015 where w₂ is weight percent butene comonomer.

[0155] 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
30 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 $M = K_{ps} M^{\alpha_{ps}+1} / [\eta]$, where α_{ps} is 0.67 and K_{ps} is 0.000175.

- 5 [0156] The branching index (g'_{vis}) is calculated using the output of the GPC-IR5-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{avg}$, of the sample is calculated by:

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

where the summations are over the chromatographic slices, i , between the integration limits. The branching index g'_{vis} is defined as:

10
$$g'_{vis} = \frac{[\eta]_{avg}}{KM_v^\alpha},$$

- where M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis and the K and α are for the reference linear polymer, which are, for purposes of this present disclosure and claims thereto, $\alpha = 0.705$ and $K = 0.0000229$ for ethylene-propylene copolymers and ethylene-propylene-diene terpolymers, $\alpha = 0.695$ and $K = 0.000579$ for linear ethylene polymers, $\alpha = 0.705$ and $K = 0.0002288$ for linear propylene polymers, $\alpha = 0.695$ and $K = 0.000181$ for linear butene polymers. 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. Calculation of the w_{2b} values is as discussed above.

20 Blends

- [0157] 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 polyethylene, isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and or butene, and or hexene, polybutene, ethylene vinyl acetate, low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, ethylene-propylene-diene monomer (EPDM)
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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-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and or polyisobutylene.

5 [0158] 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 to about 10 90 wt%.

[0159] 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); 15 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

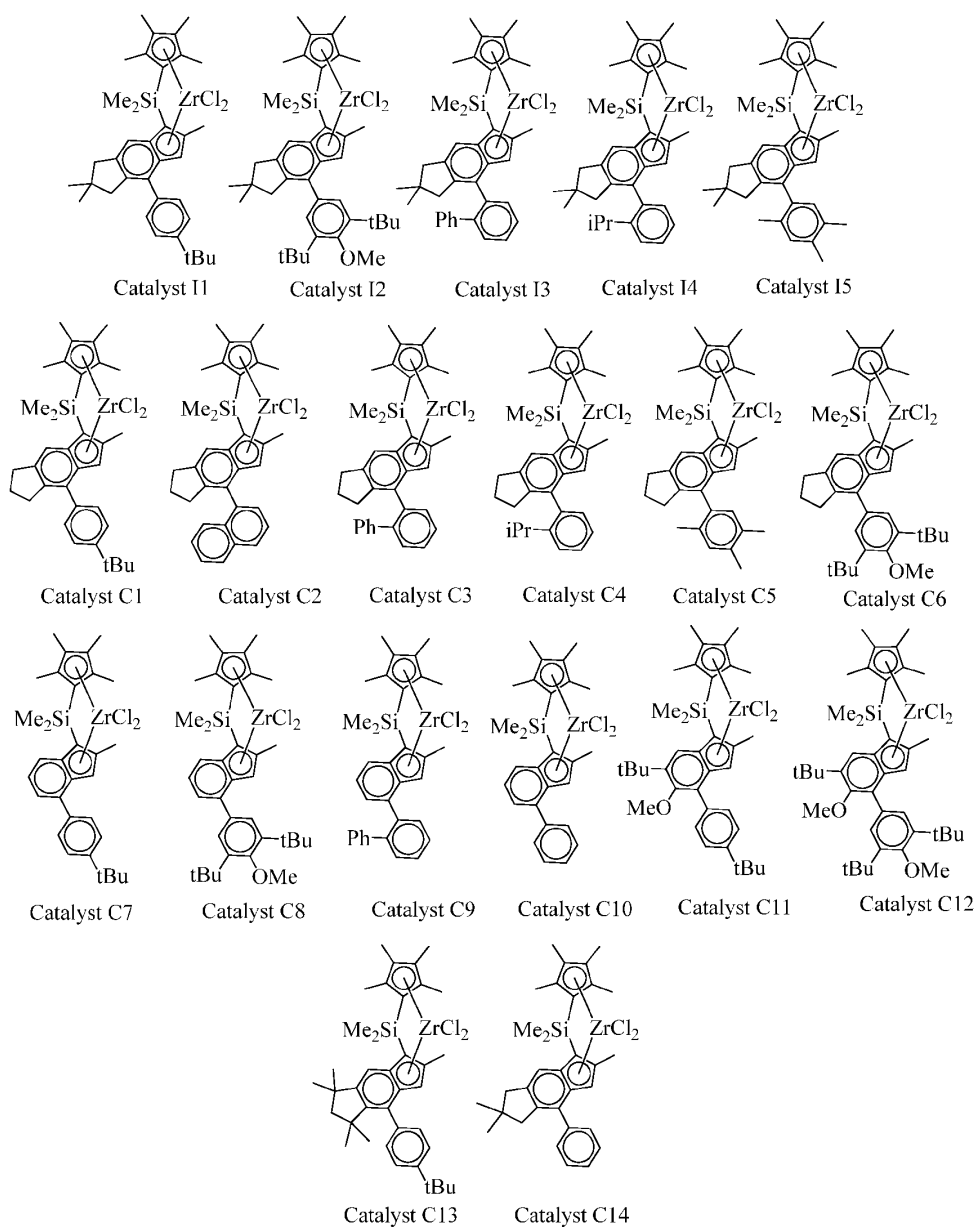
20 [0160] Any of the foregoing polymers, or blends thereof, may be used in a variety of end-use applications. Such applications include, for example, mono- or multi-layer blown, extruded, and or shrink films. These films may be formed by any number of well-known extrusion or coextrusion techniques, such 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 25 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 30 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 [0161] 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.

EXPERIMENTAL

- 10 [0162] The experimental methods and analytical techniques utilized in Examples below are described in this section.



Scheme 1 Structures of inventive catalysts I1-I5 and comparative catalysts C1-C14

Synthesis of catalysts I1 – I5 and C14

5 Synthesis of 4-methoxy-3,5-di-tert-butylphenylboronic acid

[0163] To a stirring suspension of magnesium (0.655 g, 26.9 mmol, 1.62 equiv) in tetrahydrofuran (30 mL), iodine (110 mg, 0.43 mmol, 0.026 equiv) in tetrahydrofuran (10 mL)

was added. Once the color began to fade, a solution of 1-bromo-3,5-di-tert-butyl-4-methoxybenzene (4.974 g, 16.6 mmol, 1 equiv) in tetrahydrofuran (10 mL) was added. The reaction was stirred and heated to reflux for 1 hour. The reaction was allowed to cool to room temperature. Separately, a solution of trimethylborate (2.80 mL, 25.1 mmol, 1.50 equiv) in diethyl ether (100 mL) was cooled to -35°C . Then, the Grignard mixture was filtered over Celite into the precooled, stirring solution of trimethyl borate. The reaction was allowed to warm to room temperature and stir for 14.5 hours. The reaction was poured into 1M aqueous hydrochloric acid (40 mL) in a separatory funnel. The organic layer was collected, and the aqueous phase was extracted further with diethyl ether ($2 \times 50\text{ mL}$). The combined organic extracts were washed with additional 1 M aqueous hydrochloric acid (40 mL), water (50 mL), and then brine (50 mL). The organic extract was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated *in vacuo* to afford the product as a white solid (4.23 g, 96% yield, mixture of monomer and anhydrides). ^1H NMR (400 MHz, C_6D_6) major product: δ 8.51 (s, 2H), 3.48 (s, 3H), 1.64 (s, 18H).

Synthesis of 4-(3,5-di-tert-butyl-4-methoxyphenyl)-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene

[0164] To a stirring mixture of 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene (1.00 g, 3.61 mmol), (3,5-di-tert-butyl-4-methoxyphenyl)boronic acid (0.953 g, 3.61 mmol, 1 equiv), potassium carbonate (1.15 g, 8.30 mmol, 2.30 equiv), bis(dibenzylideneacetone)palladium (21 mg, 36.5 μmol , 1 mol%), and 1,3,5,7-tetramethyl-6-phenyl-2,4,8-trioxo-6-phosphaadamantane (32 mg, 0.11 mmol, 3 mol%) in tetrahydrofuran (20 mL), degassed water (4 mL) was added. The reaction was stirred and heated to reflux overnight. The reaction was allowed to cool to room temperature. The reaction was partially concentrated *in vacuo*. The residue was partitioned between dichloromethane (40 mL) and water (50 mL). The organic phase was collected, and the aqueous phase was extracted further with additional dichloromethane ($2 \times 40\text{ mL}$). The combined dichloromethane extracts were washed with brine and dried over anhydrous magnesium sulfate. The mixture was filtered over a thin pad of silica, and the filtrate was concentrated *in vacuo* to afford the product as a white solid (1.53 g, >99% yield). ^1H NMR (400 MHz, C_6D_6): δ 7.49 (s, 2H), 7.14 (s, 1H), 6.50 (q, 1H, $J = 1.6\text{ Hz}$), 3.48 (s, 3H), 3.21 (s, 2H), 2.85 (s, 2H), 2.78 (s, 2H), 1.87 (s, 3H), 1.51 (s, 18H), 1.09 (s, 6H).

