

**TITLE: Propylene Polymers Obtained Using Transition Metal Bis(Phenolate) Catalyst
5 Complexes and Homogeneous Process for Production Thereof**

PRIORITY

[0001] This application claims priority to and the benefit of USSN 62/972,953, filed
10 February 11, 2020.

CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This invention is related to:

- 1) USSN 16/788,022, filed Feb 11, 2020;
- 2) USSN 16/788,088, filed Feb 11, 2020;
- 15 3) USSN 16/788,124, filed Feb 11, 2020;
- 4) USSN 16/787,909, filed Feb 11, 2020;
- 5) USSN 16/787,837, filed Feb 11, 2020;
- 6) concurrently filed PCT application number PCT/US2020/____ entitled “Propylene
Copolymers Obtained Using Transition Metal Bis(Phenolate) Catalyst Complexes and
20 Homogeneous Process for Production Thereof” (attorney docket number **2020EM048**);
- 8) concurrently filed PCT application number PCT/US2020/____ entitled
“Ethylene-Alpha-Olefin-Diene Monomer Copolymers Obtained Using Transition Metal
Bis(Phenolate) Catalyst Complexes and Homogeneous Process for Production Thereof”
(attorney docket number **2020EM050**);
- 25 9) concurrently filed PCT application number PCT/US2020/____ entitled
“Polyethylene Compositions Obtained Using Transition Metal Bis(Phenolate) Catalyst
Complexes and Homogeneous Process for Production Thereof” (attorney docket number
2020EM051).

FIELD OF THE INVENTION

30 **[0003]** This invention relates propylene polymers prepared using novel catalyst
compounds comprising group 4 bis(phenolate) complexes, compositions comprising such, and
processes to prepare such propylene polymers.

BACKGROUND OF THE INVENTION

[0004] Olefin polymerization catalysts are of great use in industry. Hence there is interest in finding new catalyst systems that increase the commercial usefulness of the catalyst and allow the production of polymers having improved properties.

- 5 [0005] Catalysts for olefin polymerization can be based on bis(phenolate) complexes as catalyst precursors, which are activated typically by an alumoxane or an activator containing a non-coordinating anion. Examples of bis(phenolate) complexes can be found in the following references:

10 [0006] KR 2018-022137 (LG Chem.) describes transition metal complexes of bis(methylphenyl phenolate)pyridine.

[0007] US 7,030,256 B2 (Symyx Technologies, Inc.) describes bridged bi-aromatic ligands, catalysts, processes for polymerizing and polymers therefrom.

[0008] US 6,825,296 (University of Hong Kong) describes transition metal complexes of bis(phenolate) ligands that coordinate to metal with two 6-membered rings.

- 15 [0009] US 7,847,099 (California Institute of Technology) describes transition metal complexes of bis(phenolate) ligands that coordinate to metal with two 6-membered rings.

[0010] WO 2016/172110 (Univation Technologies) describes complexes of tridentate bis(phenolate) ligands that feature a non-cyclic ether or thioether donor.

- 20 [0011] Other references of interest include: Baier, M. C. (2014) "Post-Metallocenes in the Industrial Production of Polyolefins," *Angew. Chem. Int. Ed.* 2014, v.53, pp. 9722-9744; and Golisz, S. et al. (2009) "Synthesis of Early Transition Metal Bisphenolate Complexes and Their Use as Olefin Polymerization Catalysts," *Macromolecules*, v.42(22), pp. 8751-8762.

- 25 [0012] New catalysts capable of polymerizing olefins to yield high molecular weight and/or high tacticity polymers at high process temperatures are desirable for the industrial production of polyolefins. There is still a need in the art for new and improved catalyst systems for the polymerization of olefins, in order to achieve specific polymer properties, such as high molecular weight and/or high tacticity polymers, preferably at high process temperatures.

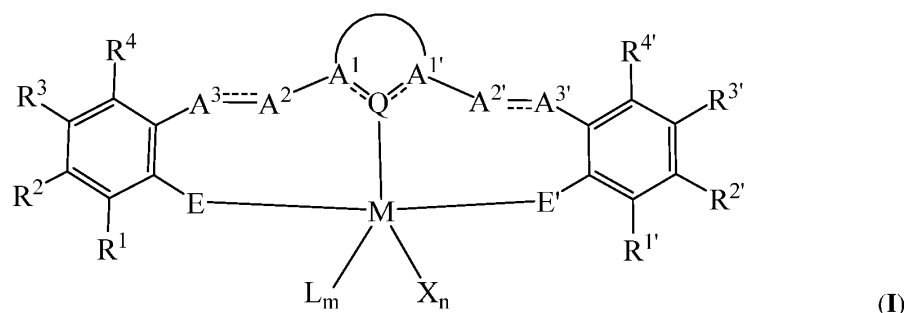
- 30 [0013] Further, it is advantageous to conduct commercial solution polymerization reactions at elevated temperatures. Major catalyst limitations often preventing access to such high temperature polymerizations are the catalyst efficiency, molecular weight of produced polymers, and for propylene homo-polymerization, high polymer crystallinity. All of these factors typically decrease with rising reactor temperature. Typical metallocene catalysts suitable for use in producing isotactic polypropylene require lower process temperatures to achieve a desired polymer crystallinity.

[0014] The newly developed single-site catalyst described herein and in related USSN 16/787,909 filed February 11, 2020 entitled “*Transition Metal Bis(Phenolate) Complexes and Their Use as Catalysts for Olefin Polymerization*,” (attorney docket number 2020EM045), has the capability of producing high molecular weight and highly crystalline isotactic polypropylene at elevated polymerization temperatures. These catalysts, when paired with various types of activators and used in a solution process can produce propylene based polymers with high crystallinity and molecular weight, among other things. Further, the catalyst activity is high which facilitates use in commercially relevant process conditions. This new process provides new propylene polymers having high crystallinity that can be produced with increased reactor throughput and at higher polymerization temperatures during polymer production.

SUMMARY OF THE INVENTION.

[0015] This invention relates to propylene polymers, such as propylene homopolymers, propylene copolymers with C₄ and higher alpha olefins, and blends comprising such propylene polymers, where the propylene polymers are prepared in a solution process using transition metal catalyst complexes of a dianionic, tridentate ligand that features a central neutral heterocyclic Lewis base and two phenolate donors, where the tridentate ligand coordinates to the metal center to form two eight-membered rings.

[0016] This invention also relates to propylene homopolymers, such as isotactic propylene polymers, isotactic propylene copolymers with C₄ and higher alpha olefins, and blends comprising such propylene polymers, where the propylene polymers are, prepared in a solution process using bis(phenolate) complexes represented by Formula (I):



wherein:

- 25 M is a group 3-6 transition metal or Lanthanide;
- E and E' are each independently O, S, or NR⁹, where R⁹ is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group;
- Q is group 14, 15, or 16 atom that forms a dative bond to metal M;

$A^1QA^{1'}$ are part of a heterocyclic Lewis base containing 4 to 40 non-hydrogen atoms that links A^2 to $A^{2'}$ via a 3-atom bridge with Q being the central atom of the 3-atom bridge, A^1 and $A^{1'}$ are independently C, N, or $C(R^{22})$, where R^{22} is selected from hydrogen, C_1 - C_{20} hydrocarbyl, C_1 - C_{20} substituted hydrocarbyl;

5 $A^3 \text{---} A^2$ is a divalent group containing 2 to 40 non-hydrogen atoms that links A^1 to the E-bonded aryl group via a 2-atom bridge;

$A^{2'} \text{---} A^{3'}$ is a divalent group containing 2 to 40 non-hydrogen atoms that links $A^{1'}$ to the E'-bonded aryl group via a 2-atom bridge;

L is a neutral Lewis base;

10 X is an anionic ligand;

n is 1, 2 or 3;

m is 0, 1, or 2;

n+m is not greater than 4;

15 each of R^1 , R^2 , R^3 , R^4 , $R^{1'}$, $R^{2'}$, $R^{3'}$, and $R^{4'}$ is independently hydrogen, C_1 - C_{40} hydrocarbyl, C_1 - C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R^1 and R^2 , R^2 and R^3 , R^3 and R^4 , $R^{1'}$ and $R^{2'}$, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$ may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings;

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

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

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

[0017] This invention also relates to a solution phase method to polymerize olefins comprising contacting a catalyst compound as described herein with an activator. This invention further relates to propylene polymer compositions produced by the methods described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] Figure 1 is a graph of the polymerization temperature ($^{\circ}\text{C}$) vs. polypropylene T_m ($^{\circ}\text{C}$) for polymer samples produced in a continuous polymerization unit.

DEFINITIONS

[0019] For the purposes of this invention and the claims thereto, the following definitions shall be used:

[0020] The new numbering scheme for the Periodic Table Groups is used as described in *Chemical And Engineering News*, v.63(5), pg. 27 (1985). Therefore, a “group 4 metal” is an element from group 4 of the Periodic Table, e.g. Hf, Ti, or Zr.

[0021] “Catalyst productivity” is a measure of the mass of polymer produced using a known quantity of polymerization catalyst. Typically, “catalyst productivity” is expressed in units of (g of polymer)/(g of catalyst) or (g of polymer)/(mmols of catalyst) or the like. If units are not specified then the “catalyst productivity” is in units of (g of polymer)/(g of catalyst). For calculating catalyst productivity only the weight of the transition metal component of the catalyst is used (i.e. the activator and/or co-catalyst are omitted). “Catalyst activity” is a measure of the mass of polymer produced using a known quantity of polymerization catalyst per unit time for batch and semi-batch polymerizations. Typically, “catalyst activity” is expressed in units of (g of polymer)/(mmol of catalyst)/hour or (kg of polymer)/(mmols of catalyst)/hour or the like. If units are not specified then the “catalyst activity” is in units of (g of polymer)/(mmol of catalyst)/hour.

[0022] “Conversion” is the percentage of a monomer that is converted to polymer product in a polymerization, and is reported as % and is calculated based on the polymer yield, the polymer composition, and the amount of monomer fed into the reactor.

[0023] An “olefin,” alternatively referred to as “alkene,” is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have a “propylene” content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from propylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer. A “polymer” has two or more of the same or different mer units. A “homopolymer” is a polymer having mer units that are the same. A “copolymer” is a polymer having two or more mer units that are different from each other. A “terpolymer” is a polymer having three mer units that are different from each other. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. “Different” as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. A “propylene polymer” or “propylene copolymer” is a polymer or copolymer comprising at least 50 mole% propylene derived units, and so on.

[0024] An alpha olefin is defined as a linear or branched C₃ or higher olefin containing at least one vinyl (CH₂=CH-) group. Non-limiting examples of alpha olefins include propylene,

1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 4-methyl-1-pentene, and styrene.

[0025] Unless otherwise specified, the term “C_n” means hydrocarbon(s) having n carbon atom(s) per molecule, wherein n is a positive integer.

- 5 **[0026]** The term “hydrocarbon” means a class of compounds containing hydrogen bound to carbon, and encompasses (i) saturated hydrocarbon compounds, (ii) unsaturated hydrocarbon compounds, and (iii) mixtures of hydrocarbon compounds (saturated and/or unsaturated), including mixtures of hydrocarbon compounds having different values of n. Likewise, a “C_m-C_y” group or compound refers to a group or compound comprising carbon
10 atoms at a total number thereof in the range from m to y. Thus, a C₁-C₅₀ alkyl group refers to an alkyl group comprising carbon atoms at a total number thereof in the range from 1 to 50.

[0027] The terms “group,” “radical,” and “substituent” may be used interchangeably.

- [0028]** The terms “hydrocarbyl radical,” “hydrocarbyl group,” or “hydrocarbyl” may be used interchangeably and are defined to mean a group consisting of hydrogen and carbon atoms
15 only. Preferred hydrocarbyls are C₁-C₁₀₀ radicals that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such radicals include, but are not limited to, alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like, aryl groups, such as phenyl, benzyl, naphthalen-2-yl, and the like.

- 20 **[0029]** Unless otherwise indicated, (e.g., the definition of “substituted hydrocarbyl”, etc.), the term “substituted” means that at least one hydrogen atom has been replaced with at least one non-hydrogen group, such as a hydrocarbyl group, a heteroatom or heteroatom-containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, -SnR*₃,
25 -PbR*₃, -(CH₂)_q-SiR*₃, and the like, where q is 1 to 10 and each R* is independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

- [0030]** The term “substituted hydrocarbyl” means a hydrocarbyl radical in which at least
30 one hydrogen atom of the hydrocarbyl radical has been substituted with at least one heteroatom (such as halogen, e.g., Br, Cl, F or I) or heteroatom-containing group (such as a functional group, e.g., -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, -SnR*₃, -PbR*₃, -(CH₂)_q-SiR*₃, and the like, where q is 1 to 10 and each R* is

independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

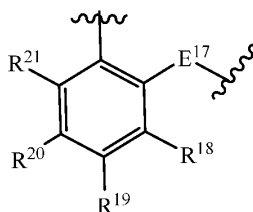
- 5 **[0031]** Silylcarbyl radicals are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one SiR*₃ containing group or where at least one -Si(R*)₂- has been inserted within the hydrocarbyl radical where R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.
- 10 **[0032]** Substituted silylcarbyl radicals are radicals in which at least one hydrogen atom has been substituted with at least one functional group such as NR*₂, OR*, SeR*, TeR*, PR*₂, AsR*₂, SbR*₂, SR*, BR*₂, GeR*₃, SnR*₃, PbR*₃ and the like or where at least one non-hydrocarbon atom or group has been inserted within the silylcarbyl radical, such as -O-, -S-, -Se-, -Te-, -N(R*)-, =N-, -P(R*)-, =P-, -As(R*)-, =As-, -Sb(R*)-, =Sb-, -B(R*)-, =B-,
- 15 -Ge(R*)₂-, -Sn(R*)₂-, -Pb(R*)₂- and the like, where R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure. Substituted silylcarbyl radicals are only bonded via a carbon or silicon atom.

- [0033]** The term "aryl" or "aryl group" means an aromatic ring (typically made of 6 carbon atoms) and the substituted variants thereof, such as phenyl, 2-methyl-phenyl, xylyl, 4-bromoxylyl. Likewise, heteroaryl means an aryl group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, such as N, O, or S. As used herein, the term "aromatic" also refers to pseudoaromatic heterocycles which are heterocyclic substituents that have similar properties and structures (nearly planar) to aromatic heterocyclic ligands, but
- 25 are not by definition aromatic.

[0034] The term "substituted aromatic," means an aromatic group having 1 or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group.

- [0035]** A "substituted phenolate" is a phenolate group where at least one, two, three, four
- 30 or five hydrogen atoms in the 2, 3, 4, 5, and/or 6 positions has been replaced with at least one non-hydrogen group, such as a hydrocarbyl group, a heteroatom or heteroatom-containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, -SnR*₃,

-PbR*₃, -(CH₂)_q-SiR*₃, and the like, where q is 1 to 10 and each R* is independently hydrogen, a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), where the 1 position is the phenolate group (Ph-O-, Ph-S-, and Ph-N(R[^])-groups, where R[^] is hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a
 5 heteroatom or a heteroatom-containing group). Preferably, a "substituted phenolate" group in the catalyst compounds described herein is represented by the formula:



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

[0036] An "alkyl substituted phenolate" is a phenolate group where at least one, two, three, four or five hydrogen atoms in the 2, 3, 4, 5, and/or 6 positions has been replaced with at least one alkyl group, such as a C₁ to C₄₀, alternately C₂ to C₂₀, alternately C₃ to C₁₂ alkyl, such as methyl, ethyl, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl,
 20 iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, adamantanyl and the like including their substituted analogues.

[0037] An "aryl substituted phenolate" is a phenolate group where at least one, two, three, four or five hydrogen atoms in the 2, 3, 4, 5, and/or 6 positions has been replaced with at least one aryl group, such as a C₁ to C₄₀, alternately C₂ to C₂₀, alternately C₃ to C₁₂ aryl group, such
 25 as phenyl, 4-fluorophenyl, 2-methylphenyl, 2-propylphenyl, 2,6-dimethylphenyl, mesityl, 2-ethylphenyl, naphthalen-2-yl and the like including their substituted analogues.

[0038] The term "ring atom" means an atom that is part of a cyclic ring structure. By this definition, a benzyl group has six ring atoms and tetrahydrofuran has 5 ring atoms.

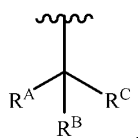
[0039] A heterocyclic ring, also referred to as a heterocyclic, is a ring having a heteroatom
 30 in the ring structure as opposed to a "heteroatom-substituted ring" where a hydrogen on a ring

atom is replaced with a heteroatom. For example, tetrahydrofuran is a heterocyclic ring and 4-N,N-dimethylamino-phenyl is a heteroatom substituted ring. A substituted heterocyclic ring means a heterocyclic ring having 1 or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group.

- 5 [0040] A substituted hydrocarbyl ring means a ring comprised of carbon and hydrogen atoms having 1 or more hydrogen groups replaced by a hydrocarbyl, substituted hydrocarbyl, heteroatom or heteroatom containing group.

- [0041] For purposes of the present disclosure, in relation to catalyst compounds (e.g., substituted bis(phenolate) catalyst compounds), the term “substituted” means that a hydrogen
 10 group has been replaced with a hydrocarbyl group, a heteroatom or heteroatom-containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, -SnR*₃, -PbR*₃, -(CH₂)_q-SiR*₃, and the like, where q is 1 to 10 and each R* is independently hydrogen,
 15 or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

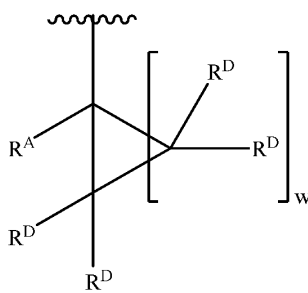
- [0042] A tertiary hydrocarbyl group possesses a carbon atom bonded to three other carbon atoms. When the hydrocarbyl group is an alkyl group, tertiary hydrocarbyl groups are also referred to as tertiary alkyl groups. Examples of tertiary hydrocarbyl groups include tert-butyl,
 20 2-methylbutan-2-yl, 2-methylhexan-2-yl, 2-phenylpropan-2-yl, 2-cyclohexylpropan-2-yl, 1-methylcyclohexyl, 1-adamantyl, bicyclo[2.2.1]heptan-1-yl and the like. Tertiary hydrocarbyl groups can be illustrated by formula A:



- wherein R^A, R^B and R^C are hydrocarbyl groups or substituted hydrocarbyl groups that may
 25 optionally be bonded to one another, and the wavy line shows where the tertiary hydrocarbyl group forms bonds to other groups.

- [0043] A cyclic tertiary hydrocarbyl group is defined as a tertiary hydrocarbyl group that forms at least one alicyclic (non-aromatic) ring. Cyclic tertiary hydrocarbyl groups are also referred to as alicyclic tertiary hydrocarbyl groups. When the hydrocarbyl group is an alkyl
 30 group, cyclic tertiary hydrocarbyl groups are also referred to as cyclic tertiary alkyl groups or alicyclic tertiary alkyl groups. Examples of cyclic tertiary hydrocarbyl groups include

1-adamantanyl, 1-methylcyclohexyl, 1-methylcyclopentyl, 1-methylcyclooctyl, 1-methylcyclodecyl, 1-methylcyclododecyl, bicyclo[3.3.1]nonan-1-yl, bicyclo[2.2.1]heptan-1-yl, bicyclo[2.3.3]hexan-1-yl, bicycle[1.1.1]pentan-1-yl, bicycle[2.2.2]octan-1-yl, and the like. Cyclic tertiary hydrocarbonyl groups can be illustrated by formula B:



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

[0044] When a cyclic tertiary hydrocarbonyl group contains more than one alicyclic ring, it can be referred to as polycyclic tertiary hydrocarbonyl group or if the hydrocarbonyl group is an alkyl group, it may be referred to as a polycyclic tertiary alkyl group.

[0045] The terms "alkyl radical," and "alkyl" are used interchangeably throughout this disclosure. For purposes of this disclosure, "alkyl radical" is defined to be C_1 - C_{100} alkyls that may be linear, branched, or cyclic. Examples of such radicals can include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like including their substituted analogues. Substituted alkyl radicals are radicals in which at least one hydrogen atom of the alkyl radical has been substituted with at least a non-hydrogen group, such as a hydrocarbonyl group, a heteroatom or heteroatom-containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as $-NR^*_2$, $-OR^*$, $-SeR^*$, $-TeR^*$, $-PR^*_2$, $-AsR^*_2$, $-SbR^*_2$, $-SR^*$, $-BR^*_2$, $-SiR^*_3$, $-GeR^*_3$, $-SnR^*_3$, $-PbR^*_3$, $-(CH_2)_q-SiR^*_3$, and the like, where q is 1 to 10 and each R^* is independently hydrogen, a hydrocarbonyl or halocarbyl radical, and two or more R^* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbonyl ring.

[0046] 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 one member of the group (e.g., n-butyl) shall

expressly disclose the remaining isomers (e.g., iso-butyl, sec-butyl, and tert-butyl) in the family. Likewise, 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).

5 [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 index (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 (g mol^{-1}).

10 [0048] The following abbreviations may be used herein: Me is methyl, Et is ethyl, Pr is propyl, cPr is cyclopropyl, nPr is n-propyl, iPr is isopropyl, Bu is butyl, nBu is normal butyl, iBu is isobutyl, sBu is sec-butyl, tBu is tert-butyl, Oct is octyl, Ph is phenyl, MAO is methylalumoxane, dme (also referred to as DME) is 1,2-dimethoxyethane, p-tBu is para-tertiary butyl, TMS is trimethylsilyl, TIBAL is triisobutylaluminum, TNOA and TNOAL are
15 tri(n-octyl)aluminum, p-Me is para-methyl, Bn is benzyl (i.e., CH_2Ph), THF (also referred to as thf) is tetrahydrofuran, RT is room temperature (and is 23°C unless otherwise indicated), tol is toluene, EtOAc is ethyl acetate, Cbz is Carbazole, and Cy is cyclohexyl. Micromoles may be abbreviated as μmol or μM .

[0049] A "catalyst system" is a combination comprising at least one catalyst compound
20 and at least one activator. 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 co-activator. 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 transition metal compound may be neutral as in a precatalyst, or a charged species with a counter ion as in an
25 activated catalyst system. For the purposes of this invention and the claims thereto, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers. A polymerization catalyst system is a catalyst system that can polymerize monomers to polymer.

30 [0050] In the description herein, the catalyst may be described as a catalyst, a catalyst precursor, a pre-catalyst compound, catalyst compound or a transition metal compound, and these terms are used interchangeably.

[0051] An “anionic ligand” is a negatively charged ligand which donates one or more pairs of electrons to a metal ion. The term “anionic donor” is used interchangeably with “anionic ligand”. Examples of anionic donors in the context of the present invention include, but are not limited to, methyl, chloride, fluoride, alkoxide, aryloxy, alkyl, alkenyl, thiolate, 5 carboxylate, amido, methyl, benzyl, hydrido, amidinate, amidate, and phenyl. Two anionic donors may be joined to form a dianionic group.

[0052] A “neutral Lewis base or “neutral donor group” is an uncharged (i.e. neutral) group which donates one or more pairs of electrons to a metal ion. Non-limiting examples of neutral Lewis bases include ethers, thioethers, amines, phosphines, ethyl ether, tetrahydrofuran, 10 dimethylsulfide, triethylamine, pyridine, alkenes, alkynes, allenes, and carbenes. Lewis bases may be joined together to form bidentate or tridentate Lewis bases.

[0053] For purposes of this invention and the claims thereto, phenolate donors include Ph-O-, Ph-S-, and Ph-N(R[^])- groups, where R[^] is hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, and Ph is optionally 15 substituted phenyl.

Detailed Description

[0054] This invention relates solution processes to produce propylene polymers using a new catalyst family comprising transition metal complexes of a dianionic, tridentate ligand that features a central neutral donor group and two phenolate donors, where the tridentate ligands 20 coordinate to the metal center to form two eight-membered rings. In complexes of this type it is advantageous for the central neutral donor to be a heterocyclic group. It is particularly advantageous for the heterocyclic group to lack hydrogens in the position alpha to the heteroatom. In complexes of this type it is also advantageous for the phenolates to be substituted with one or more cyclic tertiary alkyl substituents. The use of cyclic tertiary alkyl 25 substituted phenolates is demonstrated to improve the ability of these catalysts to produce high molecular weight polymer.

[0055] Complexes of substituted bis(phenolate) ligands (such as adamantanyl-substituted bis(phenolate) ligands) useful herein form active olefin polymerization catalysts when combined with activators, such as non-coordinating anion or alumoxane activators. Useful 30 bis(aryl phenolate)pyridine complexes comprise a tridentate bis(aryl phenolate)pyridine ligand that is coordinated to a group 4 transition metal with the formation of two eight-membered rings.

[0056] This invention also relates to solution processes to produce propylene polymers utilizing a metal complex comprising: a metal selected from groups 3-6 or Lanthanide metals,

and a tridentate, dianionic ligand containing two anionic donor groups and a neutral Lewis base donor, wherein the neutral Lewis base donor is covalently bonded between the two anionic donors, and wherein the metal-ligand complex features a pair of 8-membered metallocycle rings.

5 [0057] This invention relates to catalyst systems used in solution processes to prepare propylene polymers comprising activator and one or more catalyst compounds as described herein.

[0058] This invention also relates to solution processes (preferably at higher temperatures) to polymerize propylene using the catalyst compounds described herein comprising contacting
10 propylene with a catalyst system comprising an activator and a catalyst compound described herein.

[0059] This invention also relates to solution processes (preferably at higher temperatures) to copolymerize propylene and at least one C₄-C₂₀ alpha olefin using the catalyst compounds described herein comprising contacting propylene and at least one C₄-C₂₀ alpha olefin with a
15 catalyst system comprising an activator and a catalyst compound described herein.

[0060] The present disclosure also relates to a catalyst system comprising a transition metal compound and an activator compound as described herein, to the use of such activator compounds for activating a transition metal compound in a catalyst system for polymerizing propylene, and to processes for polymerizing propylene, the process comprising contacting
20 under polymerization conditions propylene with a catalyst system comprising a transition metal compound and activator compounds, where aromatic solvents, such as toluene, are absent (e.g. present at zero mol% relative to the moles of activator, alternately present at less than 1 mol%, preferably the catalyst system, the polymerization reaction and/or the polymer produced are free of “detectable aromatic hydrocarbon solvent,” such as toluene). For purposes of the
25 present disclosure, “detectable aromatic hydrocarbon solvent” means 1 ppm or more as determined by gas phase chromatography. For purposes of the present disclosure, “detectable toluene” means 1 ppm or more as determined by gas phase chromatography.

[0061] The catalyst systems used herein preferably contain 0 ppm (alternately less than 1 ppm) of aromatic hydrocarbon. Preferably, the catalyst systems used herein contain 0 ppm
30 (alternately less than 1 ppm) of toluene.

Catalyst Compounds

[0062] The terms “catalyst”, “compound”, “catalyst compound”, “pre-catalyst” and “complex” may be used interchangeably to describe a transition metal or Lanthanide metal complex that forms an olefin polymerization catalyst when combined with a suitable activator.

[0063] The catalyst complexes of the present invention comprise a metal selected from groups 3, 4, 5 or 6 or Lanthanide metals of the Periodic Table of the Elements, a tridentate dianionic ligand containing two anionic donor groups and a neutral heterocyclic Lewis base donor, wherein the heterocyclic donor is covalently bonded between the two anionic donors.

5 Preferably the dianionic, tridentate ligand features a central heterocyclic donor group and two phenolate donors and the tridentate ligand coordinates to the metal center to form two eight-membered rings.

[0064] The metal is preferably selected from group 3, 4, 5, or 6 elements. Preferably the metal, M, is a group 4 metal. Most preferably the metal, M, is zirconium or hafnium. When

10 higher crystallinity polypropylene or propylene-alpha-olefin copolymers is desired, M is preferably hafnium.

[0065] Preferably the heterocyclic Lewis base donor features a nitrogen or oxygen donor atom. Preferred heterocyclic groups include derivatives of pyridine, pyrazine, pyrimidine, triazine, thiazole, imidazole, thiophene, oxazole, thiazole, furan, and substituted variants of

15 thereof. Preferably the heterocyclic Lewis base lacks hydrogen(s) in the position alpha to the donor atom. Particularly preferred heterocyclic Lewis base donors include pyridine, 3-substituted pyridines, and 4-substituted pyridines.

[0066] The anionic donors of the tridentate dianionic ligand may be arylthiolates, phenolates, or anilides. Preferred anionic donors are phenolates. It is preferred that the

20 tridentate dianionic ligand coordinates to the metal center to form a complex that lacks a mirror plane of symmetry. It is preferred that the tridentate dianionic ligand coordinates to the metal center to form a complex that has a two-fold rotation axis of symmetry; when determining the symmetry of the bis(phenolate) complexes only the metal and dianionic tridentate ligand are considered (i.e. ignore remaining ligands).

[0067] A group 4 bis(phenolate) catalyst compound is a complex of a group 4 transition metal (Ti, Zr, or Hf) that is coordinated by a di-, tri- or tetradentate ligand that is dianionic, wherein the anionic groups are phenolate anions. Preferred group 4 bis(phenolate) catalyst

25 compounds feature tri- or tetradentate dianionic ligands that coordinate to the group 4 metal in such a fashion that a pair of 7- or 8-membered metallocycle rings are formed. More preferred group 4 bis(phenolate) catalyst complexes feature tridentate dianionic ligands that coordinate

30 to the group 4 metals in such a fashion that a pair of 8-membered metallocycle rings are formed.

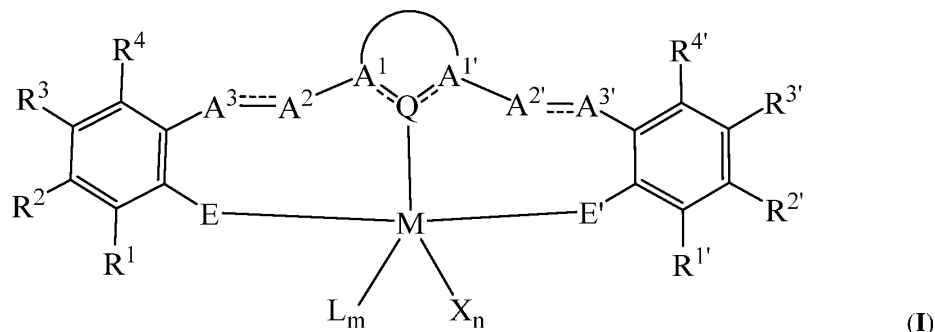
[0068] The bis(phenolate) ligands useful in the present invention are preferably tridentate dianionic ligands that coordinate to the metal M in such a fashion that a pair of 8-membered metallocycle rings are formed. Preferably, the bis(phenolate) ligands wrap around the metal to

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

[0069] Bis(phenolate) ligands in the present invention feature phenolate groups that are preferably substituted with alkyl, substituted alkyl, aryl, or other groups. It is advantageous that each phenolate group be substituted in the ring position that is adjacent to the oxygen donor atom. It is preferred that substitution at the position adjacent to the oxygen donor atom be an alkyl group containing 1-20 carbon atoms. It is preferred that substitution at the position next to the oxygen donor atom be a non-aromatic cyclic alkyl group with one or more five- or six-membered rings. It is preferred that substitution at the position next to the oxygen donor atom be a cyclic tertiary alkyl group. It is highly preferred that substitution at the position next to the oxygen donor atom be adamantan-1-yl or substituted adamantan-1-yl.

[0070] The neutral heterocyclic Lewis base donor is covalently bonded between the two anionic donors via "linker groups" that join the heterocyclic Lewis base to the phenolate groups. The "linker groups" are indicated by (A^3A^2) and ($A^{2'}A^{3'}$) in Formula (I). The choice of each linker group may affect the catalyst performance, such as the tacticity of the poly(alpha olefin) produced. Each linker group is typically a C_2 - C_{40} divalent group that is two-atoms in length. One or both linker groups may independently be phenylene, substituted phenylene, heteroaryl, vinylene, or a non-cyclic two-carbon long linker group. When one or both linker groups are phenylene, the alkyl substituents on the phenylene group may be chosen to optimize catalyst performance. Typically, one or both phenylenes may be unsubstituted or may be independently substituted with C_1 to C_{20} alkyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, or an isomer thereof, such as isopropyl, etc.

[0071] This invention further relates to catalyst compounds, and catalyst systems comprising such compounds, represented by the Formula (I):



wherein:

- 5 M is a group 3, 4, 5, or 6 transition metal or a Lanthanide (such as Hf, Zr or Ti);
 E and E' are each independently O, S, or NR⁹, where R⁹ is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group, preferably O, preferably both E and E' are O;

- Q is group 14, 15, or 16 atom that forms a dative bond to metal M, preferably Q is C,
 10 O, S or N, more preferably Q is C, N or O, most preferably Q is N;

A¹QA^{1'} are part of a heterocyclic Lewis base containing 4 to 40 non-hydrogen atoms that links A² to A^{2'} via a 3-atom bridge with Q being the central atom of the 3-atom bridge (A¹QA^{1'} combined with the curved line joining A¹ and A^{1'} represents the heterocyclic Lewis base),

- 15 A¹ and A^{1'} are independently C, N, or C(R²²), where R²² is selected from hydrogen, C₁-C₂₀ hydrocarbyl, and C₁-C₂₀ substituted hydrocarbyl. Preferably A¹ and A^{1'} are C;

- A³---A² is a divalent group containing 2 to 40 non-hydrogen atoms that links A¹ to the E-bonded aryl group via a 2-atom bridge, such as ortho-phenylene, substituted ortho-phenylene, ortho-arene, indolene, substituted indolene, benzothiophene, substituted benzothiophene, pyrrolene, substituted pyrrolene, thiophene, substituted thiophene,
 20 1,2-ethylene (-CH₂CH₂-), substituted 1,2-ethylene, 1,2-vinylene (-HC=CH-), or substituted 1,2-vinylene, preferably A³---A² is a divalent hydrocarbyl group;

- A^{2'}---A^{3'} is a divalent group containing 2 to 40 non-hydrogen atoms that links A^{1'} to the E'-bonded aryl group via a 2-atom bridge such as ortho-phenylene, substituted ortho-phenylene, ortho-arene, indolene, substituted indolene, benzothiophene, substituted
 25 phenylene, ortho-arene, indolene, substituted indolene, benzothiophene, substituted

benzothiophene, pyrrolene, substituted pyrrolene, thiophene, substituted thiophene, 1,2-ethylene (-CH₂CH₂-), substituted 1,2-ethylene, 1,2-vinylene (-HC=CH-), or substituted

1,2-vinylene, preferably $A^{2'} \equiv A^{3'}$ is a divalent hydrocarbyl group;

each L is independently a Lewis base;

5 each X is independently an anionic ligand;

n is 1, 2 or 3;

m is 0, 1, or 2;

n+m is not greater than 4;

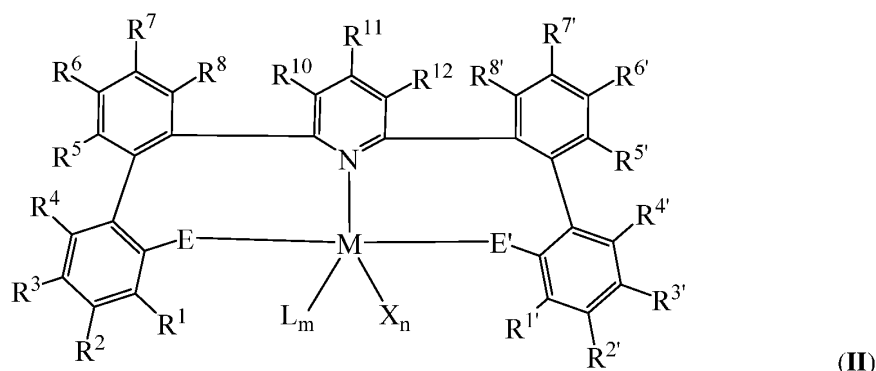
each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₄₀
 10 hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group
 (preferably R^{1'} and R¹ are independently a cyclic group, such as a cyclic tertiary alkyl group),
 or one or more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

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

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

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

[0072] This invention is further related to catalyst compounds, and catalyst systems
 20 comprising such compounds, represented by the Formula (II):



wherein:

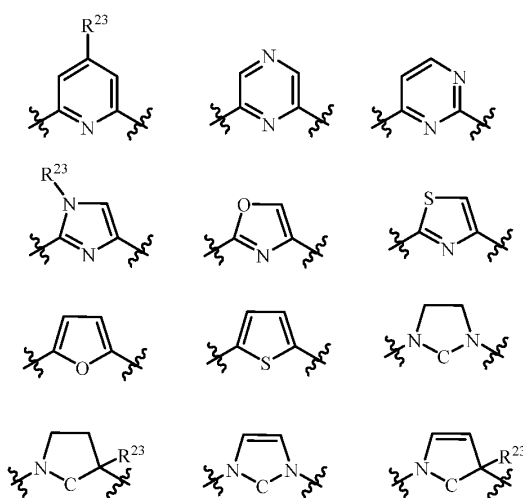
M is a group 3, 4, 5, or 6 transition metal or a Lanthanide (such as Hf, Zr or Ti);

E and E' are each independently O, S, or NR⁹, where R⁹ is independently hydrogen,
 25 C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group,
 preferably O, preferably both E and E' are O;

- each L is independently a Lewis base;
- each X is independently an anionic ligand;
- n is 1, 2 or 3;
- m is 0, 1, or 2;
- 5 n+m is not greater than 4;
- each of R^1 , R^2 , R^3 , R^4 , $R^{1'}$, $R^{2'}$, $R^{3'}$, and $R^{4'}$ is independently hydrogen, C_1 - C_{40} hydrocarbyl, C_1 - C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R^1 and R^2 , R^2 and R^3 , R^3 and R^4 , $R^{1'}$ and $R^{2'}$, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$ may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings,
- 10 substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings;
- any two L groups may be joined together to form a bidentate Lewis base;
- an X group may be joined to an L group to form a monoanionic bidentate group;
- any two X groups may be joined together to form a dianionic ligand group;
- 15 each of R^5 , R^6 , R^7 , R^8 , $R^{5'}$, $R^{6'}$, $R^{7'}$; $R^{8'}$, R^{10} , R^{11} , and R^{12} is independently hydrogen, C_1 - C_{40} hydrocarbyl, C_1 - C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R^5 and R^6 , R^6 and R^7 , R^7 and R^8 , $R^{5'}$ and $R^{6'}$, $R^{6'}$ and $R^{7'}$, $R^{7'}$ and $R^{8'}$, R^{10} and R^{11} , or R^{11} and R^{12} may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic
- 20 rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.
- [0073]** The metal, M, is preferably selected from group 3, 4, 5, or 6 elements, more preferably group 4. Most preferably the metal, M, is zirconium or hafnium.
- [0074]** The donor atom Q of the neutral heterocyclic Lewis base (in Formula (I)) is preferably nitrogen, carbon, or oxygen. Preferred Q is nitrogen.
- 25 **[0075]** Non-limiting examples of neutral heterocyclic Lewis base groups include derivatives of pyridine, pyrazine, pyrimidine, triazine, thiazole, imidazole, thiophene, oxazole, thiazole, furan, and substituted variants of thereof. Preferred heterocyclic Lewis base groups include derivatives of pyridine, pyrazine, thiazole, and imidazole.
- 30 **[0076]** Each A^1 and $A^{1'}$ of the heterocyclic Lewis base (in Formula (I)) are independently C, N, or C(R^{22}), where R^{22} is selected from hydrogen, C_1 - C_{20} hydrocarbyl, and C_1 - C_{20} substituted hydrocarbyl. Preferably A^1 and $A^{1'}$ are carbon. When Q is carbon, it is preferred that A^1 and $A^{1'}$ be selected from nitrogen and C(R^{22}). When Q is nitrogen, it is preferred that A^1 and $A^{1'}$ be carbon. It is preferred that Q = nitrogen, and $A^1 = A^{1'} =$ carbon. When Q is

nitrogen or oxygen, is preferred that the heterocyclic Lewis base in Formula (I) not have any hydrogen atoms bound to the A¹ or A^{1'} atoms. This is preferred because it is thought that hydrogens in those positions may undergo unwanted decomposition reactions that reduce the stability of the catalytically active species.

- 5 [0077] The heterocyclic Lewis base (of Formula (I)) represented by A¹QA^{1'} combined with the curved line joining A¹ and A^{1'} is preferably selected from the following, with each R²³ group selected from hydrogen, heteroatoms, C₁-C₂₀ alkyls, C₁-C₂₀ alkoxides, C₁-C₂₀ amides, and C₁-C₂₀ substituted alkyls.



- 10 [0078] In Formula (I) or (II), E and E' are each selected from oxygen or NR⁹, where R⁹ is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group. It is preferred that E and E' are oxygen. When E and/or E' are NR⁹ it is preferred that R⁹ be selected from C₁ to C₂₀ hydrocarbyls, alkyls, or aryls. In one embodiment E and E' are each selected from O, S, or N(alkyl) or N(aryl), where the alkyl is preferably a C₁ to C₂₀ alkyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, undecyl, dodecyl and the like, and aryl is a C₆ to C₄₀ aryl group, such as phenyl, naphthalen-2-yl, benzyl, methylphenyl, and the like.
- 15

[0079] In embodiments, $A^3 \text{---} A^2$ and $A^{2'} \text{---} A^{3'}$ are independently a divalent hydrocarbyl group, such as C₁ to C₁₂ hydrocarbyl group.

- 20 [0080] In complexes of Formula (I) or (II), when E and E' are oxygen it is advantageous that each phenolate group be substituted in the position that is next to the oxygen atom (i.e. R¹ and R^{1'} in Formula (I) and (II)). Thus, when E and E' are oxygen it is preferred that each

of R^1 and $R^{1'}$ is independently a C_1 - C_{40} hydrocarbyl, a C_1 - C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, more preferably, each of R^1 and $R^{1'}$ is independently a non-aromatic cyclic alkyl group with one or more five- or six-membered rings (such as cyclohexyl, cyclooctyl, adamantanyl, or 1-methylcyclohexyl, or substituted
5 adamantanyl), most preferably a non-aromatic cyclic tertiary alkyl group (such as 1-methylcyclohexyl, adamantanyl, or substituted adamantanyl).

[0081] In some embodiments of the invention of Formula (I) or (II), each of R^1 and $R^{1'}$ is independently a tertiary hydrocarbyl group. In other embodiments of the invention of Formula (I) or (II), each of R^1 and $R^{1'}$ is independently a cyclic tertiary hydrocarbyl group. In other
10 embodiments of the invention of Formula (I) or (II), each of R^1 and $R^{1'}$ is independently a polycyclic tertiary hydrocarbyl group.