Synthesis of lithium 4-(3,5-di-tert-butyl-4-methoxyphenyl)-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene

[0165] To a precooled, stirring solution of 4-(3,5-di-tert-butyl-4-methoxyphenyl)-2,2,6-

trimethyl-1,2,3,5-tetrahydro-s-indacene (1.53 g, 3.67 mmol) in diethyl ether (100 mL), n-butyllithium (1.4 mL, 2.71 M in hexane, 3.8 mmol, 1 equiv) was added. The reaction was stirred at room temperature for 14.5 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum to afford the product as a yellow solid, containing diethyl ether (0.6 equiv) (1.72g, >99% yield). ¹H NMR (400 MHz, C₄D₈O): δ 7.56 (s, 2H), 6.99 (s, 1H), 5.75 (d, 1H, J = 2.1 Hz), 5.70 (d, 1H, J = 2.1 Hz), 3.73 (s, 3H), 2.73 (s, 2H), 2.70 (s, 2H), 2.31 (s, 3H), 1.48 (s, 18H), 1.10 (s, 6H).

Synthesis of dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silyl trifluoromethanesulfonate

[0166] To a precooled, stirring solution of chlorodimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (62.727 g, 292 mmol) in dichloromethane (300 mL), silver(I) trifluoromethanesulfonate (75.0 g, 292 mmol, 1 equiv.) and dichloromethane (20 mL) were added. The reaction was stirred at room temperature for 1 hour. The reaction was filtered over Celite, extracting further with dichloromethane (2 × 50mL). The combined dichloromethane filtrate was concentrated under a stream of nitrogen and then under high vacuum to afford the product as a dark oil (91.564 g, 95% yield). ¹H NMR (400 MHz, C₆D₆): δ 2.78 (br s, 1H), 1.75 (s, 6H), 1.61 (s, 6H), 0.05 (s, 6H).

Synthesis of [4-(3,5-di-tert-butyl-4-methoxyphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl]dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

[0167] To a stirring solution of dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silyl trifluoromethanesulfonate (1.197 g, 3.64 mmol) in diethyl ether, lithium 4-(3,5-di-tert-butyl-4-methoxyphenyl)-2,6,6-trimethyl-1,2,3,5-tetrahydro-s-indacene (1.72 g, 3.7 mmol, 1 equiv) was added. The reaction was stirred at room temperature for 15 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with pentane (3 × 10mL) and filtered over Celite. The combined pentane extracts were concentrated under a stream of nitrogen and then under high vacuum to afford the product as a white solid (2.131 g, 98% yield). ¹H NMR (400 MHz, C₆D₆): δ 7.67 (s, 2H), 7.41 (s, 1H), 6.93-6.90 (m, 1H), 3.69 (s, 1H), 3.51 (s, 3H), 3.25 (br s, 1H), 2.95-2.90 (m, 2H), 2.89-2.80 (m, 2H), 2.06 (s, 3H), 1.98 (s, 3H), 1.93 (s, 3H), 1.84 (s, 6H), 1.55 (s, 18H), 1.09 (s, 3H), 1.08 (s, 3H), -0.11 (s, 3H), -0.16 (s, 3H).

Synthesis of lithium [4-(3,5-di-tert-butyl-4-methoxyphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenidyl]dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

[0168] To a precooled, stirring solution of [4-(3,5-di-tert-butyl-4-methoxyphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl]dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

(2.131 g, 3.58 mmol) in diethyl ether (40 mL), n-butyllithium (2.70 mL, 2.71 M in hexane, 7.32 mmol, 2.04 equiv) was added. The reaction was stirred at room temperature for 2.5 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was stirred in pentane (20mL) and filtered over a plastic, fritted funnel. The filtered solid was collected and concentrated under high vacuum to afford the product as a yellow solid, containing diethyl ether (1 equiv) (1.373 g, 56% yield). ¹H NMR (400 MHz, C₄D₈O): δ 7.47 (s, 2H), 7.38 (br s, 1H), 5.83 (s, 1H), 3.73 (s, 3H), 2.70 (s, 2H), 2.68 (s, 2H), 2.34 (s, 3H), 2.13 (s, 6H), 1.91 (s, 6H), 1.46 (s, 18H), 1.09 (s, 6H), 0.59 (s, 6H).

Synthesis of dimethylsilyl (4-(4-methoxy-3,5-di-tert-butylphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl) (2,3,4,5-tetramethylcyclopentadienyl) zirconium dichloride (Catalyst I2)

[0169] To a precooled, stirring suspension of lithium [4-(3,5-di-tert-butyl-4-methoxyphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenidyl]dimethyl(2,3,4,5-tetramethylcyclopentadienidyl)-silane (1.373, 2.02 mmol) in diethyl ether (40 mL), zirconium chloride (0.471 g, 2.02 mmol, 1 equiv) was added with toluene (4 mL). The reaction was stirred at room temperature for 17 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with dichloromethane (4 × 20 mL) and filtered over Celite. The combined dichloromethane extracts were concentrated under a stream of nitrogen and then under high vacuum. The residue was washed with pentane (10 mL) and then diethyl ether (10 mL) and concentrated under high vacuum to afford the product as a yellow solid (0.382 g, 44% yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.48 (br s, 2H), 7.33 (s, 1H), 6.74 (s, 1H), 3.74 (s, 1H), 2.93 (d, 1H, J = 15.8 Hz), 2.80 (d, 1H, J = 15.0 Hz), 2.66 (d, 1H, J = 16.1 Hz), 2.58-2.51 (m, 1H), 2.21 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H), 1.88 (s, 3H), 1.45 (s, 18H), 1.20 (s, 3H), 1.19 (s, 3H), 1.07 (s, 3H), 0.8 (s, 3H).

Synthesis of 4-(4-tert-butyl)-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene

[0170] To a stirring mixture of 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene (1.002 g, 3.61 mmol), 4-tert-butylphenylboronic acid (0.643 g, 3.61 mmol, 1 equiv), potassium carbonate (1.160 g, 8.39 mmol, 2.32 equiv), 1,3,5,7-tetramethyl-6-phenyl-2,4,8-trioxo-6-phosphaadamantane (34 mg, 0.12 mmol, 3 mol%), and bis(dibenzylideneacetone)palladium (20 mg, 1 mol%) in tetrahydrofuran (20 mL), degassed water (4 mL) was added. The reaction was stirred and heated to reflux for 5 hours. The reaction was allowed to cool to room temperature. The reaction was partially concentrated *in vacuo*. The residue was partitioned between dichloromethane (40 mL) and water (50 mL). The organic layer was collected, and the aqueous phased was further extracted with additional dichloromethane (2 × 40 mL). The

combined organic extracts were washed with brine and dried over anhydrous magnesium sulfate. The mixture was filtered over a thin pad of silica. The filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography to afford the product as a white foam (0.369 g, 29% yield). ¹H NMR (400 MHz, C₆D₆): δ 7.43-7.33 (m, 4H), 7.12 (s, 1H), 6.47 (q, 1H, J = 1.5 Hz), 3.05 (s, 2H), 2.76 (s, 2H), 2.71 (s, 2H), 1.86 (s, 3H), 1.30 (s, 9H), 1.08 (s, 6H).

Synthesis of lithium 4-(4-tert-butyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenide

[0171] To a precooled, stirring solution of 4-(4-tert-butyl)-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene (0.369 g, 1.05 mmol) in diethyl ether (50 mL), n-butyllithium (0.42 mL, 2.71 M in hexane, 1.1 mmol, 1.1 equiv) was added. The reaction was stirred at room temperature for 1 hour. The reaction was concentrated under a stream of nitrogen and then under high vacuum, stirred in pentane, and then concentrated under a stream of nitrogen and then under high vacuum again to afford the product as an off-white solid, containing diethyl ether (0.1 equiv) and pentane (0.3 equiv) (0.366 g, 96% yield). ¹H NMR (400 MHz, C₄D₈O): δ 7.53 (d, 2H, J = 8.4 Hz), 7.36 (d, 2H, J = 8.4 Hz), 6.99 (s, 1H), 5.75-5.67 (m, 2H), 2.69 (s, 4H), 2.29 (s, 3H), 1.37 (s, 9H), 1.08 (s, 6H).