[0082] In some embodiments of the invention of Formula (I) or (II), each of R^1 and $R^{1'}$ is independently a tertiary hydrocarbyl group. In other embodiments of the invention of Formula (I) or (II), each of R^1 and $R^{1'}$ is independently a cyclic tertiary hydrocarbyl group. In other
15 embodiments of the invention of Formula (I) or (II), each of R^1 and $R^{1'}$ is independently a polycyclic tertiary hydrocarbyl group.

[0083] The linker groups (i.e. $A^3 \text{---} A^2$ and $A^{2'} \text{---} A^{3'}$ in Formula (I)) are each preferably part of an ortho-phenylene group, preferably a substituted ortho-phenylene group. It is preferred for the R^7 and $R^{7'}$ positions of Formula (II) to be hydrogen, or C_1 to C_{20} alkyl,
20 such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, or an isomer thereof, such as isopropyl, etc. For applications targeting polymers with high tacticity it is preferred for the R^7 and $R^{7'}$ positions of Formula (II) to be a C_1 to C_{20} alkyl, most preferred for both R^7 and $R^{7'}$ to be a C_1 to C_3 alkyl.

25 [0084] In embodiments of Formula (I) herein, Q is C, N or O, preferably Q is N.

[0085] In embodiments of Formula (I) herein, A^1 and $A^{1'}$ are independently carbon, nitrogen, or $C(R^{22})$, with R^{22} selected from hydrogen, C_1 - C_{20} hydrocarbyl, C_1 - C_{20} substituted hydrocarbyl. Preferably A^1 and $A^{1'}$ are carbon.

[0086] In embodiments of Formula (I) herein, $A^1QA^{1'}$ in Formula (I) is part of a
30 heterocyclic Lewis base, such as a pyridine, pyrazine, pyrimidine, triazine, thiazole, imidazole, thiophene, oxazole, thiazole, furan, or a substituted variant of thereof.

[0087] In embodiments of Formula (I) herein, $A^1QA^{1'}$ are part of a heterocyclic Lewis base containing 2 to 20 non-hydrogen atoms that links A^2 to $A^{2'}$ via a 3-atom bridge with Q being

the central atom of the 3-atom bridge. Preferably each A^1 and $A^{1'}$ is a carbon atom and the $A^1QA^{1'}$ fragment forms part of a pyridine, pyrazine, pyrimidine, triazine, thiazole, imidazole, thiophene, oxazole, thiazole, furan, or a substituted variant of thereof group, or a substituted variant thereof.

5 [0088] In one embodiment of Formula (I) herein, Q is carbon, and each A^1 and $A^{1'}$ is N or C(R^{22}), where R^{22} is selected from hydrogen, C_1 - C_{20} hydrocarbyl, C_1 - C_{20} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group. In this embodiment, the $A^1QA^{1'}$ fragment forms part of a cyclic carbene, N-heterocyclic carbene, cyclic amino alkyl carbene, or a substituted variant of thereof group, or a substituted variant thereof.

10 [0089] In embodiments of formula I herein, $A^3\text{---}A^2$ is a divalent group containing 2 to 20 non-hydrogen atoms that links A^1 to the E-bonded aryl group via a 2-atom bridge, where the $A^3\text{---}A^2$ is a linear alkyl or forms part of a cyclic group (such as an optionally substituted ortho-phenylene group, or ortho-arylene group) or a substituted variant thereof.

[0090] $A^{2'}\text{---}A^{3'}$ is a divalent group containing 2 to 20 non-hydrogen atoms that links

15 $A^{1'}$ to the E'-bonded aryl group via a 2-atom bridge, where the $A^{2'}\text{---}A^{3'}$ is a linear alkyl or forms part of a cyclic group (such as an optionally substituted ortho-phenylene group, or ortho-arylene group or, or a substituted variant thereof).

[0091] In embodiments of the invention herein, in Formula (I) and (II), M is a group 4 metal, such as Hf or Zr.

20 [0092] In embodiments of the invention herein, in Formula (I) and (II), E and E' are O.

[0093] In embodiments of the invention herein, in Formula (I) and (II), R^1 , R^2 , R^3 , R^4 , $R^{1'}$, $R^{2'}$, $R^{3'}$, and $R^{4'}$ is independently hydrogen, C_1 - C_{40} hydrocarbyl, C_1 - C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R^1 and R^2 , R^2 and R^3 , R^3 and R^4 , $R^{1'}$ and $R^{2'}$, $R^{2'}$ and $R^{3'}$, $R^{3'}$ and $R^{4'}$ may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings, preferably hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof.

[0094] In embodiments of the invention herein, in Formula (I) and (II), R^1 , R^2 , R^3 , R^4 , $R^{1'}$, $R^{2'}$, $R^{3'}$, $R^{4'}$, and R^9 are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl,

- heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenyl, substituted phenyl (such as methylphenyl and dimethylphenyl), benzyl, substituted benzyl (such as methylbenzyl), naphthalen-2-yl, cyclohexyl, cyclohexenyl, methylcyclohexyl, and isomers thereof.
- 5 **[0095]** In embodiments of the invention herein, in Formula (I) and (II), R^4 and R^4 is independently hydrogen or a C_1 to C_3 hydrocarbyl, such as methyl, ethyl or propyl.
- [0096]** In embodiments of the invention herein, in Formula (I) and (II), R^9 is hydrogen, C_1 - C_{40} hydrocarbyl, C_1 - C_{40} substituted hydrocarbyl, or a heteroatom-containing group, preferably hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof.
- 10 Preferably R^9 is methyl, ethyl, propyl, butyl, C_1 to C_6 alkyl, phenyl, 2-methylphenyl, 2,6-dimethylphenyl, or 2,4,6-trimethylphenyl.
- [0097]** In embodiments of the invention herein, in Formula (I) and (II), each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 30 carbon atoms (such as alkyls or aryls or alkylaryls), silylcarbyl radicals having from 3 to 30 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, alkyl sulfonates, and
- 15 a combination thereof, (two or more X's may form a part of a fused ring or a ring system), preferably each X is independently selected from halides, aryls, and C_1 to C_5 alkyl groups, C_7 to C_{30} alkylaryls, preferably each X is independently a hydrido, dimethylamido, diethylamido, methyltrimethylsilyl, neopentyl, phenyl, benzyl, methylbenzyl, ethylbenzyl, propylbenzyl,
- 20 butylbenzyl (including para-tert-butylbenzyl), 4-hexylbenzyl, 4-octylbenzyl, 4-decylbenzyl, 4-dodecylbenzyl, 4-tetradecylbenzyl, 4-hexadecylbenzyl, 4-octadecylbenzyl, 4-nonadecylbenzyl, 4-icosylbenzyl, 4-henicosylbenzyl, methylene(trimethylsilane), methylene(triethylsilane), methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, fluoro, iodo, bromo, or chloro group.
- 25 **[0098]** Alternatively, each X may be, independently, a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group.
- [0099]** In embodiments of the invention herein, in Formula (I) and (II), each L is a Lewis base, independently, selected from the group consisting of ethers, thioethers, amines, nitriles, imines, pyridines, halocarbons, and phosphines, preferably ethers and thioethers, and a
- 30 combination thereof, optionally two or more L's may form a part of a fused ring or a ring system, preferably each L is independently selected from ether and thioether groups, preferably each L is a ethyl ether, tetrahydrofuran, dibutyl ether, or dimethylsulfide group.

[0100] In embodiments of the invention herein, in Formula (I) and (II), R¹ and R^{1'} are independently cyclic tertiary alkyl groups.

[0101] In embodiments of the invention herein, in Formula (I) and (II), n is 1, 2 or 3, typically 2.

5 [0102] In embodiments of the invention herein, in Formula (I) and (II), m is 0, 1 or 2, typically 0.

[0103] In embodiments of the invention herein, in Formula (I) and (II), R¹ and R^{1'} are not hydrogen.

[0104] In embodiments of the invention herein, in Formula (I) and (II), M is Hf or Zr, E and E' are O; each of R¹ and R^{1'} is independently a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, each R², R³, R⁴, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be joined to form one or more substituted hydrocarbyl rings, 15 unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings; each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms (such as alkyls or aryls), hydrides, amides, alkoxides, sulfides, phosphides, halides, and a combination thereof, (two or more X's may form a part of a fused ring or a ring system); each L is, independently, selected from the group consisting of 20 ethers, thioethers, and halo carbons (two or more L's may form a part of a fused ring or a ring system).

[0105] In embodiments of the invention herein, in Formula (II), each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more adjacent R groups may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

[0106] In embodiments of the invention herein, in Formula (II), each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, 30 hexyl, or an isomer thereof.

[0107] In embodiments of the invention herein, in Formula (II), each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl,

hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenyl, substituted phenyl (such as methylphenyl and dimethylphenyl), benzyl, substituted benzyl (such as methylbenzyl), naphthalen-2-yl, cyclohexyl, cyclohexenyl, methylcyclohexyl, and isomers thereof.

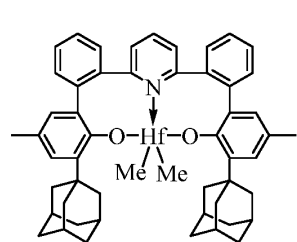
5 **[0108]** In embodiments of the invention herein, in Formula (II), M is Hf or Zr, E and E' are O; each of R¹ and R^{1'} is independently a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group,

each R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more
 10 of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings; R⁹ is hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl, or a heteroatom-containing group, such as
 15 hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof;

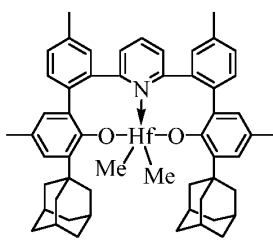
each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms (such as alkyls or aryls), hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two or more X's may form a part of a fused ring or a ring system); n is 2; m is 0; and each of
 20 R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is independently hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more adjacent R groups may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form
 25 additional rings, such as each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹ and R¹² is are independently selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, phenyl, substituted phenyl (such as methylphenyl and dimethylphenyl), benzyl, substituted benzyl (such as methylbenzyl), naphthyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, and isomers thereof.
 30

[0109] Preferred embodiment of Formula (I) is M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls.

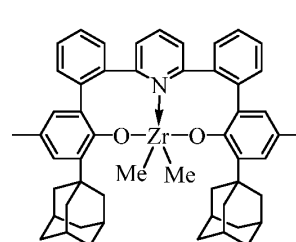
- [0110] Preferred embodiment of Formula (I) is M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are adamantan-1-yl or substituted adamantan-1-yl.
- [0111] Preferred embodiment of Formula (I) is M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are C₆-C₂₀ aryls.
- [0112] Preferred embodiment of Formula (II) is M is Zr or Hf, both E and E' are oxygen, and both R¹ and R^{1'} are C₄-C₂₀ tertiary hydrocarbyls.
- [0113] Preferred embodiment of Formula (II) is M is Zr or Hf, both E and E' are oxygen, and both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls.
- [0114] Preferred embodiment of Formula (II) is M is Zr or Hf, both E and E' are oxygen, and both R¹ and R^{1'} are adamantan-1-yl or substituted adamantan-1-yl.
- [0115] Preferred embodiment of Formula (II) is M is Zr or Hf, both E and E' are oxygen, and each of R¹, R^{1'}, R³ and R^{3'} are adamantan-1-yl or substituted adamantan-1-yl.
- [0116] Preferred embodiment of Formula (II) is M is Zr or Hf, both E and E' are oxygen, both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls, and both R⁷ and R^{7'} are C₁-C₂₀ alkyls.
- [0117] In some preferred embodiments of Formula (I) and (II), M is Hf.
- [0118] Catalyst compounds that are particularly useful in this invention include one or more of: dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3-adamantan-1-yl)-5-(tert-butyl)-[1,1'-biphenyl]-2-olate)], dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3-adamantan-1-yl)-5-(tert-butyl)-[1,1'-biphenyl]-2-olate)], dimethylzirconium[6,6'-(pyridine-2,6-diylbis(benzo[b]thiophene-3,2-diyl))bis(2-adamantan-1-yl)-4-methylphenolate)], dimethylhafnium[6,6'-(pyridine-2,6-diylbis(benzo[b]thiophene-3,2-diyl))bis(2-adamantan-1-yl)-4-methylphenolate)], dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3r,5r,7r)-adamantan-1-yl)-5-methyl-[1,1'-biphenyl]-2-olate)], dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3-((3r,5r,7r)-adamantan-1-yl)-5-methyl-[1,1'-biphenyl]-2-olate)], dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3r,5r,7r)-adamantan-1-yl)-4',5-dimethyl-[1,1'-biphenyl]-2-olate)], dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3-((3r,5r,7r)-adamantan-1-yl)-4',5-dimethyl-[1,1'-biphenyl]-2-olate)].
- [0119] Catalyst compounds that are particularly useful in this invention include those represented by one or more of the formulas:



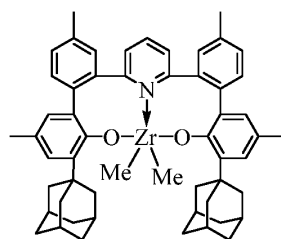
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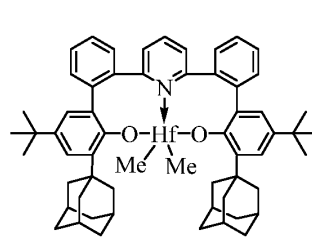
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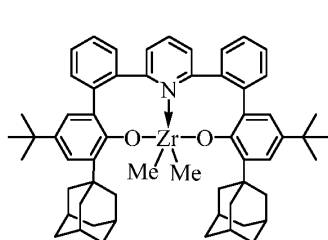
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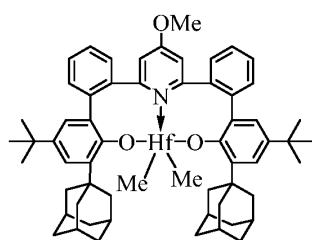
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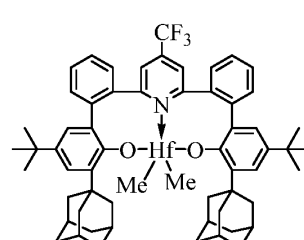
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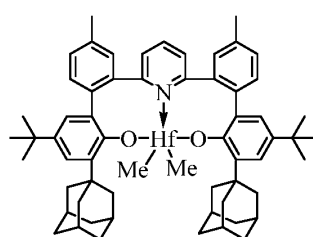
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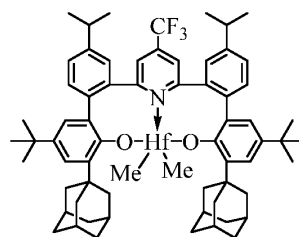
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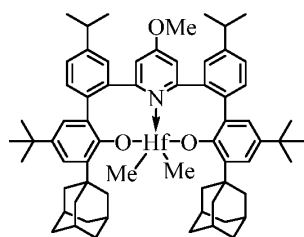
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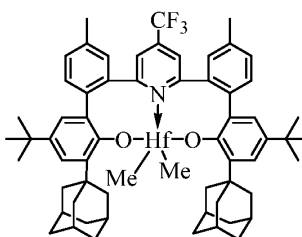
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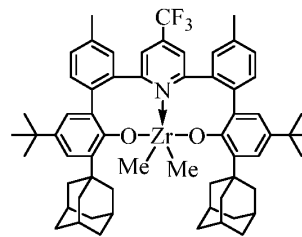
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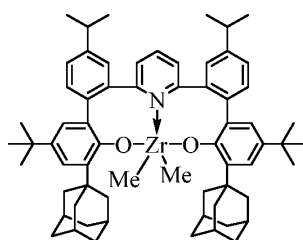
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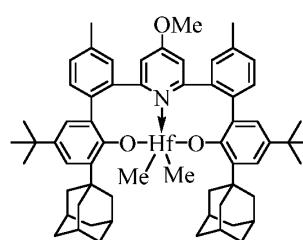
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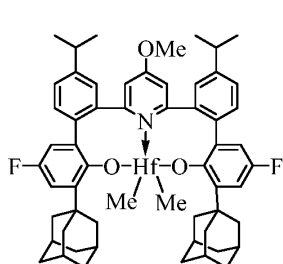
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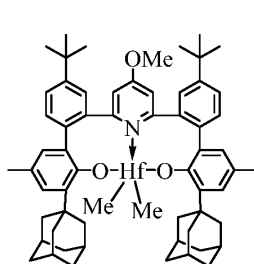
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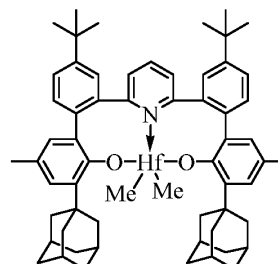
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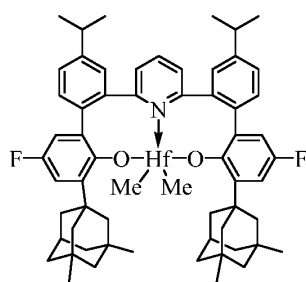
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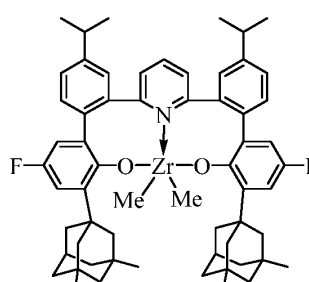
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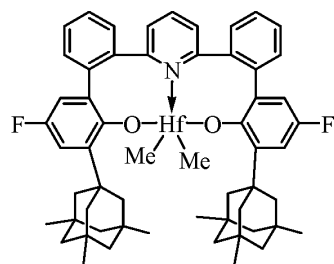
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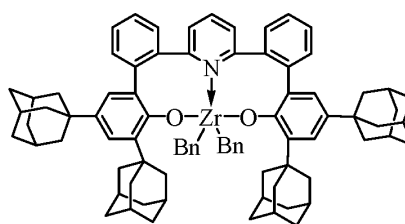
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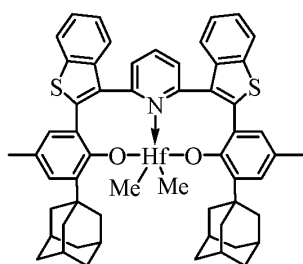
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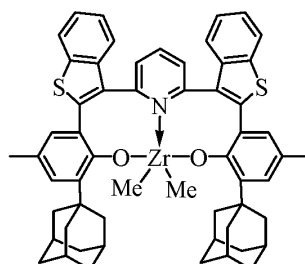
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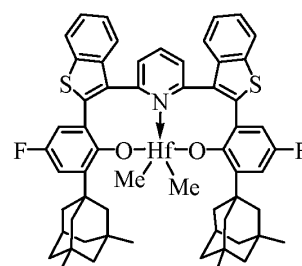
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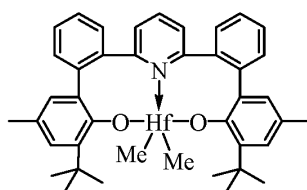
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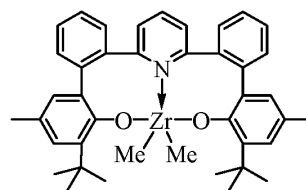
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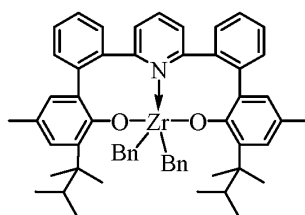
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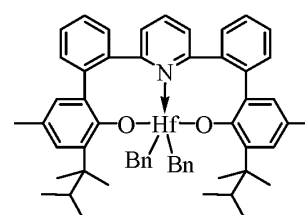
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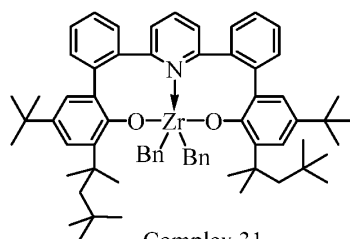
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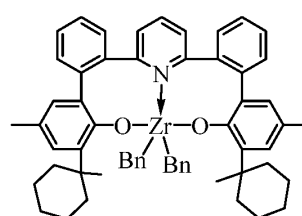
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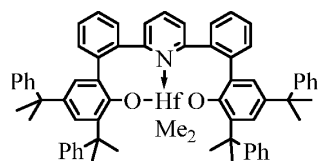
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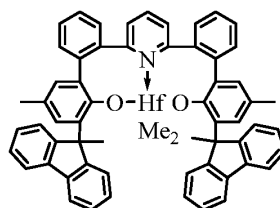
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Complex 32