Synthesis of [4-(4-tert-butylphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl] dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane

[0172] To a precooled, stirring solution of dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silyl trifluoromethanesulfonate (0.333 g, 1.02 mmol, 1 equiv) in diethyl ether (50 mL), a solution of lithium 4-(4-tert-butyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenide (0.366 g, 1.02 mmol) in diethyl ether (20 mL) was added. The reaction was stirred at room temperature for 15 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with pentane (3 × 10 mL) and filtered over Celite. The combined pentane extracts were concentrated under a stream of nitrogen and then under high vacuum to afford the product as a white foam, containing pentane (0.2 equiv) and diethyl ether (0.2 equiv) (0.533 g, 98% yield). ¹H NMR (400 MHz, C₆D₆): δ 7.65 (d, 2H, J = 8.4 Hz), 7.54 (d, 2H, J = 8.3 Hz), 7.48 (s, 1H), 6.88 (s, 1H), 3.76 (s, 1H), 3.35 (br s, 1H), 2.99-2.79 (m, 4H), 2.14 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 1.94 (s, 6H), 1.43 (s, 9H), 1.18 (s, 3H), 1.16 (s, 3H), -0.02 (s, 3H), -0.06 (s, 3H).

Synthesis of dimethyl (4-(4-tert-butylphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl) (2,3,4,5-tetramethylcyclopentadienyl) zirconium dichloride (Catalyst I1)

[0173] To a precooled, stirring solution of [4-(4-tert-butylphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl] dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (0.533 g,

1.00 mmol) in diethyl ether (30 mL), *n*-butyllithium (0.78 mL, 2.69 M in hexane, 2.1 mmol, 2.1 equiv) was added. The reaction was stirred at room temperature for 35 minutes. Then, zirconium chloride (0.244 g, 1.05 mmol, 1.05 equiv) and toluene (4 mL) were added. The reaction was stirred at room temperature for 3 days. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with dichloromethane (20 mL, then 2 × 10 mL) and filtered over Celite. The combined dichloromethane extracts were 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 a plastic, fritted funnel. The filtered solid was collected and concentrated under high vacuum to afford the product as a yellow solid (0.172 g, 25% yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.54-7.45 (m, 4H), 7.33 (s, 1H), 6.74 (s, 1H), 2.85 (d, 1H, J = 15.9 Hz), 2.80-2.73 (m, 1H), 2.70 (d, 1H, J = 15.9 Hz), 2.61-2.54 (m, 1H), 2.21 (s, 3H), 2.04 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.88 (s, 3H), 1.37 (s, 9H), 1.20 (s, 3H), 1.14 (s, 3H), 1.08 (s, 3H), 1.02 (s, 3H).

Synthesis of 2,2,6-trimethyl-4-(*o*-biphenyl)-1,2,3,5-tetrahydro-*s*-indacene

[0174] To a stirring mixture of 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-*s*-indacene (1.00 g, 3.61 mmol), *o*-biphenylboronic acid (0.714 g, 3.61 mmol, 1 equiv), potassium carbonate (1.10 g, 7.94 mmol, 2.2 equiv), bis(dibenzylideneacetone)palladium (0.104 g, 0.180 mmol, 5 mol%), and 1,3,5,7-tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane (0.158, 0.541 mmol, 15 mol%) in tetrahydrofuran (20 mL), degassed water (4 mL) was added. The reaction was stirred and heated to reflux for 17 hours. The reaction was allowed to cool to room temperature. The reaction was concentrated *in vacuo*. The residue was partitioned between water (100 mL) and isohexanes (150 mL). The organic layer was collected, and the aqueous phase was extracted further with isohexanes (50 mL). The combined organic layers were dried over anhydrous magnesium sulfate and filtered. The filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography over two columns, resulting in two fractions of product as an expansive, white foam that collapsed to a viscous, colorless oil; the first fraction (0.477 g, 37% yield) and the second fraction (0.). ¹H NMR (400 MHz, CDCl₃) δ: 7.51-7.28 (m, 7H), 7.08-6.95 (m, 2H), 6.64-6.58 (m, 1H), 6.39 (q, 1H, J = 1.6 Hz), 3.09 (d, 1H, J = 22.6 Hz), 2.77 (d, 1H, J = 22.8 Hz), 2.71 (d, 1H, J = 15.4 Hz), 2.54 (d, 1H, J = 15.3 Hz), 2.42 (d, 1H, J = 15.5 Hz), 2.07 (d, 1H, J = 15.6 Hz), 2.03 (s, 3H), 1.06 (s, 3H), 0.66 (s, 3H).

Synthesis of lithium 2,6,6-trimethyl-4-(*o*-biphenyl)-1,5,6,7-tetrahydro-*s*-indacenide

[0175] To a precooled, stirring solution of 2,2,6-trimethyl-4-(*o*-biphenyl)-1,2,3,5-tetrahydro-*s*-indacene (0.477 g, 1.36 mmol) in diethyl ether (40 mL), *n*-butyllithium (0.51 mL,

2.69 M in hexane, 1.37 mmol, 1 equiv) was added. The reaction was stirred at room temperature for 16.5 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was washed with pentane (10 mL) and filtered over a plastic, fritted funnel. The filtered solid was collected and concentrated under high vacuum to afford the product (0.389 g, 80% yield). ¹H NMR (400 MHz, C₄D₈O) δ: 7.44-7.37 (m, 2H), 7.30-7.16 (m, 4H), 6.99-6.94 (m, 3H), 6.92 (s, 1H), 5.69 (d, 1H, *J* = 2.1 Hz), 5.50 (d, 1H, *J* = 2.0 Hz), 2.54 (dd, 1H, *J* = 14.1, 1.3 Hz), 2.39 (dt, 1H, *J* = 14.1, 0.9 Hz), 2.30 (s, 3H), 2.09 (d, 1H, *J* = 14.6 Hz), 1.88 (d, 1H, *J* = 14.6 Hz), 0.93 (s, 3H), 0.43 (s, 3H).

Synthesis of (4-(*o*-biphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl)dimethyl(2,3,4,5-tetra-methylcyclopentadienyl)silane

[0176] To a precooled, stirring solution of dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silyl trifluoromethanesulfonate (0.354 g, 1.08 mmol) in diethyl ether (20 mL), a solution of lithium 2,6,6-trimethyl-4-(*o*-biphenyl)-1,5,6,7-tetrahydro-s-indacene (0.389 g, 1.09 mmol, 1 equiv) in diethyl ether (10 mL) was added. The reaction was stirred at room temperature for 16.5 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with pentane (2 × 20 mL) and filtered over Celite. The combined pentane extracts were concentrated under a stream of nitrogen and then under high vacuum to afford the product as a white foam that collapsed to a sticky, white solid (0.530 g, 93% yield, mixture of isomers). ¹H NMR (400 MHz, C₆D₆) integrated as one isomer δ: 7.55-7.41 (m, 2H), 7.34-7.23 (m, 5H), 7.09-6.86 (m, 3H), 6.54 + 6.47 (2s, 1H), 3.62 + 3.58 (2s, 1H), 3.20 (br s, 1H), 2.77-2.15 (m, 4H), 2.08-1.80 (m, 15H), 1.04 + 0.99 (2s, 3H), 0.77 + 0.64 (2s, 3H), -0.17 + -0.25 (2s, 3H), -0.18 + -0.26 (2s, 3H).

Synthesis of Dimethylsilyl (4-(*o*-biphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl) (2,3,4,5-tetramethylcyclopentadienyl) zirconium dichloride (catalyst I3)

[0177] To a precooled, stirring solution of (4-(*o*-biphenyl)-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenyl)dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silane (0.530 g, 1.00 mmol) in diethyl ether (40 mL), *n*-butyllithium (0.75 mL, 2.69 M in hexane, 2.0 mmol, 2 equiv) was added. The reaction was stirred for 2.5 hours. The reaction was then cooled to -35°C. To this cooled, stirring reaction, zirconium chloride (0.232 g, 0.993 mmol, 0.99 equiv) was added with toluene (2 mL). The reaction was stirred at room temperature for 16 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with dichloromethane (3 × 10 mL) and filtered over Celite. The combined dichloromethane extracts were 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 a plastic, fritted funnel. The filtered solid was collected and concentrated under high vacuum to afford the product as an orange-yellow solid (0.439 g, 63% yield, approximately 5:1 ratio of two isomers). ¹H NMR (400 MHz, CD₂Cl₂) isomers integrated as one δ: 7.88-6.38 (mixture of multiplets, 11 H; contains diagnostic major isomer peaks 7.85 (dt, 1H) and 6.43 (s, 1H)), 2.62-1.69 (mixture of multiplets and singlets, 19H; contains diagnostic major isomer peaks 2.85 (s, 3H), 2.00 (s, 3H), 1.93 (s, 3H), and 1.89 (br s, 6H), 1.18-0.65 (mixture of singlets, 12H; contains diagnostic major isomer peaks 1.17 (s, 3H), 1.052 (s, 3H), 1.049 (s, 3H), 0.67 (s, 3H)).

Synthesis of 2,2,6-Trimethyl-4-(2,4,5-trimethylphenyl)-1,2,3,5-tetrahydro-s-indacene

[0178] To a stirring mixture of 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene (0.246 g, 887 mmol), 2,4,5-trimethylphenylboronic acid (0.146 g, 887 mmol, 1 equiv), potassium carbonate (0.282 g, 2.04 mmol, 2.3 equiv), and methanesulfonato(1,3,5,7-tetramethyl-8-phenyl-2,4,6-trioxa-8-phosphaadamantane)(2'-amino-1,1'-biphenyl-2-yl)palladium(II) (18 mg, 27 mmol, 3 mol% in tetrahydrofuran (10 mL), water (2 mL) was added. The reaction was stirred and heated to reflux for 17 hours. The reaction was allowed to cool to room temperature. The residue was partitioned between water (50 mL) and isohexanes (50 mL). The organic phase was collected, and the aqueous phase was further extracted with isohexanes (2 × 50 mL). The combined organic phases were washed with brine (50 mL), dried over anhydrous magnesium sulfate, and filtered over a thin pad of silica. The filtrate was concentrated *in vacuo* to afford the product as a colorless oil, containing diethyl ether (0.04 equiv) (0.287 g, >99% yield). ¹H NMR (400 MHz, C₆D₆) δ: 7.04 (s, 1H), 6.93 (s, 1H), 6.49 (q, 1H, *J* = 1.5 Hz), 3.00 (d, 1H, *J* = 22.6 Hz), 2.86-2.70 (m, 3H), 2.59 (d, 1H, *J* = 15.6 Hz), 2.46 (d, 1H, *J* = 15.6 Hz), 2.15 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 1.86 (s, 3H), 1.10 (s, 3H), 1.09 (s, 3H).

Synthesis of lithium 2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenide

[0179] To a precooled, stirring solution of 2,2,6-trimethyl-4-(2,4,5-trimethylphenyl)-1,2,3,5-tetrahydro-s-indacene (0.287 g, 898 μmol) in diethyl ether (20 mL), *n*-butyllithium (0.34 mL, 2.69 M in hexane, 0.92 mmol) was added. The reaction was stirred at room temperature for 2 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum to afford the product as an off-white solid, containing diethyl ether (0.04 equiv) (0.314 g, >99% yield). ¹H NMR (400 MHz, C₄D₈O) δ: 6.99 (s, 1H), 6.96 (s, 1H), 6.90 (s, 1H), 5.67 (d, 1H, *J* = 2.1 Hz), 5.22 (dt, 1H, *J* = 2.1, 0.7 Hz), 2.72 (dd, 1H, *J* = 14.1, 1.3 Hz), 2.67 (dd, 1H, *J* = 14.0, 1.2 Hz), 2.42 (d, 1H, *J* = 14.7 Hz), 2.29 (d, 1H, *J* = 7.1 Hz), 2.25 (s, 6H), 2.20 (s, 3H), 2.00 (s, 3H), 1.09 (s, 3H), 1.05 (s, 3H).

Synthesis of dimethyl(2,3,4,5-tetramethylcyclopentadienyl)(2,6,6-trimethyl-4-(2,4,5-trimethylphenyl)-1,5,6,7-tetrahydro-s-indacenyl)silane

[0180] To a precooled, stirring solution of dimethyl(2,3,4,5-tetramethylcyclopentadienyl)silyl trifluoromethanesulfonate (0.294 g, 0.895 mmol) in diethyl ether (20 mL), a solution of lithium 2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacenide (0.314 g, 0.927 mmol, 1.04 equiv) in diethyl ether (20 mL) was added. The reaction was stirred at room temperature for 2 hours. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with pentane (3 × 10 mL) and filtered over Celite. The combined pentane extracts were concentrated under a stream of nitrogen and then under high vacuum to afford the product as an expansive white foam that collapsed to a pale orange, sticky solid (0.381 g, 86% yield, two isomers). ¹H NMR (400 MHz, C₆D₆) isomers integrated as one δ: 7.41 (s, 1H), 7.14 (s, 1H), 7.12-7.08 (m, 1H), 6.47-6.43 (m, 1H), 3.69/3.63 (s, 1H), 3.30-3.23 (m, 1H), 2.94-2.61 (m, 3H), 2.55-2.42 (m, 1H), 2.28-1.58 (m, 24H), 1.15-1.04 (m, 6H), 0.06--0.21 (m, 6H).

Dimethylsilyl (2,6,6-trimethyl-4-(2,4,5-trimethylphenyl)-1,5,6,7-tetrahydro-s-indacenyl) (2,3,4,5-tetramethylcyclopentadienyl) zirconium dichloride (catalyst 15)

[0181] To a precooled, stirring solution of dimethyl(2,3,4,5-tetramethylcyclopentadienyl)(2,6,6-trimethyl-4-(2,4,5-trimethylphenyl)-1,5,6,7-tetrahydro-s-indacenyl)silane (0.292 g, 590 μmol) in diethyl ether (20 mL), n-butyllithium (0.44 mL, 2.69 M in hexane, 1.2 mmol, 2 equiv) was added. The reaction was stirred at room temperature for 3 hours. The reaction was cooled to -35°C. Then, zirconium chloride (0.138 g, 592 μmol, 1 equiv) and toluene (2 mL) were added. The reaction was stirred at room temperature overnight. The reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with dichloromethane (10 mL, then 5 mL) and filtered over Celite. The combined dichloromethane extracts were concentrated under a stream of nitrogen and then under high vacuum. The residue was extracted with pentane (10 mL) and filtered over a plastic, fritted funnel. The filtrate was cooled to -35°C. After precipitation at this temperature, the cold supernatant was decanted away, and the precipitated solid was concentrated under high vacuum to afford the product as a yellow solid (0.092 g, 23% yield, 10:1 ratio of diastereomers). ¹H NMR (400 MHz, CD₂Cl₂) major isomer δ: 7.36 (s, 1H), 7.12 (s, 1H), 6.74 (s, 1H), 6.58 (s, 1H), 2.79-2.63 (m, 3H), 2.70 (s, 3H), 2.35 (d, 1H, J = 15.8 Hz), 2.31 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H), 2.05 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H), 1.92 (s, 3H), 1.22 (s, 3H), 1.21 (s, 3H), 1.11 (s, 3H), 1.01 (s, 3H).

Synthesis of 4-(2-isopropylphenyl)-2,2,6-trimethyl-3,5-dihydro-1H-s-indacene

[0182] A mixture of 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene (1.0 g, 3.61 mmol), 2-isopropylphenylboronic acid (0.592 g, 3.61 mmol), potassium carbonate (1.12 g, 8.12 mmol), 1,3,5,7-Tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane (0.0949 g, 9 mol%), and bis(dibenzylideneacetone)palladium (0.0622 g, 3 mol%) were suspended in tetrahydrofuran (16 mL) in a glass vial equipped with PTFE septum. Degassed water (3 mL) was added and the reaction was stirred and heated to 75°C for 3 hours. After 3 hours, the reaction mixture was concentrated. The resulting residue was diluted with 10 mL of water and extracted with 3 x 15 mL of diethylether. The combined organic layers were washed with water (3 x 10 mL) and brine (1 x 10 mL), dried over MgSO₄ and filtered. Solvent removal afforded orange oil. The oil was chromatographed (5% EtOAc / hexane) to afford a spectroscopically pure white solid in 87% yield. ¹H NMR (400 MHz, Chloroform-d) δ 7.42 (m, 2H), 7.24 (m, 1H), 7.10 (m, 2H), 6.50 (s, 1H), 2.99 (m, 1H), 2.82 (m, 4H), 2.47 (d, 1H), 2.35 (d, 1H), 2.08 (s, 3H), 1.15 (overlapping m, 12H).