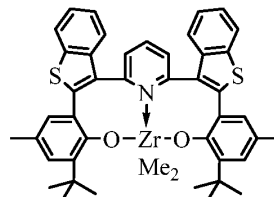
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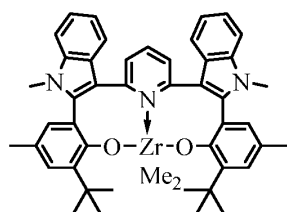
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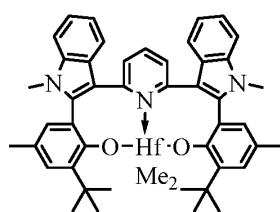
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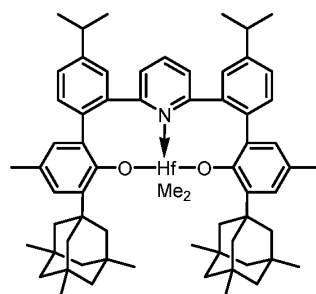
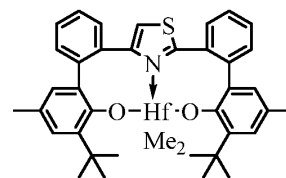
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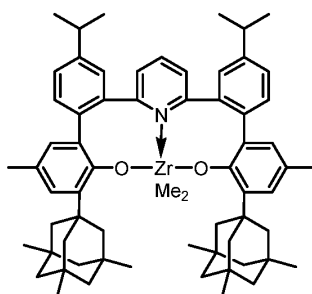
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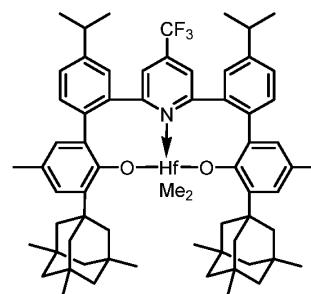
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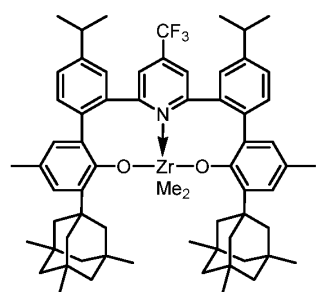
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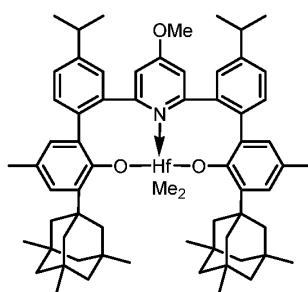
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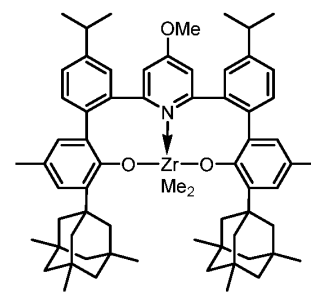
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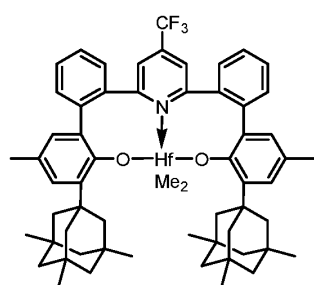
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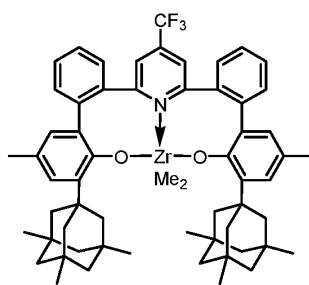
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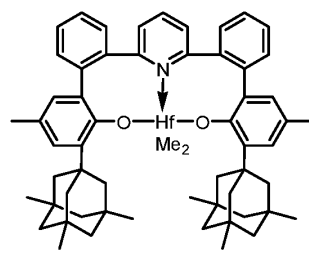
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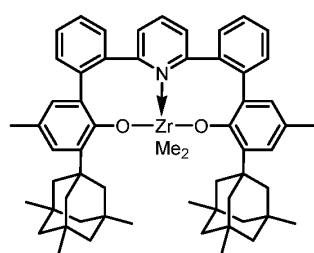
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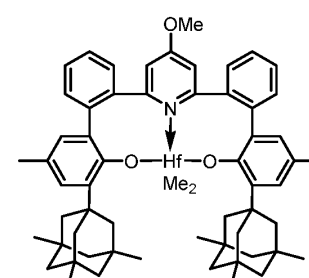
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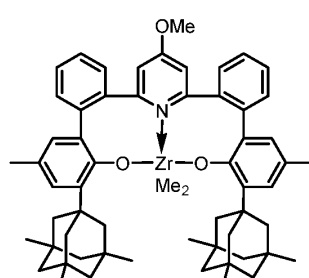
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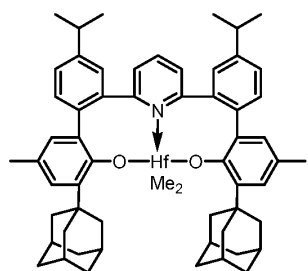
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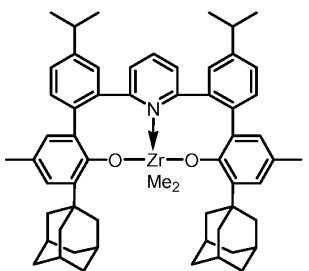
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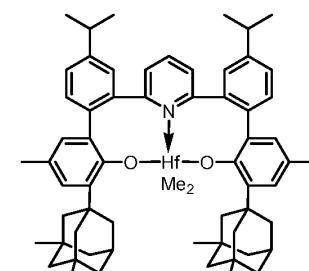
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Complex 52

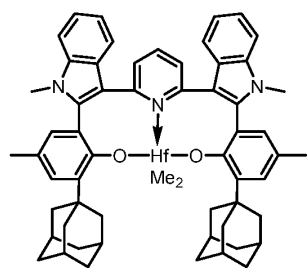


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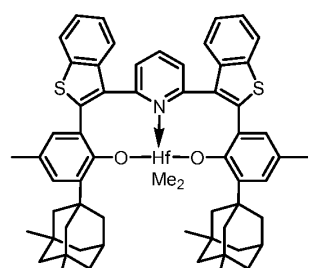


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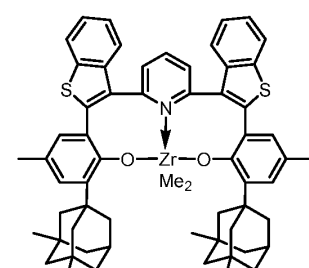
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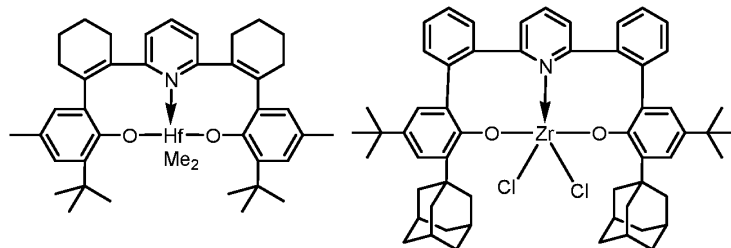
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Complex 57

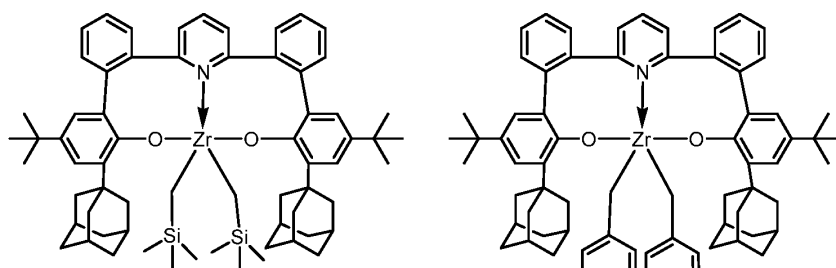


Complex 58



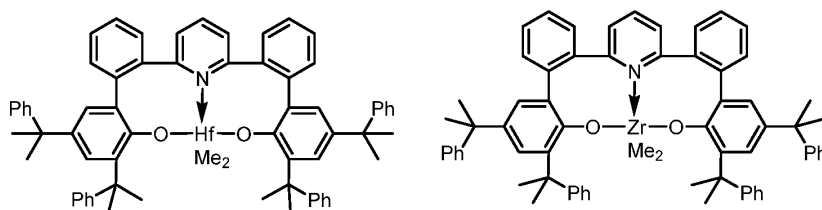
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Complex 60



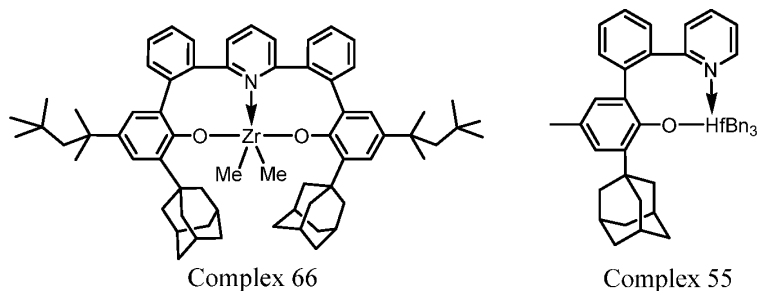
Complex 62

Complex 63



Complex 64

Complex 65



Complex 66

Complex 55

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[0120] In some embodiments, two or more different catalyst compounds are present in the catalyst system used herein. In some embodiments, two or more different catalyst compounds are present in the reaction zone where the process(es) described herein occur. When two transition metal compound based catalysts are used in one reactor as a mixed catalyst system,

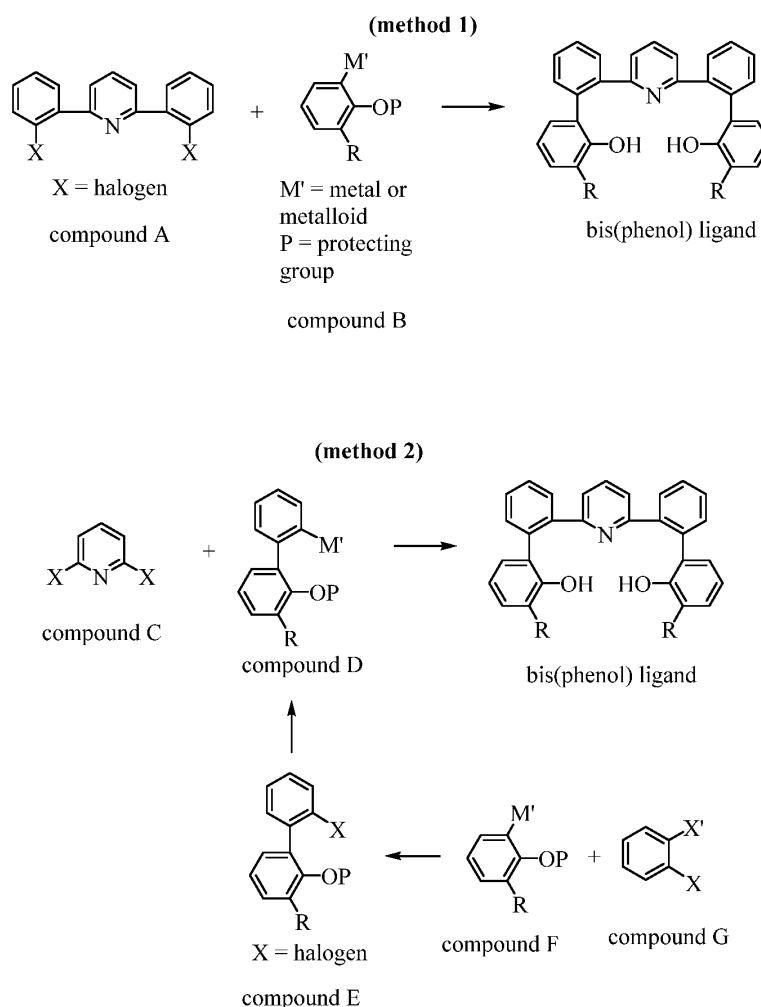
the two transition metal compounds are preferably chosen such that the two are compatible. It is preferable to use the same activator for the transition metal compounds, however, two different activators, such as a non-coordinating anion activator and an alumoxane, can be used in combination. If one or more transition metal compounds contain an X group which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the alumoxane can be contacted with the transition metal compounds prior to addition of the non-coordinating anion activator.

[0121] The two transition metal compounds (pre-catalysts) may be used in any ratio. Preferred molar ratios of (A) transition metal compound to (B) transition metal compound fall within the range of (A:B) 1:1000 to 1000:1, alternatively 1:100 to 500:1, alternatively 1:10 to 200:1, alternatively 1:1 to 100:1, and alternatively 1:1 to 75:1, and alternatively 5:1 to 50:1. The particular ratio chosen will depend on the exact pre-catalysts chosen, the method of activation, and the end product desired. In a particular embodiment, when using the two pre-catalysts, where both are activated with the same activator, useful mole percents, based upon the molecular weight of the pre-catalysts, are 10 to 99.9% A to 0.1 to 90% B, alternatively 25 to 99% A to 0.5 to 50% B, alternatively 50 to 99% A to 1 to 25% B, and alternatively 75 to 99% A to 1 to 10% B.

Methods to Prepare the Catalyst Compounds.

Ligand synthesis

[0122] The bis(phenol) ligands may be prepared using the general methods shown in Scheme 1. The formation of the bis(phenol) ligand by the coupling of compound A with compound B (method 1) may be accomplished by known Pd- and Ni-catalyzed couplings, such as Negishi, Suzuki, or Kumada couplings. The formation of the bis(phenol) ligand by the coupling of compound C with compound D (method 2) may also be accomplished by known Pd- and Ni-catalyzed couplings, such as Negishi, Suzuki, or Kumada couplings. Compound D may be prepared from compound E by reaction of compound E with either an organolithium reagent or magnesium metal, followed by optional reaction with a main-group metal halide (e.g. ZnCl_2) or boron-based reagent (e.g. $\text{B}(\text{O}^i\text{Pr})_3$, $^i\text{PrOB}(\text{pin})$). Compound E may be prepared in a non-catalyzed reaction from by the reaction of an aryllithium or aryl Grignard reagent (compound F) with a dihalogenated arene (compound G), such as 1-bromo-2-chlorobenzene. Compound E may also be prepared in a Pd- or Ni-catalyzed reaction by reaction of an arylzinc or aryl-boron reagent (compound F) with a dihalogenated arene (compound G).

Scheme 1.

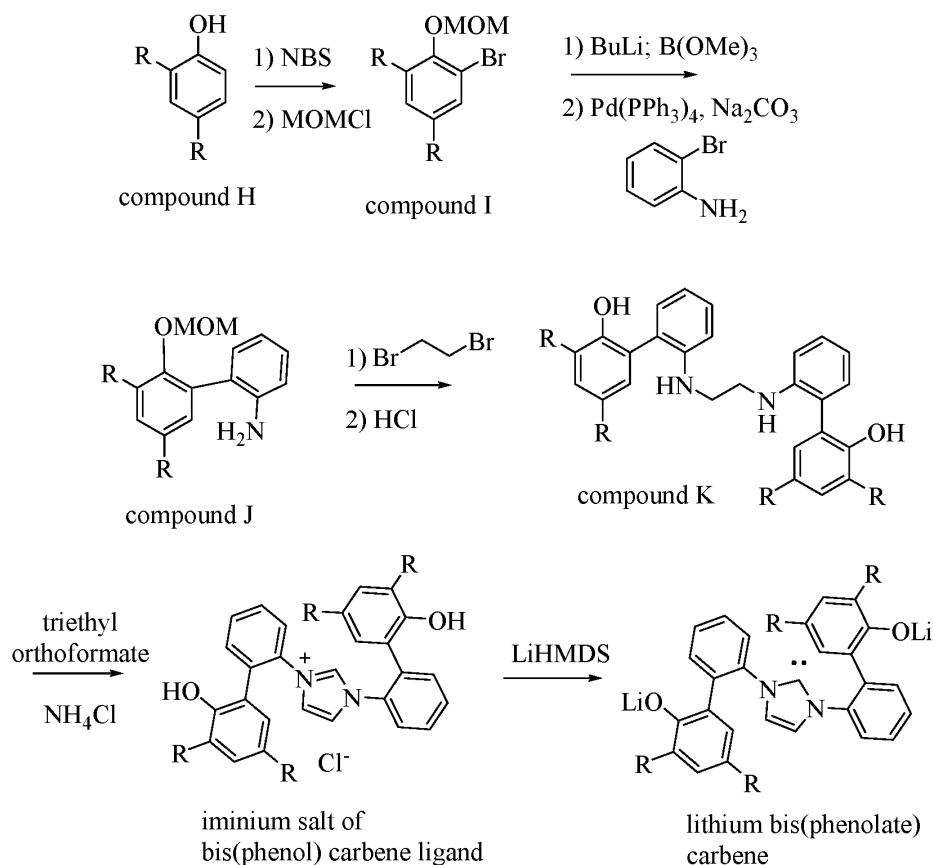
where M' is a group 1, 2, 12, or 13 element or substituted element such as Li, MgCl, MgBr, ZnCl, $\text{B}(\text{OH})_2$, B(pinacolate), P is a protective group such as methoxymethyl (MOM), tetrahydropyranyl (THP), t-butyl, allyl, ethoxymethyl, trialkylsilyl, t-butyldimethylsilyl, or benzyl, R is a $\text{C}_1\text{-C}_{40}$ alkyl, substituted alkyl, aryl, tertiary alkyl, cyclic tertiary alkyl, adamantanyl, or substituted adamantanyl and each X' and X is halogen, such as Cl, Br, F or I.

Synthesis of carbene bis(phenol) ligands

[0123] The general synthetic method to produce carbene bis(phenol) ligands is shown in Scheme 2. A substituted phenol can be ortho-brominated then protected by a known phenol protecting group, such as MOM, THP, t-butyldimethylsilyl (TBDMS), benzyl (Bn), etc. The bromide is then converted to a boronic ester (compound I) or boronic acid which can be used

in a Suzuki coupling with bromoaniline. The biphenylaniline (compound J) can be bridged by reaction with dibromoethane or condensation with oxalaldehyde, then deprotected (compound K). Reaction with triethyl orthoformate forms an iminium salt that is deprotonated to a carbene.

Scheme 2.



5

To substituted phenol (compound H) dissolved in methylene chloride, is added an equivalent of N-bromosuccinimide and 0.1 equivalent of diisopropylamine. After stirring at ambient temperature until completion, the reaction is quenched with a 10% solution of HCl. The organic portion is washed with brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give a bromophenol, typically as a solid. The substituted bromophenol, methoxymethylchloride, and potassium carbonate are dissolved in dry acetone and stirred at ambient temperature until completion of the reaction. The solution is filtered and the filtrate concentrated to give protected phenol (compound I). Alternatively, the substituted bromophenol and an equivalent of dihydropyran is dissolved in methylene chloride and cooled to 0°C. A catalytic amount of para-toluenesulfonic acid is added and the reaction stirred for

10

15

10 min, then quenched with trimethylamine. The mixture is washed with water and brine, then dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give a tetrahydropyran-protected phenol.

[0124] Aryl bromide (compound I) is dissolved in THF and cooled to -78°C .
5 n-Butyllithium is added slowly, followed by trimethoxy borate. The reaction is allowed to stir at ambient temperature until completion. The solvent is removed and the solid boronic ester washed with pentane. A boronic acid can be made from the boronic ester by treatment with HCl. The boronic ester or acid is dissolved in toluene with an equivalent of ortho-bromoaniline and a catalytic amount of palladium tetrakis(triphenyl)phosphine. An aqueous solution of
10 sodium carbonate is added and the reaction heated at reflux overnight. Upon cooling, the layers are separated and the aqueous layer extracted with ethyl acetate. The combined organic portions are washed with brine, dried (MgSO_4), filtered, and concentrated under reduced pressure. Column chromatography is typically used to purify the coupled product (compound J).

15 [0125] The aniline (compound J) and dibromoethane (0.5 equiv.) are dissolved in acetonitrile and heated at 60°C overnight. The reaction is filtered and concentrated to give an ethylene bridged dianiline. The protected phenol is deprotected by reaction with HCl to give a bridged bisamino(biphenyl)ol (compound K).

[0126] The diamine (compound K) is dissolved in triethylorthoformate. Ammonium chloride is added and the reaction heated at reflux overnight. A precipitate is formed which is collected by filtration and washed with ether to give the iminium salt. The iminium chloride is suspended in THF and treated with lithium or sodium hexamethyldisilylamide. Upon completion, the reaction is filtered and the filtrate concentrated to give the carbene ligand.

Preparation of bis(phenolate) complexes

25 [0127] Transition metal or Lanthanide metal bis(phenolate) complexes are used as catalyst components for olefin polymerization in the present invention. The terms "catalyst" and "catalyst complex" are used interchangeably. The preparation of transition metal or Lanthanide metal bis(phenolate) complexes may be accomplished by reaction of the bis(phenol) ligand with a metal reactant containing anionic basic leaving groups. Typical anionic basic leaving groups include dialkylamido, benzyl, phenyl, hydrido, and methyl. In this reaction, the role of the basic leaving group is to deprotonate the bis(phenol) ligand. Suitable metal reactants for this type of reaction include, but are not limited to, HfBn_4 ($\text{Bn} = \text{CH}_2\text{Ph}$), ZrBn_4 , TiBn_4 , $\text{ZrBn}_2\text{Cl}_2(\text{OEt}_2)$, $\text{HfBn}_2\text{Cl}_2(\text{OEt}_2)$, $\text{Zr}(\text{NMe}_2)_2\text{Cl}_2(\text{dimethoxyethane})$, $\text{Hf}(\text{NMe}_2)_2\text{Cl}_2(\text{dimethoxyethane})$, $\text{Hf}(\text{NMe}_2)_4$, $\text{Zr}(\text{NMe}_2)_4$, and $\text{Hf}(\text{NEt}_2)_4$. Suitable metal

reagents also include ZrMe₄, HfMe₄, and other group 4 alkyls that may be formed *in situ* and used without isolation.

[0128] A second method for the preparation of transition metal or Lanthanide bis(phenolate) complexes is by reaction of the bis(phenol) ligand with an alkali metal or
5 alkaline earth metal base (e.g., Na, BuLi, ⁱPrMgBr) to generate deprotonated ligand, followed by reaction with a metal halide (e.g., HfCl₄, ZrCl₄) to form a bis(phenolate) complex. Bis(phenolate) metal complexes that contain metal-halide, alkoxide, or amido leaving groups may be alkylated by reaction with organolithium, Grignard, and organoaluminum reagents. In the alkylation reaction the alkyl groups are transferred to the bis(phenolate) metal center and
10 the leaving groups are removed. Reagents typically used for the alkylation reaction include, but are not limited to, MeLi, MeMgBr, AlMe₃, Al(ⁱBu)₃, AlOct₃, and PhCH₂MgCl. Typically 2 to 20 molar equivalents of the alkylating reagent are added to the bis(phenolate) complex. The alkylations are generally performed in etherial or hydrocarbon solvents or solvent mixtures at temperatures typically ranging from -80°C to 120°C.