Synthesis of [4-(2-isopropylphenyl)-2,6,6-trimethyl-5,7-dihydro-1H-s-indacen-1-yl]lithium

[0183] nBuLi (1.2 mL of 2.7 M solution) was slowly added to a stirring, pre-cooled diethylether solution of 4-(2-isopropylphenyl)-2,2,6-trimethyl-3,5-dihydro-1H-s-indacene (0.99 g, 3.1 mmol). The reaction mixture was allowed to warm up to room temperature and was stirred overnight. After 18 hours, the clear yellow solution was concentrated *in vacuo*, and the residue was triturated with excess pentane. The solution was decanted leaving oily yellow material. This material was dried *in vacuo* to afford spectroscopically pure product as an off-white foam in quantitative yield. ¹H NMR (400 MHz, THF-d₈) δ 7.33 (m, 1H), 7.19 (m, 1H), 7.01 (m, 3H), 5.68 (s, 1H), 5.22 (s, 1H), 3.05 (m, 1H), 2.72 (m, 2H), 2.44 (m, 1H), 2.27 (m, 1H), 2.26 (s, 3H), 1.11 (s, 6H), 1.04 (s, 6H).

Synthesis of [4-(2-isopropylphenyl)-2,6,6-trimethyl-5,7-dihydro-1H-s-indacen-1-yl]-dimethyl-(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)silane

[0184] Solid [4-(2-isopropylphenyl)-2,6,6-trimethyl-5,7-dihydro-1H-s-indacen-1-yl]lithium (1.0 g, 3.1 mmol) was slowly added to a stirring, pre-cooled solution of Me₂CpSiMe₂OTf (1.0 g, 3.0 mmol) in diethylether. The reaction mixture was allowed to warm up to room temperature and was stirred for 1 hour. After 1 hour, solvent was removed *in vacuo*, and the residue was extracted with pentane (2 x 10 mL) and filtered over celite. Solvent removal afforded spectroscopically pure white foam in 96% yield. ¹H NMR (400 MHz, C₆D₆) δ 7.39 (m, 2H), 7.28 (m, 2H), 7.22 (m, 1H), 6.37 (s, 1H), 3.67 (s, 1H), 3.27 (s, 1H), 3.09 (m, 1H), 2.81

(m, 2H), 2.60 (m, 1H), 2.48 (m, 1H), 1.99 (s, 6H), 1.91 (s, 3H), 1.84 (s, 6H), 1.21 (s, 6H), 1.10 (s, 6H), -0.18 (s, 6H).

Synthesis of dimethylsilyl (2,6,6-trimethyl-4-(2-isopropylphenyl)-1,5,6,7-tetrahydro-s-indacenyl) (2,3,4,5-tetramethylcyclopentadienyl) zirconium dichloride (catalyst I4)

- 5 [0185] nBuLi (2.3 mL of 2.7 M solution) was slowly added to a pre-cooled (-35°C) solution of [4-(2-isopropylphenyl)-2,6,6-trimethyl-5,7-dihydro-1H-s-indacen-1-yl]-dimethyl-(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)silane (1.5 g, 3.0 mmol) in diethylether. The reaction mixture was allowed to warm up to room temperature and was stirred for 1 hour. After 1 hour, the solution was cooled back to -35°C. While stirring, solid ZrCl₄(OEt)₂ (1.1 g, 3.0 mmol)
- 10 was slowly added in portions. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. After 18 hours, the bright yellow mixture was concentrated *in vacuo* to give yellow solids. The solids were extracted with methylene chloride (2 x 20 mL), filtered over celite, and concentrated. Pentane (ca 20 mL) was added, the resulting yellow solids were stirred for 5 minutes, filtered over plastic frit, washed with additional
- 15 pentane and dried *in vacuo* to afford spectroscopically pure complex as a single isomer. ¹H NMR (400 MHz, Methylene Chloride-d₂) δ 7.66 (d, 1H), 7.43 (m, 3H), 7.28 (m, 1H), 6.37 (s, 1H), 2.70 (m, 3H), 2.52 (m, 1H), 2.37 (m, 1H), 2.23 (s, 3H), 2.05 (s, 3H), 1.97 (overlapping s, 6H), 1.94 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H), 1.11 (s, 3H), 1.06 (s, 6H), 1.05 (s, 3H).

Synthesis of 2,2,6-trimethyl-8-phenyl-3,5-dihydro-1H-s-indacene

- 20 [0186] To a stirring mixture of 4-bromo-2,2,6-trimethyl-1,2,3,5-tetrahydro-s-indacene (1.04 g, 3.75 mmol), phenylboronic acid (0.457 g, 3.75 mmol), potassium carbonate (2.26 g, 16.3 mmol), 1,3,5,7-Tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane (0.0658 g, 6 mol%), and bis(dibenzylideneacetone)palladium (0.0431 g 2 mol%) in tetrahydrofuran (16 mL) in a glass vial equipped with PTFE septum, degassed water (3 mL) was added. The
- 25 reaction was stirred and heated to 75°C. After 3 hours, the reaction mixture was concentrated. The residue was diluted with 10 mL of water and extracted with 3 x 15 mL of diethylether. The combined organic layers were washed with water (3 x 10 mL) and brine (1 x 10 mL), dried over MgSO₄ and filtered. Solvent removal afforded orange oil. The oil was chromatographed (5% EtOAc / hexane) to afford a spectroscopically pure white oil in 90% yield. ¹H NMR (CDCl₃)
- 30 δ 7.43 (m, 2H) 7.40 (m, 3H), 7.09 (s, 1H), 6.50 (s, 1H), 3.19 (s, 2H), 2.82 (s, 2H), 2.64 (s, 2H), 2.11 (s, 3H) 1.15 (s, 6H).

Synthesis of (2,6,6-trimethyl-4-phenyl-5,7-dihydro-1H-s-indacen-1-yl)lithium

[0187] nBuLi (1.4 mL of 2.7 M solution) was slowly added to a stirring, pre-cooled diethylether solution of 2,2,6-trimethyl-8-phenyl-3,5-dihydro-1H-s-indacene (0.98 g,

3.6 mmol). The reaction mixture was allowed to warm up to room temperature and was stirred overnight. After 18 hours, the solution is white with copious amount of precipitate. Solvent was removed *in vacuo*, and the residue was triturated with pentane and filtered. The resulting white solid was washed with additional pentane (10 mL) and dried *in vacuo* to afford spectroscopically pure product as a white solid. ¹H NMR (THF-d₈) δ 7.63 (m, 2H) 7.33 (m, 2H), 7.16 (t, 3H) 7.04 (s, 1H), 5.74 (s, 1H), 2.74 – 2.72 (overlapping s, 4H), 2.33 (s, 3H), 1.12 (s, 6H).

Synthesis of dimethyl-(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)-(2,6,6-trimethyl-4-phenyl-5,7-dihydro-1H-s-indacen-1-yl)silane

[0188] Solid (2,6,6-trimethyl-4-phenyl-5,7-dihydro-1H-s-indacen-1-yl)lithium (0.86 g, 3.1 mmol) was slowly added to a stirring, pre-cooled solution of dimethyl-(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)silyl trifluoromethanesulfonate (0.96 g, 2.9 mmol) in diethylether. The reaction mixture was allowed to warm up to room temperature and was stirred for 1 hour. After 1 hour, solvent was removed *in vacuo*, and the residue was extracted with pentane (2 x 10 mL) and filtered over celite. Solvent removal afforded spectroscopically pure white foam in quantitative yield. ¹H NMR (C₆D₆) δ 7.52 (m 2H), 7.37 (m, 3H) 7.19 (m, 1H), 6.71 (s, 1H) 3.63 (s, 1H), 3.22 (s, 1H), 2.80 (m, 4H), 2.03 (s, 3H), 1.97 (s, 3H) 1.92 (s, 3H) 1.83 (s, 6H), 1.08 (overlapping s, 6H), -0.14 (overlapping s, 6H).

Synthesis of dilithium-dimethyl-(2,3,4,5-tetramethylcyclopentadienyl)-(2,6,6-trimethyl-4-phenyl-5,7-dihydro-indacen-1-yl)silane

[0189] nBuLi (2.4 mL, 2.7M solution) was slowly added to a pre-cooled solution of dimethyl-(2,3,4,5-tetramethylcyclopenta-2,4-dien-1-yl)-(2,6,6-trimethyl-4-phenyl-5,7-dihydro-1H-s-indacen-1-yl)silane (1.4 g, 3.0 mmol) in diethylether. The reaction mixture was allowed to warm up to room temperature and was stirred for 1 hour. After 1 hour, solvent was removed *in vacuo* to afford yellow residue. The residue was washed with pentane (3 x 10 mL) and dried *in vacuo* to afford yellow solid, which was spectroscopically pure. ¹H NMR (THF-d₈) δ 7.56 – 7.52 (m, 2H), 7.42 (s, 1H), 7.31 (m, 2H), 7.18 – 7.12 (m, 1H), 5.83 (s, 1H), 2.74 (s, 2H), 2.68 (s, 2H), 2.36 (s, 3H), 2.16 (s, 6H), 1.95 (s, 6H), 1.11 (s, 6H), 0.63 (s, 6H).

Synthesis of dimethylsilyl-(2,3,4,5-tetramethylcyclopentadienyl)-(2,6,6-trimethyl-4-phenyl-5,7-dihydro-indacenyl) zirconium dichloride (catalyst C₁₄)

[0190] Solid dilithium-dimethyl-(2,3,4,5-tetramethylcyclopentadienyl)-(2,6,6-trimethyl-4-phenyl-5,7-dihydro-indacen-1-yl)silane ligand (1.4 g, 3.0 mmol) was slowly added to a pre-cooled solution of ZrCl₄(OEt₂)₂ (1.1 g, 3.0 mmol) in diethylether. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. After 18 hours, the reaction

mixture was concentrated *in vacuo* to afford dark yellow residue. The residue was extracted with methylene chloride (2 x 15 mL), filtered over celite and concentrated. Addition of pentane precipitated dark yellow powder, which was collected and washed with additional minimal pentane to afford 1.3 g of crude product. Minimal diethylether was then added to the bulk, and the residue was filtered again to afford yellow solid. The solid was dried *in vacuo* and confirms desired product (0.9 g, 50% yield) ¹H NMR (400 MHz, CD₂Cl₂) δ 7.65 – 7.56 (m, 2H), 7.53 – 7.44 (m, 2H), 7.44 – 7.34 (m, 2H), 6.73 (t, *J* = 0.8 Hz, 1H), 2.89 – 2.59 (m, 5H), 2.25 (d, *J* = 0.6 Hz, 3H), 2.08 (s, 3H), 1.99 (s, 3H), 1.95 (s, 3H), 1.93 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H), 1.12 (s, 3H), 1.08 (s, 3H).

10 Preparation of support material (SMAO)

[0191] 12.8 g of PD17062 silica (PQ corporation, calcined at 600°C calcination) was slurried in 50 mL of toluene and cooled to -35°C in the freezer. While stirring, 21.0 g of MAO (30 % solution in toluene) was then added slowly via pipette. The mixture was allowed to warm up to room temperature and was stirred for 1 hour. After 1 hour, the mixture was heated to 100°C for additional 2.5 hours. After 2.5 hours, the mixture was cooled to 55°C and filtered while hot. The collected solid was washed with toluene (2 x 30 mL) and pentane (2 x 30 mL) and dried *in vacuo* to afford 18.2 g of SMAO as a white free flowing powder.

Preparation of supported catalysts.

[0192] 1 g of SMAO was placed in 6 mL of toluene and placed on a shaker. While shaking, 0.52 mL of 1 M solution of triisobutylaluminum was added. The mixture was allowed to shake for 15 minutes at room temperature. After 15 minutes, 22 μmol of metallocene was added in ca 2 mL of toluene. The reaction mixture was allowed to shake for 3.5 hours. After 3.5 hours, the slurry was filtered, and the solid was washed with toluene (2 x 5 mL) and hexane (2 x 5 mL) and dried *in vacuo*. Each catalyst was used in reactor testing as 5 wt% slurry in mineral oil.

25 Propylene polymerization in a 2L reactor.

[0193] A 2L autoclave equipped with a steam jacket and mechanical stirrer was nitrogen purged and heated to 130°C for at least 1 hour. Upon cooling to room temperature, liquid propylene (400 mL), triisobutylaluminum (0.4 mL of 1 M solution in hexane) and desired amount of hydrogen (typically 1 – 30 mmol) were added and allowed to mix for 5 minutes. After 5 minutes, catalyst slurry (typically 12.5 – 25.0 mg of dry catalyst) was flushed in the reactor along with 400 mL of liquid propylene. The contents of the reactor were allowed to mix for 5 minutes (pre-polymerization stage), before reactor temperature was raised to 70°C to start the polymerization. After 30 minutes, the reactor was cooled to room temperature, unreacted propylene was vented, and the polymer was collected and allowed to dry overnight.

Polymerization Results

[0194] The preliminary screening using parallel pressure reactors (PPR) revealed higher than anticipated activities of inventive catalysts I1 and I2 relative to control catalysts C1-C9 (Table 1). The advantage in higher activity while maintaining relatively comparable Mw capability and narrow polydispersities (PDI) represents a clear advantage of using catalyst systems based on 6,6-dimethylindacenes.

Table 1 Propylene polymerization in solution (70°C, MAO activation, 115 psi in isohexane)

Catalyst	PP activity (kg/mmol·h)	Mn (g/mol)	Mw (g/mol)	PDI
C1	278.3	46,487	95,195	2.05
C2	305.1	43,975	92,102	2.09
C3	296.8	49,099	84,542	1.72
C4	271.1	71,112	124,129	1.75
C5	332.3	51,058	117,976	2.31
C7	273.0	43,615	81,155	1.86
C9	229.5	40,841	66,803	1.64
C10	122.1	56,731	96,000	1.69
C13	97.4	57,109	90,061	1.58
C14	261.0	48,679	80,396	1.65
I2	377.9	42,819	93,579	2.19
I1	302.7	33,226	75,965	2.29

[0195] In order to illustrate the performance of new catalysts in slurry polymerization – inventive catalysts I1- I5 were supported using silica supported MAO (SMAO) and tested under industrially relevant propylene polymerization conditions at 70°C. The results are illustrated in the Figures.

[0196] FIG. 1 is graphs illustrating catalyst productivity of inventive catalysts and comparative catalysts, according to some embodiments.

[0197] FIG. 2 is histogram illustrating catalyst productivity as a function of example type (top chart) and as a function of hydrogen in reactor (bottom), according to some embodiments.

[0198] FIG. 3 is a graph illustrating average polymer melting points taken across the hydrogen gradient in reactor. Error bars represent the range of melting points obtained at two hydrogen extremes (2 mmol and 15 mmol).

[0199] FIG. 4 is a graph illustrating polymer Mw as a function of hydrogen loading in the

reactor, according to some embodiments.

[0200] FIG. 5 is a graph illustrating molecular weight distribution (MWD) dependence on hydrogen loading in the reactor, according to some embodiments.

[0201] FIG. 6 is a graph illustrating flexural modulus of iPP produced as a function of mmol H₂ in reactor, according to some embodiments.

[0202] FIG. 7 is a graph illustrating Young's modulus of iPP produced as a function of mmol H₂ in reactor, according to some embodiments.

[0203] FIG. 8 is a graph illustrating tensile strength at yield of iPP produced as a function of mmol H₂ in reactor, according to some embodiments.

[0204] Inventive catalysts I1 and I2 showed 2 – 4-fold improvement in catalyst productivity in slurry polymerization relative to representative comparatives (liquid propylene, 70°C) while using identical catalyst preparation route, silica support and hydrogen loadings. In addition to this, high activity was maintained at all hydrogen levels and catalyst had sufficient chain transfer response to produce resins of broad molecular weight capability (from about 330 kg/mol to about 100 kg/mol) under tested conditions. This molecular weight capability range corresponds to broad MFR range (1 – 1000 MFR), thus significantly extending the applicability of the inventive systems. In addition to above mentioned benefits, inventive catalysts were able to maintain very narrow MWD while eliminating higher fractions of low molecular weight tails. For example, MWD for inventive catalysts I1 and I2 were usually between 2.8 – 2.9, which is narrower compared to indacenyl catalysts C₁, C₄ and C₆ and similar to low activity catalysts C₇-C₁₃. The added benefits allow for preparation of resins for fiber spinning (spunbound and meltblown) and injection molding articles used in medical applications, all which involve cleanliness, narrow polydispersities, low volatile organic compounds (VOCs) and low odor. In addition to this, high melting points of inventive catalysts (T_m = 158 - 160°C) allows for improved stiffness for rigid parts, allowing application in impact copolymers commonly used in automotive industry. Finally, inventive catalysts I1 and I2 contain a substituted aryl group in the 4-position of the indacenyl ring. Relative to unsubstituted aryl group (*e.g.*, phenyl) highlighted in catalyst C₁₄, inventive catalysts showed generally improved activity (highest 33 kg/g and 43 kg/g for I1 and I2) relative to 27 kg/g for C₁₄. In addition to activity improvements, average polymer melting points were also improved (158°C and 160°C for I1 and I2) relative to 157°C for catalyst C₁₄. These results demonstrate that substitutions of the aryl ring in the 4-position results in unexpected improvements in both catalyst activities and stereoselectivities (and thus polymer crystallinities) in propylene polymerization.