15 Activators

[0129] The terms “cocatalyst” and “activator” are used herein interchangeably.

[0130] The catalyst systems described herein typically comprises a catalyst complex, such as the transition metal or Lanthanide bis(phenolate) complexes described above, and an activator such as alumoxane or a non-coordinating anion. These catalyst systems may be
20 formed by combining the catalyst components described herein with activators in any manner known from the literature. 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
25 compounds described above by converting the neutral metal compound to a catalytically active metal compound cation. Non-limiting activators, for example, include alumoxanes, ionizing activators, which may be neutral or ionic, and conventional-type cocatalysts. Preferred activators typically include alumoxane compounds, modified alumoxane compounds, and ionizing anion precursor compounds that abstract a reactive metal ligand making the metal
30 compound cationic and providing a charge-balancing non-coordinating or weakly coordinating anion, e.g. a non-coordinating anion.

Alumoxane Activators

- [0131] Alumoxane activators are utilized as activators in the catalyst systems described herein. Alumoxanes are generally oligomeric compounds containing $-Al(R^1)-O-$ sub-units, where R^1 is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO),
5 modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is an alkyl, halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear
10 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 Patent No. 5,041,584). Another useful alumoxane is solid polymethylaluminoxane as described in US 9,340,630; US 8,404,880; and US 8,975,209.
- 15 [0132] When the activator is an alumoxane (modified or unmodified), typically the maximum amount of activator is at up to a 5,000-fold molar excess Al/M over the catalyst compound (per metal catalytic site). The minimum activator-to-catalyst-compound is a 1:1 molar ratio. Alternate preferred ranges include from 1:1 to 500:1, alternately from 1:1 to 200:1, alternately from 1:1 to 100:1, or alternately from 1:1 to 50:1.
- 20 [0133] In an alternate embodiment, little or no alumoxane is used in the polymerization processes described herein. Preferably, alumoxane is present at zero mole %, alternately the alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1.

Ionizing/Non Coordinating Anion Activators

- 25 [0134] 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 neutral Lewis base. 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
30 accordance with this invention 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. 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. Any metal or metalloid that can form a compatible, weakly coordinating complex may be used or contained
 5 in the non-coordinating 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.

[0135] It is within the scope of this invention to use an ionizing activator, neutral or ionic. It is also within the scope of this invention to use neutral or ionic activators alone or in
 10 combination with alumoxane or modified alumoxane activators.

[0136] In embodiments of the invention, the activator is represented by the Formula (III):



wherein Z is (L-H) or a reducible Lewis Acid, L is a neutral Lewis base; H is hydrogen; (L-H)⁺ is a Bronsted acid; A^{d-} is a non-coordinating anion having the charge d-; and d is an
 15 integer from 1 to 3 (such as 1, 2 or 3), preferably Z is (Ar₃C⁺), where Ar is aryl or aryl substituted with a heteroatom, a C₁ to C₄₀ hydrocarbyl, or a substituted C₁ to C₄₀ hydrocarbyl. The anion component A^{d-} includes those having the formula [M^{k+}Q_n]^{d-} wherein k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6 (preferably 1, 2, 3, or 4); n - k = d; M is an element selected from Group 13 of the Periodic Table of the Elements, preferably boron or aluminum, and Q is
 20 independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 40 carbon atoms (optionally with the proviso that in not more than 1 occurrence is Q a halide). Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 40 (such as 1 to 20) carbon atoms, more preferably each Q is a fluorinated
 25 aryl group, such as a perfluorinated aryl group and most preferably each Q is a pentafluoryl aryl group or perfluoronaphthalen-2-yl group. Examples of suitable A^{d-} also include diboron compounds as disclosed in US Patent No. 5,447,895, which is fully incorporated herein by reference.

[0137] When Z is the activating cation (L-H), it can be a Bronsted acid, capable of donating
 30 a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, sulfoniums, and mixtures thereof, such as ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline,

N-methyl-4-nonadecyl-N-octadecylaniline, N-methyl-4-octadecyl-N-octadecylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, dioctadecylmethylamine, phosphoniums from triethylphosphine, triphenylphosphine, and
 5 diphenylphosphine, oxoniums from ethers such as dimethyl ether, diethyl ether, tetrahydrofuran and dioxane, sulfoniums from thioethers, such as diethyl thioethers, tetrahydrothiophene, and mixtures thereof.

[0138] In particularly useful embodiments of the invention, the activator is soluble in non-aromatic-hydrocarbon solvents, such as aliphatic solvents.

10 **[0139]** In one or more embodiments, a 20 wt% mixture of the activator compound in n-hexane, isohexane, cyclohexane, methylcyclohexane, or a combination thereof, forms a clear homogeneous solution at 25°C, preferably a 30 wt% mixture of the activator compound in n-hexane, isohexane, cyclohexane, methylcyclohexane, or a combination thereof, forms a clear homogeneous solution at 25°C.

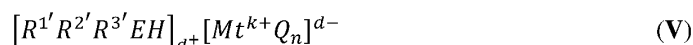
15 **[0140]** In embodiments of the invention, the activators described herein have a solubility of more than 10 mM (or more than 20 mM, or more than 50 mM) at 25°C (stirred 2 hours) in methylcyclohexane.

[0141] In embodiments of the invention, the activators described herein have a solubility of more than 1 mM (or more than 10 mM, or more than 20 mM) at 25°C (stirred 2 hours) in
 20 isohexane.

[0142] In embodiments of the invention, the activators described herein have a solubility of more than 10 mM (or more than 20 mM, or more than 50 mM) at 25°C (stirred 2 hours) in methylcyclohexane and a solubility of more than 1 mM (or more than 10 mM, or more than 20 mM) at 25°C (stirred 2 hours) in isohexane.

25 **[0143]** In a preferred embodiment, the activator is a non-aromatic-hydrocarbon soluble activator compound.

[0144] Non-aromatic-hydrocarbon soluble activator compounds useful herein include those represented by the Formula (V):



30 wherein:

E is nitrogen or phosphorous;

d is 1, 2 or 3; *k* is 1, 2, or 3; *n* is 1, 2, 3, 4, 5, or 6; *n* − *k* = *d* (preferably *d* is 1, 2 or 3; *k* is 3; *n* is 4, 5, or 6);

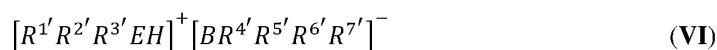
$R^{1'}$, $R^{2'}$, and $R^{3'}$ are independently a C_1 to C_{50} hydrocarbyl group optionally substituted with one or more alkoxy groups, silyl groups, a halogen atoms, or halogen containing groups, wherein $R^{1'}$, $R^{2'}$, and $R^{3'}$ together comprise 15 or more carbon atoms;

Mt is an element selected from group 13 of the Periodic Table of the Elements, such as

5 B or Al; and

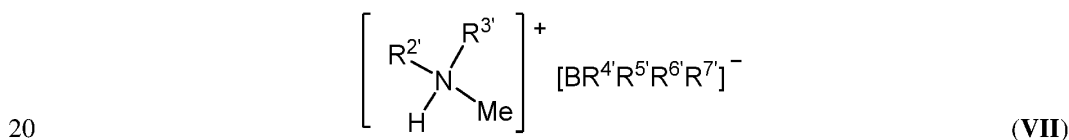
each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical.

[0145] Non-aromatic-hydrocarbon soluble activator compounds useful herein include those represented by the Formula (VI):

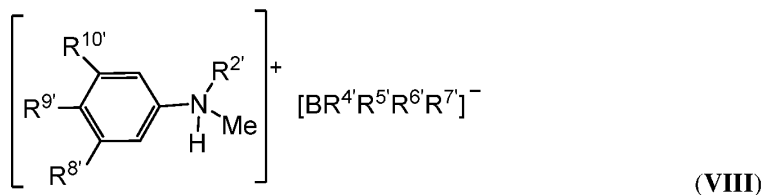


wherein: E is nitrogen or phosphorous; $R^{1'}$ is a methyl group; $R^{2'}$ and $R^{3'}$ are independently is C_4 - C_{50} hydrocarbyl group optionally substituted with one or more alkoxy groups, silyl groups, a halogen atoms, or halogen containing groups wherein $R^{2'}$ and $R^{3'}$ together comprise 14 or more carbon atoms; B is boron; and $R^{4'}$, $R^{5'}$, $R^{6'}$, and $R^{7'}$ are independently hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical.

[0146] Non-aromatic-hydrocarbon soluble activator compounds useful herein include those represented by the Formula (VII) or Formula (VIII):



and



wherein:

N is nitrogen;

25 $R^{2'}$ and $R^{3'}$ are independently is C_6 - C_{40} hydrocarbyl group optionally substituted with one or more alkoxy groups, silyl groups, a halogen atoms, or halogen containing groups wherein $R^{2'}$ and $R^{3'}$ (if present) together comprise 14 or more carbon atoms;

$R^{8'}$, $R^{9'}$, and $R^{10'}$ are independently a C₄-C₃₀ hydrocarbyl or substituted C₄-C₃₀ hydrocarbyl group;

B is boron;

and $R^{4'}$, $R^{5'}$, $R^{6'}$, and $R^{7'}$ are independently hydride, bridged or unbridged
5 dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical.

[0147] Optionally, in any of Formulas (V), (VI), (VII), or (VIII) herein, $R^{4'}$, $R^{5'}$, $R^{6'}$, and $R^{7'}$ are pentafluorophenyl.

[0148] Optionally, in any of Formulas (V), (VI), (VII), or (VIII) herein, $R^{4'}$, $R^{5'}$, $R^{6'}$, and
10 $R^{7'}$ are pentafluoronaphthalen-2-yl.

[0149] Optionally, in any embodiment of Formula (VIII) herein, $R^{8'}$ and $R^{10'}$ are hydrogen atoms and $R^{9'}$ is a C₄-C₃₀ hydrocarbyl group which is optionally substituted with one or more alkoxy groups, silyl groups, a halogen atoms, or halogen containing groups.

[0150] Optionally, in any embodiment of Formula (VIII) herein, $R^{9'}$ is a C₈-C₂₂
15 hydrocarbyl group which is optionally substituted with one or more alkoxy groups, silyl groups, a halogen atoms, or halogen containing groups.

[0151] Optionally, in any embodiment of Formula (VII) or (VIII) herein, $R^{2'}$ and $R^{3'}$ are independently a C₁₂-C₂₂ hydrocarbyl group.

[0152] Optionally, $R^{1'}$, $R^{2'}$ and $R^{3'}$ together comprise 15 or more carbon atoms (such as
20 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 38 or more carbon atoms, such as 40 or more carbon atoms, such as 15 to 100 carbon atoms, such as 25 to 75 carbon atoms).

[0153] Optionally, $R^{2'}$ and $R^{3'}$ together comprise 15 or more carbon atoms (such as 18 or
25 more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon atoms, such as 38 or more carbon atoms, such as 40 or more carbon atoms, such as 15 to 100 carbon atoms, such as 25 to 75 carbon atoms).

[0154] Optionally, $R^{8'}$, $R^{9'}$, and $R^{10'}$ together comprise 15 or more carbon atoms (such as
30 18 or more carbon atoms, such as 20 or more carbon atoms, such as 22 or more carbon atoms, such as 25 or more carbon atoms, such as 30 or more carbon atoms, such as 35 or more carbon

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

[0155] Optionally, when Q is a fluorophenyl group, then $R^{2'}$ is not a C_1 - C_{40} linear alkyl group (alternately $R^{2'}$ is not an optionally substituted C_1 - C_{40} linear alkyl group).

- 5 [0156] Optionally, each of $R^{4'}$, $R^{5'}$, $R^{6'}$, and $R^{7'}$ is an aryl group (such as phenyl or naphthalen-2-yl), wherein at least one of $R^{4'}$, $R^{5'}$, $R^{6'}$, and $R^{7'}$ is substituted with at least one fluorine atom, preferably each of $R^{4'}$, $R^{5'}$, $R^{6'}$, and $R^{7'}$ is a perfluoroaryl group (such as perfluorophenyl or perfluoronaphthalen-2-yl).

- [0157] Optionally, each Q is an aryl group (such as phenyl or naphthalen-2-yl), wherein at
10 least one Q is substituted with at least one fluorine atom, preferably each Q is a perfluoroaryl group (such as perfluorophenyl or perfluoronaphthalen-2-yl).

[0158] Optionally, $R^{1'}$ is a methyl group; $R^{2'}$ is C_6 - C_{50} aryl group; and $R^{3'}$ is independently C_1 - C_{40} linear alkyl or C_5 - C_{50} -aryl group.

- [0159] Optionally, each of $R^{2'}$ and $R^{3'}$ is independently unsubstituted or substituted with
15 at least one of halide, C_1 - C_{35} alkyl, C_5 - C_{15} aryl, C_6 - C_{35} arylalkyl, C_6 - C_{35} alkylaryl, wherein R^2 , and R^3 together comprise 20 or more carbon atoms.

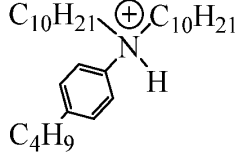
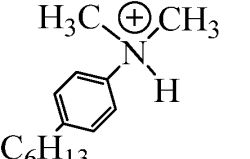
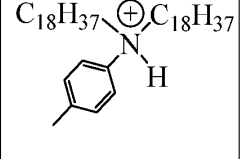
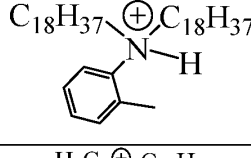
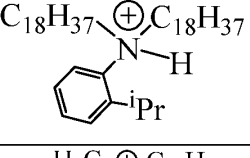
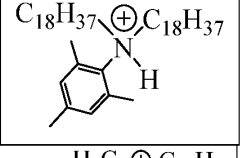
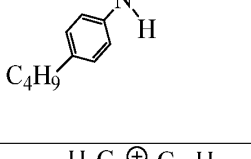
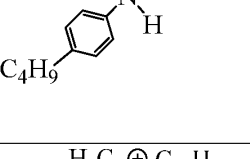
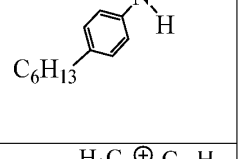
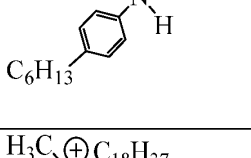
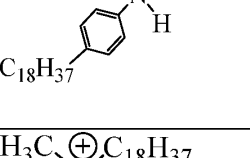
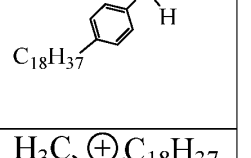
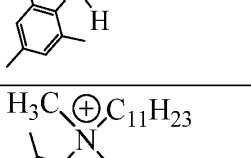
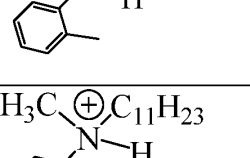
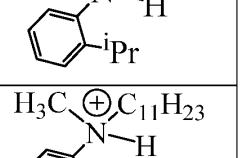
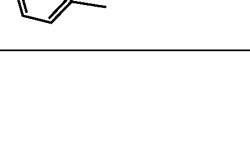
- [0160] Optionally, each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical, provided that when Q is a fluorophenyl
20 group, then $R^{2'}$ is not a C_1 - C_{40} linear alkyl group, preferably $R^{2'}$ is not an optionally substituted C_1 - C_{40} linear alkyl group (alternately when Q is a substituted phenyl group, then $R^{2'}$ is not a C_1 - C_{40} linear alkyl group, preferably $R^{2'}$ is not an optionally substituted C_1 - C_{40} linear alkyl group). Optionally, when Q is a fluorophenyl group (alternately when Q is a substituted phenyl group), then $R^{2'}$ is a meta- and/or para-substituted phenyl group, where the meta and para
25 substituents are, independently, an optionally substituted C_1 to C_{40} hydrocarbyl group (such as a C_6 to C_{40} aryl group or linear alkyl group, a C_{12} to C_{30} aryl group or linear alkyl group, or a C_{10} to C_{20} aryl group or linear alkyl group), an optionally substituted alkoxy group, or an optionally substituted silyl group. Optionally, each Q is a fluorinated hydrocarbyl group having 1 to 30 carbon atoms, more preferably each Q is a fluorinated aryl (such as phenyl or
30 naphthalen-2-yl) group, and most preferably each Q is a perfluorinated aryl (such as phenyl or naphthalen-2-yl) group. Examples of suitable $[Mt^{k+}Q_n]^{d-}$ also include diboron compounds as disclosed in US Patent No. 5,447,895, which is fully incorporated herein by reference.

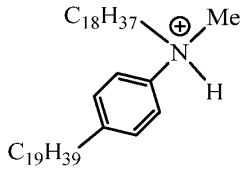
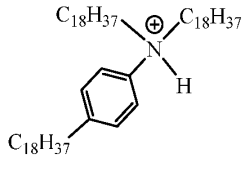
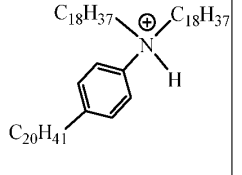
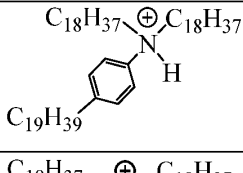
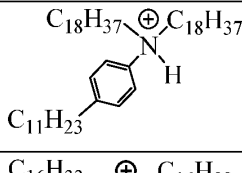
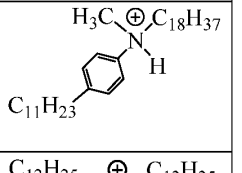
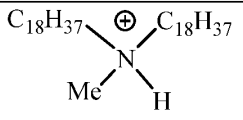
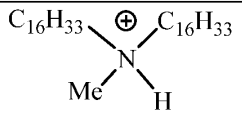
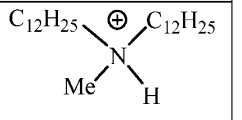
Optionally, at least one *Q* is not substituted phenyl. Optionally all *Q* are not substituted phenyl.

Optionally at least one *Q* is not perfluorophenyl. Optionally all *Q* are not perfluorophenyl.

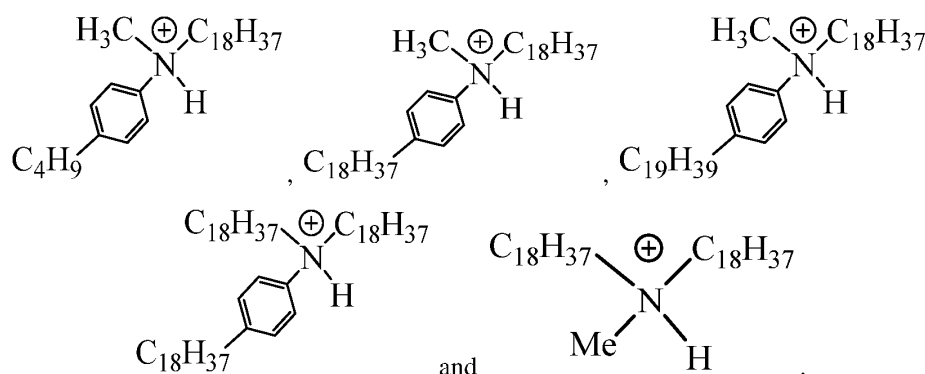
- [0161] In some embodiments of the invention, $R^{1'}$ is not methyl, $R^{2'}$ is not C_{18} alkyl and $R^{3'}$ is not C_{18} alkyl, alternately $R^{1'}$ is not methyl, $R^{2'}$ is not C_{18} alkyl and $R^{3'}$ is not C_{18} alkyl and at least one *Q* is not substituted phenyl, optionally all *Q* are not substituted phenyl.

[0162] Useful cation components in Formulas (III) and (V) to (VIII) include those represented by the formula:

10		11		12	
13		14		15	
16		17		18	
19		20		21	
22		23		24	
25		26		27	

29		28		30	
31		32		33	
34		35		36	

[0163] Useful cation components in Formulas (III) and (V) to (VIII) include those represented by the formulas:



5

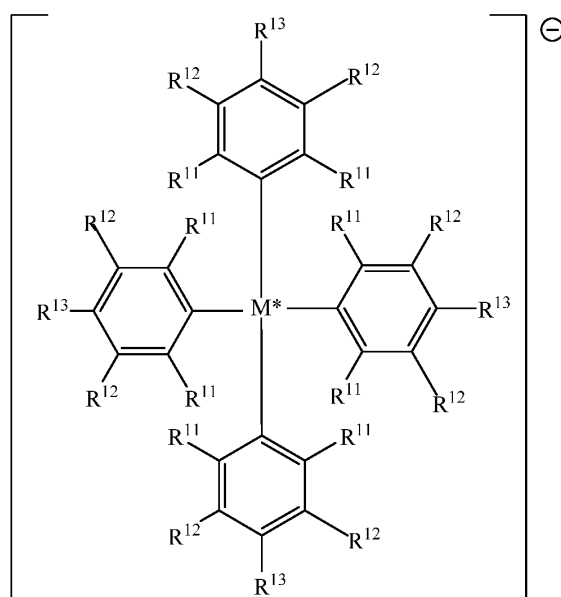
[0164] The anion component of the activators described herein includes those represented by the formula $[Mt^{k+}Q_n]^-$ wherein k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6 (preferably 1, 2, 3, or 4), (preferably k is 3; n is 4, 5, or 6, preferably when M is B , n is 4); Mt is an element selected from Group 13 of the Periodic Table of the Elements, preferably boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q a halide. Preferably, each Q is a fluorinated hydrocarbyl group, optionally having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a perfluorinated aryl group. Preferably at least one Q is not

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

[0165] In one embodiment, the borate activator comprises tetrakis(heptafluoronaphthalen-2-yl)borate.