¹³C NMR analysis of polymer samples

[0205] In addition to polymer characterization by GPC-4D and DSC, ¹³C NMR was employed to evaluate microstructure of produced resins. The average results are reported in Table 2. As indicated in Table 2, the inventive catalysts demonstrate slight improvement in tacticity (mmmm) relative to analogous tetrahydroindacenyl catalysts C₁- C₆ and significantly improved balance of stereo / regio errors relative to comparative catalysts C₁₁-C₁₄. Such properties enabled generally improved mechanical properties of resulting polymers discussed later in the document.

Table 2 – ¹³C NMR analysis

Catalyst	<i>mmmm</i>	Total 1,2 stereo errors	Total 2,1 regio errors
C1	0.958	76	3
C2	0.939	136	8
C3	0.948	97	10
C4	0.940	121	8
C5	0.963	70	5
C6	0.897	194	0
C11	0.943	107	14
C12	0.952	88	11
C13	0.934	131	30
C14	0.957	80	10
I1	0.953	86	6
I2	0.965	62	5
I3	0.962	68	9
I4	0.966	62	10
I5	0.959	79	2

10

Mechanical Properties of Polypropylenes.

[0206] Mechanical testing on Type-3 injection molded specimens prepared from compounded polypropylene samples (500 ppm Irganox 1010 and 500 ppm Irgafos 168) revealed additional advantages of using inventive catalysts based on 2,6,6-trimethylindacenyl moieties. Each measurement represents an average of 5 sample bars.

[0207] For example, polypropylenes prepared with inventive catalysts I1 and I2 showed higher resistance to deformation both under bending (Flexural Modulus) and under tension (Young's Modulus) across the broad range of hydrogen loading in reactor as described in FIGs. 6 and 7. Therefore, polypropylenes prepared with inventive catalysts demonstrate improved stiffness when compared to analogous C₁ symmetric catalysts from indacenyl (C₁ and C₆), indenyl (C₇ and C₈), 5-OMe-6-tBu-indenyl (C₁₁ and C₁₂) and pentamethylindacenyl (C₁₃) sub-families. Given that the 4-aryl substitution was kept consistent in the sample series (either 4-tBu-phenyl or 3,5-tBu2-4-OMe phenyl) the effect of improved stiffness is provided by

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2,6,6-trimethylsubstitution of inventive catalyst compounds.

[0208] In addition to improved stiffness, polymers prepared with inventive systems show significantly improved tensile properties, especially at higher hydrogen loadings (and thus polymer MFR) as illustrated in FIG. 8.

- 5 [0209] To summarize, inventive catalysts provide polypropylenes with significant improvements in mechanical properties as indicated by Table 2 below. Overall, inventive systems provide approximately about 10% improved polypropylene stiffness relative to incumbent C₁ symmetric comparatives under identical reaction and catalyst preparation conditions.

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Table 3: Comparative Examples

Flexural Modulus (MPa)		Young's Modulus (MPa)		Tensile Yield Stress (MPa)	
Mean	1420.3993	Mean	1738.2105	Mean	33.497568
Std Dev	139.79034	Std Dev	80.171872	Std Dev	1.4690745
Std Err	21.317827	Std Err	12.226096	Std Err	0.2415144
Mean		Mean		Mean	
Upper 95% Mean	1463.4204	Upper 95% Mean	1762.8837	Upper 95% Mean	33.987381
Lower 95% Mean	1377.3782	Lower 95% Mean	1713.5372	Lower 95% Mean	33.007754
N	43	N	43	N	37

Table 3 (Continued): Inventive Examples

Flexural Modulus (MPa)		Young's Modulus (MPa)		Tensile Yield Stress (MPa)	
Mean	1572.6	Mean	1887.4733	Mean	34.817333
Std Dev	109.50753	Std Dev	87.383248	Std Dev	1.0633671
Std Err	28.274723	Std Err	22.562258	Std Err	0.2745602
Mean		Mean		Mean	
Upper 95% Mean	1633.2433	Upper 95% Mean	1935.8646	Upper 95% Mean	35.406206
Lower 95% Mean	1511.9567	Lower 95% Mean	1839.0821	Lower 95% Mean	34.22846
N	15	N	15	N	15

Gel Permeation Chromatography

[0210] High temperature size exclusion chromatography was performed on samples described in Table 1 using an automated "Rapid GPC" system as described in U.S. 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; 5 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 15 (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 7.5 mm 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. 20 The molecular weights obtained are relative to linear polystyrene standards.

GPC-4D

[0211] Unless otherwise indicated the reactor samples were analyzed according to the GPC-4D method described above.

Differential Scanning Calorimetry (DSC)

25 [0212] 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 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 30 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.

[0213] Overall, catalyst compounds of the present disclosure can have high activity and low sensitivity to exothermic deactivation. Catalyst compounds can be capable of providing polymers suitable for use in medical materials. Catalyst compounds can provide polymers having high melting points broad molecular weight capabilities, particularly for propylene polymerization. Polymers of the present disclosure can have narrow polydispersity, robust isotacticity, and broad MFR capability. Such benefits allow for preparation of resins for fiber spinning (spunbound and meltblown) and injection molding articles used in medical applications, all which provide cleanliness, narrow polydispersities, low volatile organic compounds (VOCs) and low odor. In addition, high melting points of polypropylene provided by catalyst compounds of the present disclosure allows for improved stiffness for rigid parts, allowing application of polypropylene for impact copolymers commonly used in automotive industry. In addition to improved stiffness, polypropylenes can have significantly improved tensile properties, especially at higher hydrogen loadings (and thus polymer MFR).

[0214] 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.

[0215] 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.

[0216] All documents described herein are incorporated by reference herein, including any priority documents and or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the present disclosure have been illustrated and described, various modifications can

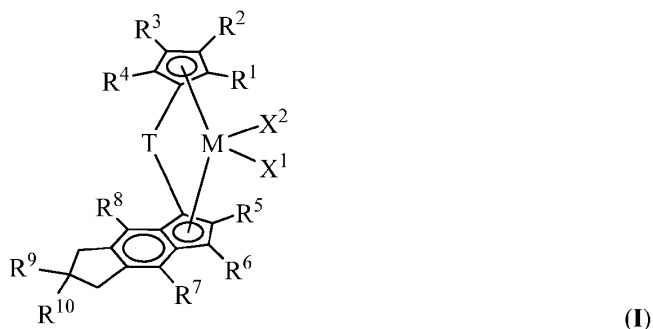
be made without departing from the spirit and scope of the present disclosure. Accordingly, it is not intended that the present disclosure be limited thereby. Likewise, the term “comprising” is considered synonymous with the term “including” for purposes of United States law. Likewise, whenever a composition, an element or a group of elements is preceded with the
5 transitional phrase “comprising,” it is understood that we also contemplate the same composition or group of elements with transitional phrases “consisting essentially of,” “consisting of,” “selected from the group of consisting of,” or “is” preceding the recitation of the composition, element, or elements and vice versa.

[0217] While the present disclosure has been described with respect to a number of
10 embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the present disclosure.

CLAIMS:

We claim:

1. A compound represented by Formula (I):



wherein:

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

T is a bridging group;

each of X¹ and X² is independently a univalent anionic ligand, or X¹ and X² are joined to form a metallocycle ring;

R¹, R², R³, and R⁴ are each independently a hydrogen atom or substituted or unsubstituted C₁ to C₆ hydrocarbyl group and, optionally, any adjacent R¹, R², R³ and R⁴ can be joined to form a cyclic structure;

R⁵ is a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group;

R⁶ and R⁸ are each independently a hydrogen atom or a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group;

R⁷ is a substituted aryl group, unsubstituted naphthyl, unsubstituted anthracenyl, or substituted or unsubstituted heteroaryl group; and

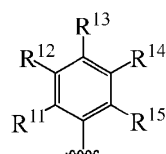
R⁹ and R¹⁰ are each independently a substituted or unsubstituted C₁ to C₂₀ hydrocarbyl group.

2. The compound of claim 1, wherein R¹, R², R³, and R⁴ are each independently selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, and hexyl.
3. The compound of claims 1 or 2, wherein R⁵ is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, and decyl.
4. The compound of claim 3, wherein R⁵ is methyl.

5. The compound of any of claims 1 to 4, wherein R^6 and R^8 are each independently selected from the group consisting of hydrogen, methyl, ethyl, propyl, butyl, pentyl, and hexyl.