5 **[0166]** In one embodiment, the borate activator comprises tetrakis(pentafluorophenyl)borate.

[0167] Anions for use in the non-coordinating anion activators described herein also include those represented by Formula (7), below:



Formula (7)

wherein:

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

each R^{11} is, independently, a halide, preferably a fluoride;

each R^{12} is, independently, a halide, a C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula $-O-Si-R^a$, where R^a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group, preferably R^{12} is a fluoride or a perfluorinated phenyl group;

each R^{13} is a halide, a C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula $-O-Si-R_a$, where R^a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group, preferably R^{13} is a fluoride or a C_6 perfluorinated aromatic hydrocarbyl group;

wherein R^{12} and R^{13} can form one or more saturated or unsaturated, substituted or unsubstituted rings, preferably R^{12} and R^{13} form a perfluorinated phenyl ring. Preferably the

anion has a molecular weight of greater than 700 g/mol, and, preferably, at least three of the substituents on the M* atom each have a molecular volume of greater than 180 cubic Å.

[0168] "Molecular volume" is used herein as an approximation of spatial steric bulk of an activator molecule in solution. Comparison of substituents with differing molecular volumes allows the substituent with the smaller molecular volume to be considered "less bulky" in comparison to the substituent with the larger molecular volume. Conversely, a substituent with a larger molecular volume may be considered "more bulky" than a substituent with a smaller molecular volume.

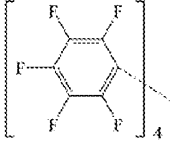
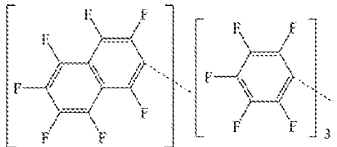
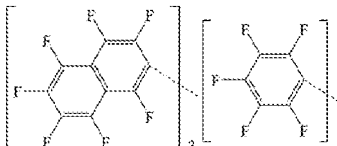
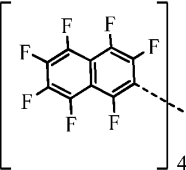
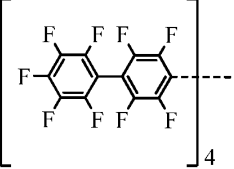
[0169] Molecular volume may be calculated as reported in "A Simple "Back of the Envelope" Method for Estimating the Densities and Molecular Volumes of Liquids and Solids," *Journal of Chemical Education*, v.71(11), November 1994, pp. 962-964. Molecular volume (MV), in units of cubic Å, is calculated using the formula: $MV = 8.3V_s$, where V_s is the scaled volume. V_s is the sum of the relative volumes of the constituent atoms, and is calculated from the molecular formula of the substituent using Table A below of relative volumes. For fused rings, the V_s is decreased by 7.5% per fused ring. The Calculated Total MV of the anion is the sum of the MV per substituent, for example, the MV of perfluorophenyl is 183 Å³, and the Calculated Total MV for tetrakis(perfluorophenyl)borate is four times 183 Å³, or 732 Å³.

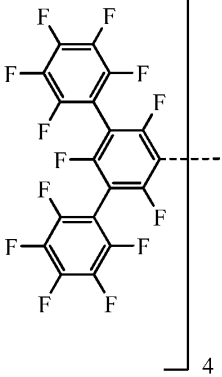
Table A

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

[0170] Exemplary anions useful herein and their respective scaled volumes and molecular volumes are shown in Table B below. The dashed bonds indicate bonding to boron.

Table B

Ion	Structure of Boron Substituents	Molecular Formula of Each Substituent	V _s	MV Per subst. (Å ³)	Calculated Total MV (Å ³)
tetrakis(perfluorophenyl) borate		C ₆ F ₅	22	183	732
tris(perfluorophenyl)-(perfluoronaphthalen-2-yl) borate		C ₆ F ₅ C ₁₀ F ₇	22 34	183 261	810
(perfluorophenyl)tris-(perfluoronaphthalen-2-yl) borate		C ₆ F ₅ C ₁₀ F ₇	22 34	183 261	966
tetrakis(perfluoronaphthalen-2-yl) borate		C ₁₀ F ₇	34	261	1044
tetrakis(perfluorobiphenyl) borate		C ₁₂ F ₉	42	349	1396

$[(C_6F_3(C_6F_5)_2)_4B]$		$C_{18}F_{13}$	62	515	2060
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- [0171]** The activators may be added to a polymerization in the form of an ion pair using, for example, $[M2H^+][NCA]^-$ in which the di(hydrogenated tallow)methylamine (“M2H⁺”) cation reacts with a basic leaving group on the transition metal complex to form a transition metal complex cation and $[NCA]^-$. Alternatively, the transition metal complex may be reacted with a neutral NCA precursor, such as $B(C_6F_5)_3$, which abstracts an anionic group from the complex to form an activated species. Useful activators include di(hydrogenated tallow)methylammonium[tetrakis(pentafluorophenyl)borate] (i.e., $[M2H^+][B(C_6F_5)_4]^-$) and di(octadecyl)tolylammonium [tetrakis(pentafluorophenyl)borate] (i.e., $[DOTH^+][B(C_6F_5)_4]^-$).
- [0172]** Activator compounds that are particularly useful in this invention include one or more of:
- N,N*-di(hydrogenated tallow)methylammonium [tetrakis(perfluorophenyl) borate],
 - N*-methyl-4-nonadecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-hexadecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-tetradecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-dodecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-decyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-octyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-hexyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-butyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-octadecyl-*N*-decylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-nonadecyl-*N*-dodecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-nonadecyl-*N*-tetradecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-methyl-4-nonadecyl-*N*-hexadecylanilinium [tetrakis(perfluorophenyl)borate],
 - N*-ethyl-4-nonadecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],

- N*-methyl-*N,N*-dioctadecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-dihexadecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-ditetradecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-didodecylammonium [tetrakis(perfluorophenyl)borate],
5 *N*-methyl-*N,N*-didecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-dioctylammonium [tetrakis(perfluorophenyl)borate],
N-ethyl-*N,N*-dioctadecylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(octadecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(hexadecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
10 *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],
15 *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],
20 *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],
25 *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].

[0173] Additional useful activators and the synthesis non-aromatic-hydrocarbon soluble
30 activators, are described in USSN 16/394,166 filed April 25, 2019, USSN 16/394,186, filed
April 25, 2019, and USSN 16/394,197, filed April 25, 2019, which are incorporated by
reference herein.

[0174] Likewise, particularly useful activators also include dimethylaniliniumtetrakis
(pentafluorophenyl) borate and dimethyl anilinium tetrakis(heptafluoro-2-naphthalen-2-yl)

tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkyl-(2,4,6-trimethylanilinium)
 tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium
 tetrakis(pentafluorophenyl)borate, (where alkyl is methyl, ethyl, propyl, n-butyl, sec-butyl, or
 t-butyl).

- 5 **[0179]** The typical activator-to-catalyst ratio, e.g., all NCA activators-to-catalyst ratio is about a 1:1 molar ratio. Alternate preferred ranges include from 0.1:1 to 100:1, alternately from 0.5:1 to 200:1, alternately from 1:1 to 500:1 alternately from 1:1 to 1000:1. A particularly useful range is from 0.5:1 to 10:1, preferably 1:1 to 5:1.

- [0180]** It is also within the scope of the present disclosure that the catalyst compounds can
 10 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 (the disclosures of which are incorporated herein by reference in their entirety) which discuss the use of an alumoxane in combination with an ionizing activator).

Optional Scavengers, Co-Activators, Chain Transfer Agents

- 15 **[0181]** In addition to activator compounds, scavengers or co-activators may be used. A scavenger is a compound that is typically added to facilitate polymerization by scavenging impurities. Some scavengers may also act as activators and may be referred to as co-activators. A co-activator, that is not a scavenger, may also be used in conjunction with an activator in order to form an active catalyst. In some embodiments a co-activator can be pre-mixed with
 20 the transition metal compound to form an alkylated transition metal compound.

- [0182]** Co-activators can include alumoxanes such as methylalumoxane, modified alumoxanes such as modified methylalumoxane, and aluminum alkyls such as trimethylaluminum, tri-isobutylaluminum, triethylaluminum, and tri-isopropylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tri-n-decylaluminum or tri-n-dodecylaluminum.
 25 Co-activators are typically used in combination with Lewis acid activators and ionic activators when the pre-catalyst is not a dihydrocarbyl or dihydride complex. Sometimes co-activators are also used as scavengers to deactivate impurities in feed or reactors.

- [0183]** Aluminum alkyl or organoaluminum compounds which may be utilized as scavengers or co-activators include, for example, trimethylaluminum, triethylaluminum,
 30 triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, and dialkyl zinc, such as diethyl zinc.

[0184] Chain transfer agents may be used in the compositions and or processes described herein. Useful chain transfer agents are typically hydrogen, alkylalumoxanes, a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic

radical, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

Polymerization Processes

5 [0185] For the polymerization processes described herein, the term "continuous" means a system that operates without interruption or cessation. For example a continuous process to produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually withdrawn.

[0186] A solution polymerization means a polymerization process in which the polymer is
10 dissolved in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Such systems are preferably not turbid as described in J. Vladimir Oliveira, et al. (2000) *Ind. Eng. Chem. Res.*, v.29, pg. 4627.

15 [0187] A bulk polymerization means a polymerization process in which the monomers and/or comonomers being polymerized are used as a solvent or diluent using little or no inert solvent as a solvent or diluent. A small fraction of inert solvent might be used as a carrier for catalyst and scavenger. A bulk polymerization system contains less than 25 wt% of inert solvent or diluent, preferably less than 10 wt%, preferably less than 1 wt%, preferably 0 wt%.
20 If a bulk polymerization process is performed such that the polymer remains dissolved in the polymerization medium then may be considered to be a type of a homogeneous polymerization process.

[0188] In embodiments herein, the invention relates to solution polymerization processes where propylene monomer, and optionally one or more C₄ or higher alpha olefin comonomers,
25 are contacted with a catalyst system comprising an activator and at least one catalyst compound, as described above. The catalyst compound and activator may be combined in any order, and are combined typically prior to contacting with the monomer. Often such solution polymerization processes are referred to as homogeneous polymerization processes.

[0189] Monomers useful herein include substituted or unsubstituted C₃ to C₄₀ alpha olefins,
30 preferably C₃ to C₂₀ alpha olefins, preferably C₃ to C₁₂ alpha olefins, preferably propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In a preferred embodiment of the invention, the monomer comprises propylene and an optional comonomers comprising one or more C₄ to C₄₀ olefins, preferably C₄ to C₂₀

olefins, or preferably C₆ to C₁₂ olefins. The C₄ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₄ to C₄₀ cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups. In another preferred embodiment, the monomer comprises propylene and an optional comonomers comprising one or more C₄ to C₄₀ olefins, preferably C₄ to C₂₀ olefins, or preferably C₄ to C₈ olefins. The C₄ to C₄₀ olefin comonomers 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.

[0190] Exemplary C₃ to C₄₀ olefin monomers and optional comonomers include propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, cyclobutene, cyclopentene, cycloheptene, cyclooctene, cyclododecene, substituted derivatives thereof, and isomers thereof, preferably hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 5-methylcyclopentene, cyclopentene, norbornene, 5-ethylidene-2-norbornene, and their respective homologs and derivatives.

[0191] In an embodiment one or more dienes are present in the polymer produced herein at up to 10 weight %, preferably at 0.00001 to 1.0 weight %, preferably 0.002 to 0.5 weight %, even more preferably 0.003 to 0.2 weight %, based upon the total weight of the composition. In some embodiments 500 ppm or less of diene is added to the polymerization, preferably 400 ppm or less, preferably or 300 ppm or less. In other embodiments at least 50 ppm of diene is added to the polymerization, or 100 ppm or more, or 150 ppm or more.

[0192] Preferred diolefin monomers useful in this invention include any hydrocarbon structure, preferably C₅ to C₃₀, having at least two unsaturated bonds. In certain embodiments the diolefin monomer contains at least two unsaturated bonds that are readily incorporated into a polymer. In certain embodiments, the diolefin monomer contains only one unsaturated bond that is readily incorporated into a polymer. Dienes may be conjugated or non-conjugated, acyclic or cyclic. Preferably, the dienes are non-conjugated. Dienes can include 5-ethylidene-2-norbornene (ENB); 5-vinyl-2-norbornene (VNB); 1,4-hexadiene; 5-methylene-2-norbornene (MNB); 1,6-octadiene; 3,7-dimethyl-1,6-octadiene (MOD); 1,3-cyclopentadiene; 1,4-cyclohexadiene; dicyclopentadiene (DCPD); and combinations thereof. Other exemplary dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene,

nonacosadiene, triacontadiene, and isomers thereof. Examples of α,ω -dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene and divinylbenzene. Low molecular weight polybutadienes (Mw less than 1,000 g/mol) may also be used as the diene, which is sometimes also referred to as a polyene. Cyclic dienes include cyclopentadiene, norbornadiene, 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

[0193] In some embodiments the diene is preferably 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, norbornadiene, 1,4-hexadiene, 5-methylene-2-norbornene, 1,6-octadiene, 3,7-dimethyl-1,6-octadiene, dicyclopentadiene, cyclopentadiene, and combinations thereof.

[0194] Polymerization processes of this invention can be carried out in any manner known in the art. Any suspension, homogeneous, bulk, or solution polymerization process known in the art can be used. Such processes can be run in a batch, semi-batch, or continuous mode. Homogeneous polymerization processes are preferred. (A homogeneous polymerization process is preferably a process where at least 90 wt% of the product is soluble in the reaction media.) In some embodiments, a bulk homogeneous process is preferred. (A bulk process is preferably a process where monomer concentration in all feeds to the reactor is 70 volume % or more.) In useful embodiments the process is a solution process wherein solvent is added. Alternately, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst system or other additives, or amounts typically found with the monomer; e.g., propane in propylene).

[0195] Suitable diluents/solvents for polymerization include non-coordinating, inert liquids. Examples include straight and branched-chain hydrocarbons, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof, such as can be found commercially (Isopar™ fluids); perhalogenated hydrocarbons, such as perfluorinated C₄₋₁₀ alkanes, chlorobenzene, and aromatic and alkyl-substituted aromatic compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including propylene. In a preferred embodiment, aliphatic hydrocarbon solvents are used as the solvent, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and

alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof. In another embodiment, the solvent is not aromatic, preferably aromatics are present in the solvent at less than 1 wt%, preferably less than 0.5 wt%, preferably less than 0 wt% based upon the weight of the solvents.

- 5 **[0196]** In a preferred embodiment, the feed concentration of the propylene for the polymerization is 60 vol% solvent or less, preferably 40 vol% or less, or preferably 20 vol% or less, based on the total volume of the feedstream.

[0197] Preferred polymerizations can be run at any temperature and/or pressure suitable to obtain the desired propylene polymers. Typical temperatures and/or pressures include a
10 temperature in the range of from about 0°C to about 300°C, preferably about 20°C to about 200°C, preferably about 70°C to about 200°C, preferably from about 90°C to about 180°C, preferably from about 100°C to about 170°C; preferably from about 120°C to about 170°C; and at a pressure in the range of from about 0.35 MPa to about 18 MPa, preferably from about 0.45 MPa to about 6 MPa, or preferably from about 0.5 MPa to about 4 MPa.

- 15 **[0198]** Alternately, typical temperatures and/or pressures include a temperature in the range of from about 0°C to about 300°C, preferably about 20°C to about 200°C, preferably about 35°C to about 150°C, preferably from about 40°C to about 120°C, preferably from about 45°C to about 80°C; and at a pressure in the range of from about 0.35 MPa to about 18 MPa, preferably from about 0.45 MPa to about 6 MPa, or preferably from about 0.5 MPa to about
20 4 MPa.

[0199] In a typical polymerization, the run time of the reaction is up to 300 minutes, preferably in the range of from about 5 to 250 minutes, or preferably from about 10 to 120 minutes. In a continuous polymerization the run time is the same thing as the average residence time.

- 25 **[0200]** In some embodiments, hydrogen is present in the polymerization reactor at a partial pressure of 0.001 to 50 psig (0.007 to 345 kPa), preferably from 0.01 to 25 psig (0.07 to 172 kPa), more preferably 0.1 to 10 psig (0.7 to 70 kPa).

[0201] In an alternate embodiment, the catalyst activity is at least 10,000 g/mmol/hour, preferably 100,000 or more g/mmol/hour, preferably 500,000 or more g/mmol/hr, preferably
30 1,000,000 or more g/mmol/hr, preferably 2,000,000 or more g/mmol/hr, preferably 5,000,000 or more g/mmol/hr. In an alternate embodiment, the catalyst productivity is at least 10,000 or more g polymer/g catalyst, preferably 50,000 or more g polymer/g catalyst, preferably 100,000 or more g polymer/g catalyst, preferably 200,000 or more g polymer/g catalyst, preferably 500,000 or more g polymer/g catalyst. In an alternate embodiment, the conversion of olefin

monomer is at least 10%, based upon polymer yield and the weight of the monomer entering the reaction zone, preferably 20% or more, preferably 30% or more, preferably 50% or more, preferably 80% or more. In a preferred embodiment, little or no alumoxane is used in the process to produce the polymers. Preferably, alumoxane is present at zero mol%, alternately
5 the alumoxane is present at a molar ratio of aluminum to transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1.

[0202] In some embodiments, little or no scavenger is used in the process to produce the polymer. Preferably, scavenger (such as tri alkyl aluminum) is present at zero mol%, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of
10 less than 100:1, preferably less than 50:1, preferably less than 15:1, preferably less than 10:1.

[0203] In a preferred embodiment, the homogeneous (solution or bulk) propylene polymerization: 1) is conducted at temperatures of 0 to 300°C (preferably 25 to 150°C, preferably 40 to 140°C, preferably 50 to 130°C, preferably 60 to 120°C, alternatively 65 to 110°C, alternatively 70 to 100°C,); 2) is conducted at a pressure of atmospheric pressure to
15 18 MPa (preferably 0.35 to 16 MPa, preferably from 0.45 to 14 MPa, preferably from 0.5 to 12 MPa, preferably from 0.5 to 10 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; preferably where aromatics are
20 preferably present in the solvent at less than 1 wt%, preferably less than 0.5 wt%, preferably 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%, preferably 0 mol% alumoxane, alternately the alumoxane is present at a molar ratio of aluminum to transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1; 5) the polymerization
25 preferably occurs in one reaction zone; 6) the catalyst productivity is at least 10,000 g polymer/ g catalyst (preferably at least 100,000 g polymer/ g catalyst, preferably at least 200,000 g polymer/ g catalyst, preferably at least 500,000 g polymer/ g catalyst, preferably at least 1,000,000 g polymer/ g catalyst); 7) optionally scavengers (such as trialkyl aluminum compounds) are absent (e.g. present at zero mol%, alternately the scavenger is present at a
30 molar ratio of scavenger metal to transition metal of less than 100:1, preferably less than 50:1, preferably less than 15:1, preferably less than 10:1); and 8) optionally hydrogen is present in the polymerization reactor at a partial pressure of 0.001 to 50 psig (0.007 to 345 kPa) (preferably from 0.01 to 25 psig (0.07 to 172 kPa), more preferably 0.1 to 10 psig (0.7 to 70 kPa)). In a preferred embodiment, the catalyst system used in the polymerization comprises

no more than one catalyst compound per reaction zone. A "reaction zone" also referred to as a "polymerization zone" is a vessel where polymerization takes place, for example a batch reactor. When multiple reactors are used in either series or parallel configuration, each reactor is considered as a separate polymerization zone. For a multi-stage polymerization in both a batch reactor and a continuous reactor, each polymerization stage is considered as a separate polymerization zone. In a preferred embodiment, the polymerization occurs in one reaction zone. In an alternate embodiment, the polymerization occurs in two reaction zones, with each zone using the same polymerization catalyst.

[0204] The terms "dense fluid" "solid-fluid phase transition temperature" "phase transition" "solid-fluid phase transition pressure" "fluid-fluid phase transition pressure" "fluid-fluid phase transition temperature" "cloud point" "cloud point pressure" "cloud point temperature" "supercritical state" "critical temperature (Tc)" "critical pressure (Pc)" "supercritical polymerization" "homogeneous polymerization" "homogeneous polymerization system" are defined in US 7,812,104, which is incorporated by reference herein.

[0205] A supercritical polymerization means a polymerization process in which the polymerization system is in a dense (i.e. its density is 300 kg/m³ or higher), supercritical state.

[0206] A super solution polymerization or super solution polymerization system is one where the polymerization occurs at a temperature of 65°C to 150°C and a pressure of between 250 to 5,000 psi (1.72 to 34.5 MPa), preferably the super solution polymerization polymerizes a C₃ to C₂₀ monomer (preferably propylene), and has: 1) 0 to 20 wt% of one or more comonomers (based upon the weight of all monomers and comonomers present in the feed) selected from the group consisting of C₄ to C₁₂ olefins, 2) from 20 to 65 wt% diluent or solvent, based upon the total weight of feeds to the polymerization reactor, 3) 0 to 5 wt% scavenger, based upon the total weight of feeds to the polymerization reactor, 4) the olefin monomers and any comonomers are present in the polymerization system at 15 wt% or more, 5) the polymerization temperature is above the solid-fluid phase transition temperature of the polymerization system and above a pressure greater than 1 MPa below the cloud point pressure of the polymerization system, provided however that the polymerization occurs: (1) at a temperature below the critical temperature of the polymerization system, or (2) at a pressure below the critical pressure of the polymerization system.

[0207] In a preferred embodiment of the invention, the polymerization process is conducted under homogeneous (such as solution, super solution, or supercritical) conditions preferably including a temperature of about 60°C to about 200°C, preferably for 65°C to 195°C, preferably for 90°C to 190°C, preferably from greater than 100°C to about 180°C, such as

105°C to 170°C, preferably from about 110°C to about 160°C. The process may be conducted at a pressure in excess of 1.7 MPa, especially under super solution conditions including a pressure of between 1.7 MPa and 30 MPa, or especially under supercritical conditions including a pressure of between 15 MPa and 1,500 MPa, especially when the monomer composition comprises propylene or a mixture of propylene with at least one C₄ to C₂₀ α -olefin. In a preferred embodiment the monomer is propylene and the propylene is present at 15 wt% or more in the polymerization system, preferably at 20 wt% or more, preferably at 30 wt% or more, preferably at 40 wt% or more, preferably at 50 wt% or more, preferably at 60 wt% or more, preferably at 70 wt% or more, preferably 80 wt% or more. In an alternate embodiment, the monomer and any comonomer present are present at 15 wt% or more in the polymerization system, preferably at 20 wt% or more, preferably at 30 wt% or more, preferably at 40 wt% or more, preferably at 50 wt% or more, preferably at 60 wt% or more, preferably at 70 wt% or more, preferably 80 wt% or more.

[0208] In a preferred embodiment of the invention, the polymerization process is conducted under super solution conditions including temperatures from about 65°C to about 150°C, preferably from about 75°C to about 140°C, preferably from about 90°C to about 140°C, more preferably from about 100°C to about 140°C, and pressures of between 1.72 MPa and 35 MPa, preferably between 5 and 30 MPa.

[0209] In another particular embodiment of the invention, the polymerization process is conducted under supercritical conditions (preferably homogeneous supercritical conditions, e.g. above the supercritical point and above the cloud point) including temperatures from about 90°C to about 200°C, and pressures of between 15 MPa and 1,500 MPa, preferably between 20 MPa and 140 MPa.

[0210] A particular embodiment of this invention relates to a process to polymerize propylene comprising contacting, at a temperature of 60°C or more and a pressure of between 15 MPa (150 Bar, or about 2,175 psi) to 1,500 MPa (15,000 Bar, or about 217,557 psi), one or more olefin monomers having three or more carbon atoms, with: 1) the catalyst system, 2) optionally one or more comonomers, 3) optionally diluent or solvent, and 4) optionally scavenger, wherein: a) the olefin monomers and any comonomers are present in the polymerization system at 40 wt% or more, b) the propylene is present at 80 wt% or more based upon the weight of all monomers and comonomers present in the feed, c) the polymerization occurs at a temperature above the solid-fluid phase transition temperature of the polymerization system and a pressure no lower than 2 MPa below the cloud point pressure of the polymerization system.

[0211] Another particular embodiment of this invention relates to a process to polymerize olefins comprising contacting propylene, at a temperature of 65°C to 150°C and a pressure of between 250 to 5,000 psi (1.72 to 34.5 MPa), with: 1) the catalyst system, 2) 0 to 20 wt% of one or more comonomers (based upon the weight of all monomers and comonomers present in the feed) selected from the group consisting of C₄ to C₁₂ olefins, 3) from 20 to 65 wt% diluent or solvent, based upon the total weight of feeds to the polymerization reactor, and 4) 0 to 5 wt% scavenger, based upon the total weight of feeds to the polymerization reactor, wherein: a) the olefin monomers and any comonomers are present in the polymerization system at 15 wt% or more, b) the propylene is present at 80 wt% or more based upon the weight of all monomers and comonomers present in the feed, c) the polymerization occurs at a temperature above the solid-fluid phase transition temperature of the polymerization system and above a pressure greater than 1 MPa below the cloud point pressure of the polymerization system, provided however that the polymerization occurs: (1) at a temperature below the critical temperature of the polymerization system, or (2) at a pressure below the critical pressure of the polymerization system.

[0212] In another embodiment, the polymerization occurs at a temperature above the solid-fluid phase transition temperature of the polymerization system and a pressure no lower than 10 MPa below the cloud point pressure (CPP) of the polymerization system (preferably no lower than 8 MPa below the CPP, preferably no lower than 6 MPa below the CPP, preferably no lower than 4 MPa below the CPP, preferably no lower than 2 MPa below the CPP). Preferably, the polymerization occurs at a temperature and pressure above the solid-fluid phase transition temperature and pressure of the polymerization system and, preferably above the fluid-fluid phase transition temperature and pressure of the polymerization system.

[0213] In an alternate embodiment, the polymerization occurs at a temperature above the solid-fluid phase transition temperature of the polymerization system and a pressure greater than 1 MPa below the cloud point pressure (CPP) of the polymerization system (preferably greater than 0.5 MPa below the CPP, preferably greater than the CCP), and the polymerization occurs: (1) at a temperature below the critical temperature of the polymerization system, or (2) at a pressure below the critical pressure of the polymerization system, preferably the polymerization occurs at a pressure and temperature below the critical point of the polymerization system, most preferably the polymerization occurs: (1) at a temperature below the critical temperature of the polymerization system, and (2) at a pressure below the critical pressure of the polymerization system.

[0214] Alternately, the polymerization occurs at a temperature and pressure above the solid-fluid phase transition temperature and pressure of the polymerization system. Alternately, the polymerization occurs at a temperature and pressure above the fluid-fluid phase transition temperature and pressure of the polymerization system. Alternately, the polymerization occurs at a temperature and pressure below the fluid-fluid phase transition temperature and pressure of the polymerization system.

[0215] In another embodiment, the polymerization system is preferably a homogeneous, single phase polymerization system, preferably a homogeneous dense fluid polymerization system.

[0216] In another embodiment, the reaction temperature is preferably below the critical temperature of the polymerization system. Preferably, the temperature is above the solid-fluid phase transition temperature of the polymer-containing fluid reaction medium at the reactor pressure or at least 5°C above the solid-fluid phase transition temperature of the polymer-containing fluid reaction medium at the reactor pressure, or at least 10°C above the solid-fluid phase transformation point of the polymer-containing fluid reaction medium at the reactor pressure. In another embodiment, the temperature is above the cloud point of the single-phase fluid reaction medium at the reactor pressure, or 2°C or more above the cloud point of the fluid reaction medium at the reactor pressure. In yet another embodiment, the temperature is between 60°C and 150°C, between 60°C and 140°C, between 70°C and 130°C, or between 80°C and 130°C. In one embodiment, the temperature is above 60°C, 65°C, 70°C, 75°C, 80°C, 85°C, 90°C, 95°C, 100°C, 105°C, or 110°C. In another embodiment, the temperature is below 150°C, 140°C, 130°C, or 120°C. In another embodiment, the cloud point temperature is below the supercritical temperature of the polymerization system or between 70°C and 150°C.

[0217] In another embodiment, the polymerization occurs at a temperature and pressure above the solid-fluid phase transition temperature of the polymerization system, preferably the polymerization occurs at a temperature at least 5°C higher (preferably at least 10°C higher, preferably at least 20°C higher) than the solid-fluid phase transition temperature and at a pressure at least 2 MPa higher (preferably at least 5 MPa higher, preferably at least 10 MPa higher) than the cloud point pressure of the polymerization system. In a preferred embodiment, the polymerization occurs at a pressure above the fluid-fluid phase transition pressure of the polymerization system (preferably at least 2 MPa higher, preferably at least 5 MPa higher, preferably at least 10 MPa higher than the fluid-fluid phase transition pressure). Alternately, the polymerization occurs at a temperature at least 5°C higher (preferably at least 10°C higher, preferably at least 20°C higher) than the solid-fluid phase transition temperature and at a

pressure higher than, (preferably at least 2 MPa higher, preferably at least 5 MPa higher, preferably at least 10MPa higher) than the fluid-fluid phase transition pressure of the polymerization system.

5 [0218] In another embodiment, the polymerization occurs at a temperature above the solid-fluid phase transition temperature of the polymer-containing fluid reaction medium at the reactor pressure, preferably at least 5°C above the solid-fluid phase transition temperature of the polymer-containing fluid reaction medium at the reactor pressure, or preferably at least 10°C above the solid-fluid phase transformation point of the polymer-containing fluid reaction medium at the reactor pressure.

10 [0219] In another useful embodiment, the polymerization occurs at a temperature above the cloud point of the single-phase fluid reaction medium at the reactor pressure, more preferably 2°C or more (preferably 5°C or more, preferably 10°C or more, preferably 30°C or more) above the cloud point of the fluid reaction medium at the reactor pressure. Alternately, in another useful embodiment, the polymerization occurs at a temperature above the cloud
15 point of the polymerization system at the reactor pressure, more preferably 2°C or more (preferably 5°C or more, preferably 10°C or more, preferably 30°C or more) above the cloud point of the polymerization system.

[0220] In another embodiment, the polymerization process temperature is above the solid-fluid phase transition temperature of the polymer-containing fluid polymerization system at the
20 reactor pressure, or at least 2°C above the solid-fluid phase transition temperature of the polymer-containing fluid polymerization system at the reactor pressure, or at least 5°C above the solid-fluid phase transition temperature of the polymer-containing fluid polymerization at the reactor pressure, or at least 10°C above the solid-fluid phase transformation point of the polymer-containing fluid polymerization system at the reactor pressure. In another
25 embodiment, the polymerization process temperature should be above the cloud point of the single-phase fluid polymerization system at the reactor pressure, or 2°C or more above the cloud point of the fluid polymerization system at the reactor pressure. In still another embodiment, the polymerization process temperature is between 50°C and 350°C, or between 60°C and 250°C, or between 70°C and 250°C, or between 80°C and 250°C. Exemplary lower
30 polymerization temperature limits are 50°C, or 60°C, or 70°C, or 80°C, or 90°C, or 95°C, or 100°C, or 110°C, or 120°C. Exemplary upper polymerization temperature limits are 350°C, or 250°C, or 240°C, or 230°C, or 220°C, or 210°C, or 200°C.

[0221] In some embodiments of the invention, the preferred polymerization is 100°C or higher, and when 100°C, the polymer produced can have a peak melting point T_m of greater than 155°C, preferably greater than 158°C, preferably greater than 160°C.

[0222] In other embodiments of the invention, the preferred polymerization is 70°C or higher, and when 70°C, the polymer produced can have a peak melting point T_m of greater than 155°C, preferably greater than 160°C, preferably greater than 163°C.

[0223] Room temperature is 23°C unless otherwise noted.

[0224] Other additives may also be used in the polymerization, as desired, such as one or more scavengers, hydrogen, aluminum alkyls, silanes, or chain transfer agents (such as alkylalumoxanes, a compound represented by the formula AlR_3 or ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic radical, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, methylalumoxane, MMAO-3A, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof).

15 Polyolefin Products

[0225] This invention also relates to compositions of matter produced by the methods described herein. The processes described herein may be used to produce polymers of olefins or mixtures of olefins. Polymers that may be prepared include polypropylene homopolymers having the properties described below.

20 [0226] This invention also relates to polymer compositions of matter described herein.

[0227] Generally, the process of this invention produces olefin polymers, preferably polypropylene homopolymers and propylene copolymers with C_4 - C_{20} alpha olefins.

[0228] While the molecular weight of propylene polymers is influenced by numerous process conditions that include temperature, monomer concentration and pressure, the presence of chain transfer agents and the like, the polypropylene homopolymer and copolymer products produced by the present process typically have a weight-average molecular weight (M_w) of about 1,000 to about 1,000,000 g/mol, alternately of about 10,000 to about 600,000 g/mol, or alternately of about 100,000 to about 500,000 g/mol (where all molecular weight values (M_n , M_w and M_z) are presented in terms of calculated polypropylene molecular weights).

30 [0229] Alternatively, in some embodiments of the invention, the polymers produced herein have an M_w of 1,000 to 2,000,000 g/mol (preferably 5,000 to 1,000,000 g/mol, alternatively 10,000 to 500,000 g/mol, alternatively 10,000 to 300,000 g/mol, and/or an M_w/M_n of greater than 1 to 40 (alternately 1.2 to 20, alternately 1.3 to 10, alternately 1.4 to 5, 1.5 to 4, alternately 1.5 to 3) wherein the molecular weight values are relative to linear polystyrene standards.

[0230] Likewise, while process conditions can influence polymer melting point, the polypropylene homopolymer and copolymer products produced by the present process typically have a T_m of about 100°C to about 175°C, alternately of about 120°C to about 170°C, alternately of about 140°C to about 168°C. Alternately the polymers produced have a T_m of 150°C or more. In addition, the polymer products typically have a heat of fusion, (H_f or ΔH_f), of up to 160 J/g, alternately from 20 up to 150 J/g, alternately from about 80 to 120 J/g, alternately from about 90 to 110 J/g, alternately greater than 90 J/g, alternately greater than 100 J/g, alternately greater than 110 J/g, alternately greater than 120 J/g.

[0231] In an embodiment, this invention relates to a propylene-alpha-olefin copolymer having 1) 20 wt.% alpha-olefin or less (alternatively 15 wt.% alpha-olefin or less, alternatively 10 wt.% alpha-olefin or less), 2) a T_m of 50°C or more (alternatively 70°C or more, alternatively 80°C or more, alternatively 90°C or more, alternatively 100°C or more, alternatively 110°C or more); and 3) greater than 0.02 unsaturated end-groups per 1,000C as determined by 1H NMR (alternatively greater than 0.05 unsaturated end-groups per 1,000C, alternatively greater than 0.10 unsaturated end-groups per 1,000C, alternatively greater than 0.30 unsaturated end-groups per 1,000C, alternatively greater than 0.50 unsaturated end-groups per 1,000C) and wherein the alpha-olefin is a C₄-C₂₀ alpha olefin.

[0232] In a preferred embodiment, the monomer is propylene and the comonomer is butene or hexene, preferably from 0.5 to 50 mole% butene or hexene, alternately 1 to 40 mole%, alternately 1 to 30% mole, alternately 1 to 25 mole%, alternately 1 to 20 mole%, alternately 1 to 15 mole%, alternately 1 to 10 mole%.

[0233] In a preferred embodiment, the monomer is propylene and no comonomer is present.

[0234] In a preferred embodiment, the monomer is propylene, no comonomer is present, and the polymer is isotactic.

[0235] In a preferred embodiment the polymer produced herein has a unimodal or multimodal molecular weight distribution ($MWD=M_w/M_n$) 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).

[0236] In a preferred embodiment the polypropylene produced herein has a T_m of 150°C or more (preferably 155°C or more, or 160°C or more, or 162°C or more, or 165°C or more), and an M_n of 20,000 g/mol or more, preferably 50,000 g/mol or more, more preferably 100,000

g/mol or more, more preferably 150,000 g/mole or more (GPC-DRI, relative to linear polystyrene standards). GPC-DRI, relative to linear polystyrene standards means that the numerical values have not been corrected to polypropylene values.

[0237] In a preferred embodiment the polypropylene produced herein has a T_m of 150°C or more (preferably 155°C or more, 160°C or more, or 162°C or more, or 165°C or more), and an M_w of 50,000 g/mol or more, preferably 100,000 g/mol or more, preferably 150,000 g/mol or more, more preferably 200,000 g/mol or more, more preferably 250,000 g/mole or more (GPC-DRI, relative to linear polystyrene standards). In a preferred embodiment the polypropylene produced herein has a T_m of 145°C or more (preferably 150°C or more, 155°C or more, or 160°C or more, or 163°C or more), and an M_w of 50,000 to 350,000 g/mol, preferably 100,000 to 300,000 g/mol, preferably 150,000 to 275,000 g/mol, more preferably 200,000 to 260,000 g/mol (GPC-DRI, relative to linear polystyrene standards). GPC-DRI, relative to linear polystyrene standards means that the numerical values have not been corrected to polypropylene values.

[0238] In a preferred embodiment of the invention, the polymer M_w (GPC-DRI, relative to linear polystyrene standards) is less than $1E-08e^{0.1962x}$ where x is the T_m (°C) of the polymer as measured by DSC (2nd melt) (alternatively less than $4E-09e^{0.2019x}$, alternatively less than $1E-09e^{0.2096x}$), and greater than $2E-16e^{0.2956x}$ where x is the T_m of the polymer as measured by DSC (2nd melt) (alternatively greater than $y = 5E-16e^{0.291x}$, alternatively greater than $1E-15e^{0.2869x}$) and where in the T_m of the polypropylene is 155°C or greater.

[0239] Alternately, the polymer M_w (GPC-DRI, relative to linear polystyrene standards) is less than $(10^{-8})(e^{0.1962z})$, where z is the T_m (°C) of the polymer as measured by DSC (2nd melt) (alternatively less than $(4 \times 10^{-9})(e^{0.2019z})$, alternatively less than $(10^{-9})(e^{0.2096z})$), and greater than $(2 \times 10^{-16})(e^{0.2956z})$ where z is the T_m of the polymer as measured by DSC (2nd melt) (alternatively greater than $(5 \times 10^{-16})(e^{0.291z})$, alternatively greater than $(10^{-15})(e^{0.2869z})$) and where in the T_m of the polypropylene is 155°C or greater.

[0240] In another embodiment, the polypropylene produced herein has a T_m of 150°C or more (preferably 155°C or more, 160°C or more, or 162°C or more, 165°C or more), and a M_w of 50,000 or more g/mol, preferably 80,000 g/mol or more, more preferably 100,000 g/mol or more (GPC-DRI, corrected to polypropylene values). GPC-DRI, corrected to polypropylene values means that while the GPC instrument was calibrated to linear polystyrene samples, values reported are corrected to polypropylene values using the appropriate Mark Houwink coefficients.

[0241] In a preferred embodiment of the invention, the polymer produced herein is isotactic, preferably highly isotactic. An “isotactic” polymer has at least 10% isotactic pentads, a “highly isotactic” polymer has at least 50% isotactic pentads, and a “syndiotactic” polymer has at least 10% syndiotactic pentads, according to analysis by ¹³C-NMR. Preferably isotactic
5 polymers have at least 50% (preferably at least 60%, preferably at least 70%, preferably at least 80%, preferably at least 90%) isotactic pentads. A polyolefin is “atactic” if it has less than 5% isotactic pentads and less than 5% syndiotactic pentads.

[0242] In an embodiment of the invention, the polymer produced herein has an mmmm pentad tacticity index of 75% or greater (preferably 80% or greater, preferably 85% or greater,
10 preferably 90% or greater, preferably 95% or greater, preferably 96% or greater, preferably 97% or greater, preferably 98% or greater as determined by ¹³C NMR as described below.

[0243] In a preferred embodiment of the invention, the polymer produced herein is isotactic, and contains 2,1- and in some instances, 1,3-regio defects (1,3-regio defects are also sometimes called 3,1-regio defects, and the term regio defect is also called regio-error). In
15 some embodiments of the invention, the polymer produced herein has less than 200 total regio defects/10,000 monomer units (defined as the sum of 2,1-erythro and 2,1-threo insertions, and 3,1-isomerizations (also called 1,3-insertions) as measured by ¹³C-NMR (preferably less than 100 total regio defects/10,000 monomer units, preferably less than 50 total regio defects/10,000 monomer units, preferably less than 35 total regio defects/10,000 monomer units, preferably
20 less than 30 total regio defects/10,000 monomer units, preferably less than 25 total regio defects/10,000 monomer units, preferably less than 20 total regio defects/10,000 monomer units) with the proviso that the total regio defects is not less than 1 total regio defects/10,000 monomer units, preferably not less than 2 total regio defects/10,000 monomer units, alternatively not less than 5 total regio defects/10,000 monomer units. In some embodiments
25 of the invention, the isotactic polymers contain no measureable 1,3-regio defects.

[0244] In a preferred embodiment, the isotactic polypropylene polymer has 1,3-regio defects of 30/10,000 monomer units or less (preferably less than 20/10,000 monomer units, preferably less than 10/10,000 monomer units, preferably less than 5/10,000 monomer units, preferably less than 4/10,000 monomer units, preferably less than 3/10,000 monomer units, preferably less than 2/10,000 monomer units, preferably less than 1/10,000 monomer units) as determined by ¹³C NMR.
30

[0245] In a preferred embodiment, the isotactic polypropylene polymer has a T_m as measured by DSC of 155°C or greater (preferably 157°C or greater, alternatively 159°C or greater, alternatively 160°C or greater, alternatively 161°C or greater, and wherein the total

regio defects/10,000 monomer units is less than $-1.18 \times T_m(^{\circ}\text{C}) + 210$, alternatively less than $-1.18 \times T_m(^{\circ}\text{C}) + 209.5$, alternatively $1.18 \times T_m(^{\circ}\text{C}) + 209$ with the proviso that the total regio defects is not less than 3 total regio defects/10,000 monomer units, preferably not less than 4 total regio defects/10,000 monomer units, alternatively not less than 5 total regio defects/10,000 monomer units.

[0246] In addition to total regio defects defined above, isotactic polymers also exhibit stereo-defects. "Total defects" is defined to be total regio defects plus stereo-defects. Total regio defects times 100 and divided by the "total defects" is referred to as the percentage of total regio defects. In some embodiments of the invention the percentage of total regio defects is less than 40%, preferably less than 35%, preferably less than 32%, preferably less than 30%, alternatively less than 25%.