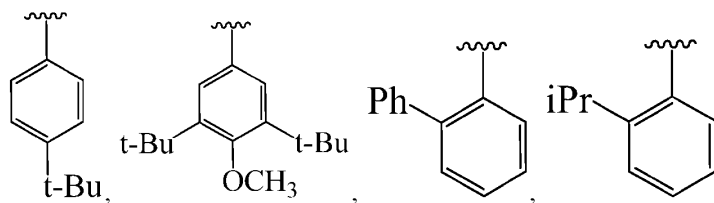
6. The compound of claim 5, wherein R^6 and R^8 are each hydrogen.

7. The compound of any of claims 1 to 6, wherein R^7 is a substituted aryl group represented by the formula:

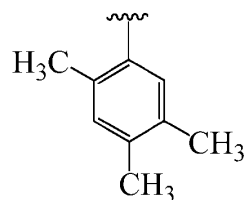


, wherein each of R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} is independently selected from the group consisting of hydrogen, substituted or unsubstituted C_1 - C_{10} alkyl, substituted or unsubstituted C_1 - C_6 alkoxy, and substituted or unsubstituted phenyl, wherein at least one of R^{11} , R^{12} , R^{13} , R^{14} , or R^{15} is not hydrogen.

8. The compound of claim 7, wherein R^7 is selected from the group consisting of:



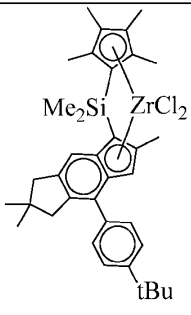
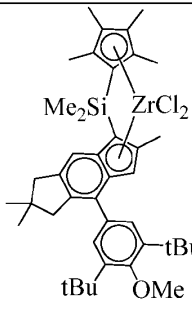
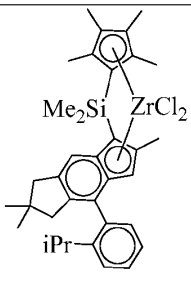
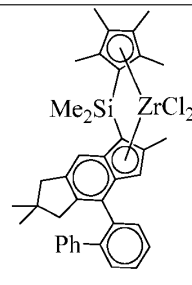
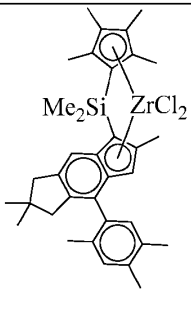
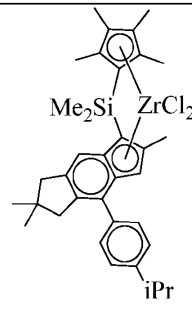
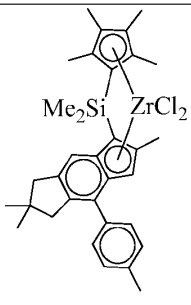
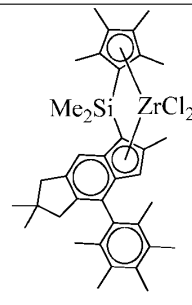
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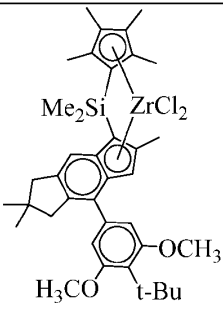
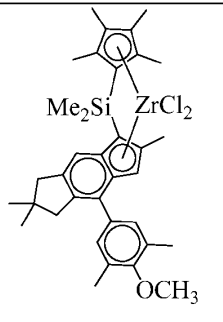
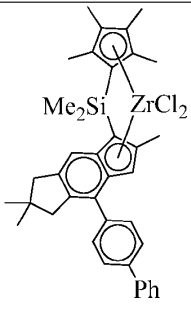
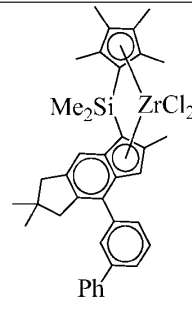
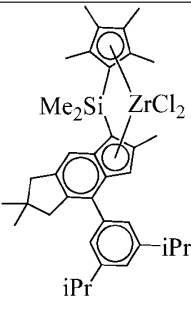
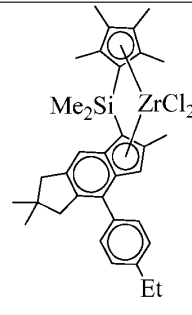
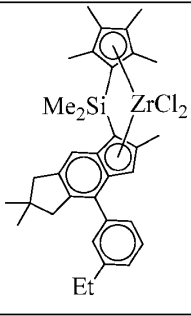
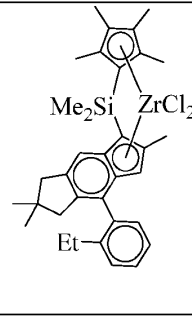


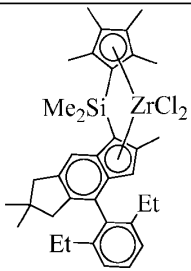
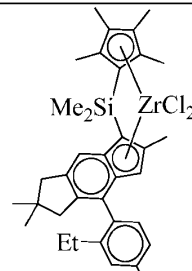
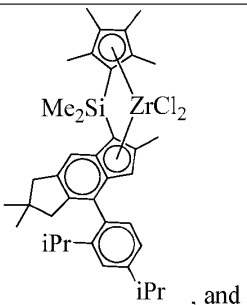
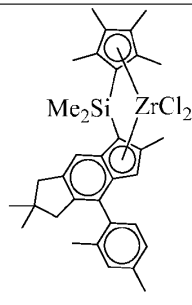
9. The compound of any of claims 1 to 6, wherein R^7 is selected from the group consisting of 3-biphenyl, 4-biphenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 3,4,5-trimethylphenyl, 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, 3-isopropylphenyl,

4-isopropylphenyl, 3,5-di-isopropylphenyl, 2,5-di-isopropylphenyl, 2-tert-butylphenyl, 3-tert-butylphenyl, 3,5-di-tert-butylphenyl, 3,5-di-tert-butyl-4-dimethylamino-phenyl, 2,5-di-tert-butylphenyl, 2-trimethylsilylphenyl, 3-trimethylsilylphenyl, 4-trimethylsilylphenyl, 3,5-bis(trimethylsilyl)phenyl, 2-trifluoromethylphenyl, 3-trifluoromethylphenyl, 4-trifluoromethylphenyl, and 3,5-bis(trifluoromethyl)phenyl.

10. The compound of any of claims 1 to 9, wherein R^9 and R^{10} are each independently unsubstituted C_1 to C_6 hydrocarbyl group.
11. The compound of claim 10, wherein R^9 and R^{10} are methyl.
12. The compound of any of claims 1 to 11, wherein T is selected from the group consisting of $SiMe_2$, $Si(CH_2CH_3)_2$, and $Si(CH_2CH_2CH_3)_2$.
13. The compound of any of claims 1 to 12, wherein M is Zr or Hf.
14. The compound of any of claims 1 to 13, wherein X^1 and X^2 are chloride.
15. The compound of claim 1, wherein:
 - (1) M is Zr or Hf,
 - (2) T is $SiMe_2$, $Si(CH_2CH_3)_2$, or $Si(CH_2CH_2CH_3)_2$,
 - (3) each of R^6 and R^8 is independently a hydrogen atom or an unsubstituted C_1 - C_{10} alkyl,
 - (4) each of R^9 and R^{10} is independently an unsubstituted C_1 - C_{10} alkyl,
 - (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 aryl, and
 - (8) each of X^1 and X^2 is independently chloride or methyl.
16. The compound of claim 1, wherein the compound is selected from the group consisting of:

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19	 , and	20	 .

17. A catalyst system comprising an activator, the compound of any of claims 1 to 16, and an optional support material.

18. A process for producing olefin homopolymer or copolymer, the process comprising:
polymerizing one or more olefins selected from the group consisting of one or more C₂-C₂₀ alpha-olefins, by introducing one or more C₂-C₂₀ alpha olefins and optionally hydrogen with the catalyst system of claim 17, in solution, gas phase or slurry reactor, in series, or in parallel, at a reactor pressure of about 0.05 MPa to about 1,500 MPa and a reactor temperature of about 30°C to about 230°C to form the alpha olefin homopolymer or copolymer.

19. The process of claim 18, wherein the C₂-C₂₀ alpha-olefin consists of propylene to form the olefin homopolymer, wherein the olefin homopolymer is an isotactic polypropylene.

20. The process of claim 19, wherein the isotactic polypropylene has a molecular weight distribution (MWD) of less than 3 and a melting point (T_m) of about 157°C to about 162°C.