[0247] In some embodiments of the invention, the isotactic polypropylene has greater than 0.05 unsaturated end-groups per 1000C as determined by ^1H NMR (alternatively greater than 0.10 unsaturated end-groups per 1000C, alternatively greater than 0.30 unsaturated end-groups per 1000C, alternatively greater than 0.50 unsaturated end-groups per 1000C).

[0248] In some embodiments of the invention, the propylene based polymers are propylene-alpha-olefin copolymers wherein the alpha-olefin is a $\text{C}_4\text{-C}_{20}$ alpha olefin. Preferably, the propylene-alpha-olefin copolymer contains 50 mol% propylene or greater, alternatively 60 mol% propylene or greater, alternatively 70 mol% propylene or greater, alternatively 80 mol% propylene or greater, alternatively 90 mol% propylene or greater, with the lower limit of $\text{C}_4\text{-C}_{20}$ alpha-olefin being 1 mol%, alternatively 3 mol%, alternatively 5 mol%, alternatively 10 mol%, alternatively 15 mol%, alternatively 20 mol%, alternatively 30 mol%. In a preferred embodiment of the invention, the propylene-alpha-olefin copolymers have at least 50% (preferably at least 60%, preferably at least 70%, preferably at least 80%, preferably at least 90%) isotactic triads as measured by ^{13}C NMR.

^{13}C -NMR Spectroscopy on Polyolefins

[0249] Polypropylene microstructure is determined by ^{13}C -NMR spectroscopy, including the concentration of isotactic and syndiotactic diads ([m] and [r]), triads ([mm] and [rr]), and pentads ([mmmm] and [rrrr]). The designation "m" or "r" describes the stereochemistry of pairs of contiguous propylene groups, "m" referring to meso and "r" to racemic. Samples are dissolved in $\text{d}_2\text{-1,1,2,2-tetrachloroethane}$, and spectra recorded at 120°C using a ^{13}C frequency of 125 MHz (or higher) NMR spectrometer. Polymer resonance peaks are referenced to mmmm = 21.8 ppm. Calculations involved in the characterization of polymers by NMR are described by F. A. Bovey in *Polymer Conformation and Configuration* (Academic Press, New

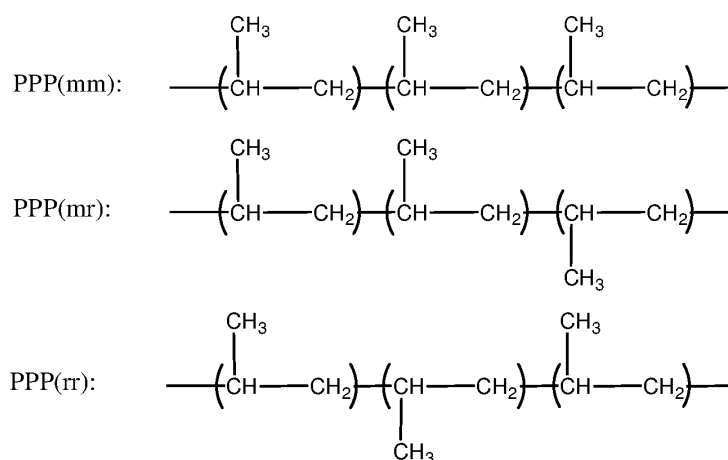
York 1969) and J. Randall in *Polymer Sequence Determination, ¹³C-NMR Method* (Academic Press, New York, 1977).

[0250] The “propylene tacticity index”, expressed herein as [m/r], is calculated as defined in H.N. Cheng (1984) *Macromolecules*, v.17, p. 1950. When [m/r] is 0 to less than 1.0, the polymer is generally described as syndiotactic, when [m/r] is 1.0 the polymer is atactic, and when [m/r] is greater than 1.0 the polymer is generally described as isotactic.

[0251] The “mm triad tacticity index” of a polymer is a measure of the relative isotacticity of a sequence of three adjacent propylene units connected in a head-to-tail configuration. More specifically, in the present invention, the mm triad tacticity index (also referred to as the “mm Fraction”) of a polypropylene homopolymer or copolymer is expressed as the ratio of the number of units of meso tacticity to all of the propylene triads in the copolymer:

$$\text{mm Fraction} = \frac{\text{PPP(mm)}}{\text{PPP(mm)} + \text{PPP(mr)} + \text{PPP(rr)}}$$

where PPP(mm), PPP(mr) and PPP(rr) denote peak areas derived from the methyl groups of the second units in the possible triad configurations for three head-to-tail propylene units, shown below in Fischer projection diagrams:



[0252] The calculation of the mm Fraction of a propylene polymer is described in US Patent 5,504,172 (homopolymer: column 25, line 49 to column 27, line 26; copolymer: column 28, line 38 to column 29, line 67). For further information on how the mm triad tacticity can be determined from a ¹³C-NMR spectrum, see 1) J. A. Ewen (1986), *Catalytic Polymerization of Olefins: Proceedings of the International Symposium on Future Aspects of Olefin*

Polymerization, T. Keii and K. Soga, Eds. (Elsevier), pp. 271-292; and 2) US Patent Application Publication No. US2004/054086 (paragraphs [0043] to [0054]).

[0253] Similarly m diads and r diads can be calculated as follows where mm, mr and mr are defined above:

$$m = mm + \frac{1}{2} mr$$

$$r = rr + \frac{1}{2} mr .$$

[0254] In another embodiment of the invention, the propylene polymers produced herein (preferably a homopolypropylene) have regio defects (as determined by ^{13}C NMR), based upon the total propylene monomer. Three types defects are defined to be the regio defects: 2,1-erythro, 2,1-threo, and 3,1-isomerization. The structures and peak assignments for these are given in [L. Resconi, et al. (2000) *Chem. Rev.*, v.100, pp. 1253-1345]. The regio defects each give rise to multiple peaks in the 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

[0255] The average integral for each defect is divided by the integral for one of the main propylene signals (CH_3 , CH , CH_2), and multiplied by 10,000 to determine the defect concentration per 10,000 monomers.

[0256] Mn (^1H NMR) is determined according to the following NMR method. ^1H NMR data is collected at either room temperature or 120°C (for purposes of the claims, 120°C shall be used) in a 10 mm probe using a Bruker spectrometer with a ^1H frequency of 500 MHz or higher (for the purpose of the claims, a proton frequency of 600 MHz is used and the polymer sample is dissolved in 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2) and transferred into a 10 mm glass NMR tube). Data are recorded using a maximum pulse width of 45°C , 5 seconds between pulses and signal averaging 512 transients. Spectral signals are integrated and the number of unsaturation types per 1,000 carbons is calculated by multiplying the different groups by 1,000 and dividing the result by the total number of carbons. Mn is calculated by dividing the total

number of unsaturated species into 14,000, and has units of g/mol. The chemical shift regions for the olefin types are defined to be between the following spectral regions.

Unsaturation Type	Region (ppm)	Number of hydrogens per structure
Vinyl	4.98-5.13	2
Vinylidene (VYD)	4.69-4.88	2
Vinylene	5.31-5.55	2
Trisubstituted	5.11-5.30	1

Blends

- 5 **[0257]** In another embodiment, the propylene homopolymer or propylene copolymer with a C₄ or higher alpha olefin produced herein is combined with one or more additional polymers prior to being formed into a film, molded part or other article. Other useful polymers include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene,
- 10 polybutene, ethylene vinyl acetate, LDPE, LLDPE, HDPE, ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM,
- 15 block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and/or polyisobutylene.

- [0258]** In a preferred embodiment, the propylene polymer (preferably the homopolypropylene) is present in the above blends, at from 10 to 99 wt%, based upon the weight of the polymers in the blend, preferably 20 to 95 wt%, even more preferably at least 30 to 90 wt%, even more preferably at least 40 to 90 wt%, even more preferably at least 50 to 90 wt%, even more preferably at least 60 to 90 wt%, even more preferably at least 70 to 90 wt%.

- [0259]** The blends described above may be produced by mixing the polymers of the invention with one or more polymers (as described above), by connecting reactors together in series to make reactor blends or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers can be mixed together prior to being put into the extruder or may be mixed in an extruder.

[0260] The blends may be formed using conventional equipment and methods, such as by dry blending the individual components and subsequently melt mixing in a mixer, or by mixing the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which may include a compounding extruder and a side-arm extruder used directly downstream of a polymerization process, which may include blending powders or pellets of the resins at the hopper of the film extruder. Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives are well known in the art, and can include, for example: fillers; antioxidants (e.g., hindered phenolics such as IRGANOX™ 1010 or IRGANOX™ 1076 available from Ciba-Geigy); phosphites (e.g., IRGAFOS™ 168 available from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates, and hydrogenated rosins; UV stabilizers; heat stabilizers; anti-blocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; talc; and the like.

[0261] The polymer products produced by the present process may be blended with one or more other polymers, including but not limited to, thermoplastic polymer(s) and/or elastomer(s), such as those disclosed at page 59 of WO 2004/014998.

[0262] The polymers of this invention (and blends thereof as described above) whether formed in situ or by physical blending are preferably used in any known thermoplastic or elastomer application. Examples include uses in molded parts, films, tapes, sheets, tubing, hose, sheeting, wire and cable coating, adhesives, shoe soles, bumpers, gaskets, bellows, films, fibers, elastic fibers, nonwovens, spunbonds, sealants, surgical gowns and medical devices. Films of polymers produced herein may be made according to WO 2004/014998 at page 63, line 1 to page 66, line 26, including that the films of polymers produced herein may be combined with one or more other layers as described at WO 2004/014998 at page 63, line 21 to page 65, line 2.

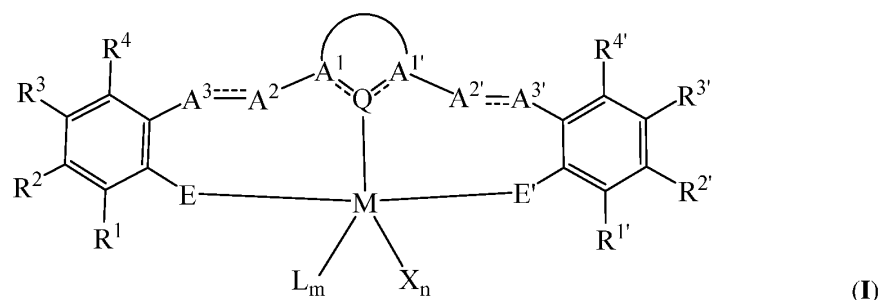
[0263] Any of the foregoing polymers and compositions in combination with optional additives (see, for example, US Patent Application Publication No. 2016/0060430, paragraphs [0082]-[0093]) may be used in a variety of end-use applications. Such end uses may be produced by methods known in the art. End uses include polymer products and products having specific end-uses. Exemplary end uses are films, film-based products, diaper backsheet, housewrap, wire and cable coating compositions, articles formed by molding techniques, e.g., injection or blow molding, extrusion coating, foaming, casting, and combinations thereof. End

uses also include products made from films, e.g., bags, packaging, and personal care films, pouches, medical products, such as for example, medical films and intravenous (IV) bags.

Films

- [0264]** Specifically, any of the foregoing polymers, such as the foregoing polypropylenes or blends thereof, may be used in a variety of end-use applications. Such applications include, for example, mono- or multi-layer blown, extruded, and/or shrink films. These films may be formed by any number of well-known extrusion or coextrusion techniques, such as a blown bubble film processing technique, wherein the composition can be extruded in a molten state through an annular die and then expanded to form a uni-axial or biaxial orientation melt prior to being cooled to form a tubular, blown film, which can then be axially slit and unfolded to form a flat film. Films may be subsequently unoriented, uniaxially oriented, or biaxially oriented to the same or different extents. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. The uniaxially orientation can be accomplished using typical cold drawing or hot drawing methods. Biaxial orientation can be accomplished using tenter frame equipment or a double bubble processes and may occur before or after the individual layers are brought together. For example, a polyethylene layer can be extrusion coated or laminated onto an oriented polypropylene layer or the polyethylene and polypropylene can be coextruded together into a film then oriented. Likewise, oriented polypropylene could be laminated to oriented polyethylene or oriented polyethylene could be coated onto polypropylene then optionally the combination could be oriented even further. Typically the films are oriented in the Machine Direction (MD) at a ratio of up to 15, preferably between 5 and 7, and in the Transverse Direction (TD) at a ratio of up to 15, preferably 7 to 9. However, in another embodiment the film is oriented to the same extent in both the MD and TD directions.
- [0265]** The films may vary in thickness depending on the intended application; however, films of a thickness from 1 to 50 μm are usually suitable. Films intended for packaging are usually from 10 to 50 μm thick. The thickness of the sealing layer is typically 0.2 to 50 μm . There may be a sealing layer on both the inner and outer surfaces of the film or the sealing layer may be present on only the inner or the outer surface.
- [0266]** In another embodiment, one or more layers may be modified by corona treatment, electron beam irradiation, gamma irradiation, flame treatment, or microwave. In a preferred embodiment, one or both of the surface layers is modified by corona treatment.
- [0267]** In another embodiment, this invention relates to:

1. A polymerization process comprising contacting in a homogeneous phase, propylene with a catalyst system comprising activator and catalyst compound represented by the Formula (I):



5 wherein:

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

E and E' are each independently O, S, or NR⁹ where R⁹ is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl or a heteroatom-containing group;

Q is group 14, 15, or 16 atom that forms a dative bond to metal M;

10 A¹QA^{1'} are part of a heterocyclic Lewis base containing 4 to 40 non-hydrogen atoms that links A² to A^{2'} via a 3-atom bridge with Q being the central atom of the 3-atom bridge, A¹ and A^{1'} are independently C, N, or C(R²²), where R²² is selected from hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl;

15 A³---A² is a divalent group containing 2 to 40 non-hydrogen atoms that links A¹ to the E-bonded aryl group via a 2-atom bridge;

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

L is a Lewis base; X is an anionic ligand; n is 1, 2 or 3; m is 0, 1, or 2; n+m is not greater than 4;

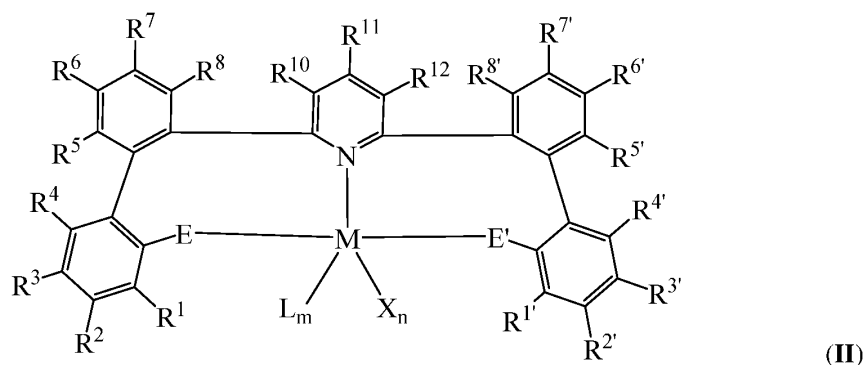
20 each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, and one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may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

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

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

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

2. The process of paragraph 1 where the catalyst compound represented by the Formula (II):



5 wherein:

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

E and E' are each independently O, S, or NR⁹, where R⁹ is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group;

each L is independently a Lewis base; each X is independently an anionic ligand; n is

10 1, 2 or 3; m is 0, 1, or 2; n+m is not greater than 4;

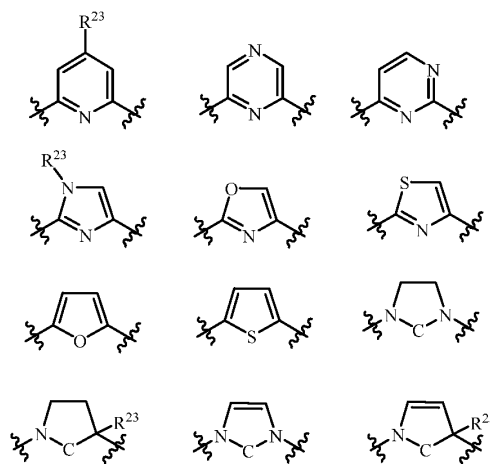
each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be joined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

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

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

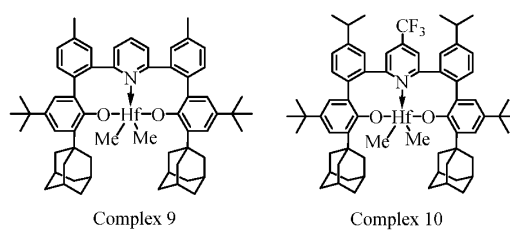
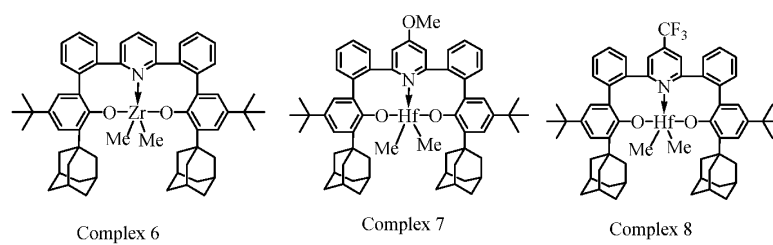
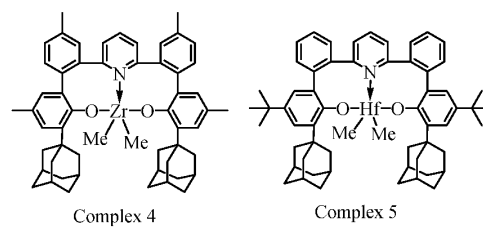
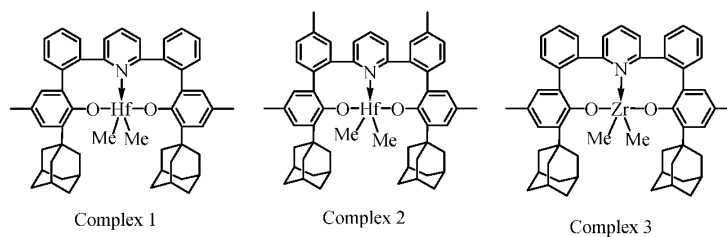
20 each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹, and R¹² is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R⁵ and R⁶, R⁶ and R⁷, R⁷ and R⁸, R^{5'} and R^{6'}, R^{6'} and R^{7'}, R^{7'} and R^{8'}, R¹⁰ and R¹¹, or R¹¹ and R¹² may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

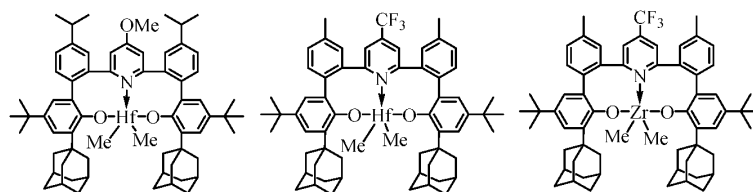
3. The process of paragraph 1 or 2 wherein the M is Hf, Zr or Ti, preferably Hf.
4. The process of paragraph 1, 2 or 3 wherein E and E' are each O.
5. The process of paragraph 1, 2, 3, or 4 wherein R¹ and R^{1'} is independently a C₄-C₄₀ tertiary hydrocarbyl group, preferably a C₄-C₄₀ cyclic tertiary hydrocarbyl group, preferably a C₄-C₄₀ polycyclic tertiary hydrocarbyl group.
6. The process any of paragraphs 1 to 5 wherein each X is, independently, selected from the group consisting of substituted or unsubstituted hydrocarbyl radicals having from 1 to 30 (such as 1 to 20) carbon atoms, substituted or unsubstituted silylcarbyl radicals having from 3 to 30 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, substituted benzyl radicals having from 8 to 30 carbon atoms, and a combination thereof, (two X's may form a part of a fused ring or a ring system).
7. The process any of paragraphs 1 to 6 wherein each L is, independently, selected from the group consisting of: ethers, thioethers, amines, phosphines, ethyl ether, tetrahydrofuran, dimethylsulfide, triethylamine, pyridine, alkenes, alkynes, allenes, and carbenes and a combinations thereof, optionally two or more L's may form a part of a fused ring or a ring system).
8. The process of paragraph 1, wherein M is Zr or Hf, preferably Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls.
9. The process of paragraph 1, wherein M is Zr or Hf, preferably Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are adamantan-1-yl or substituted adamantan-1-yl.
10. The process of paragraph 1 or 2, wherein M is Hf.
11. The process of paragraph 1 or 2, wherein both R¹ and R^{1'} are adamantan-1-yl or substituted adamantan-1-yl.
12. The process of paragraph 1, wherein Q is carbon, A¹ and A^{1'} are both nitrogen, and both E and E' are oxygen.
13. The process of paragraph 1, wherein Q is carbon, A¹ is nitrogen, A^{1'} is C(R²²), and both E and E' are oxygen, where R²² is selected from hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl.
14. The process of any of paragraphs 1 to 13, wherein the heterocyclic Lewis base is selected from the groups represented by the following formulas:



where each R^{23} is independently selected from hydrogen, C_1 - C_{20} alkyls, and C_1 - C_{20} substituted alkyls.

15. The process of paragraph 2, wherein M is Zr or Hf, preferably Hf, both E and E' are oxygen, and both R^1 and $R^{1'}$ are C_4 - C_{20} cyclic tertiary alkyls.
16. The process of paragraph 2, wherein M is Zr or Hf, preferably Hf, both E and E' are oxygen, and both R^1 and $R^{1'}$ are adamantan-1-yl or substituted adamantan-1-yl.
17. The process of paragraph 2, wherein M is Zr or Hf, preferably Hf, both E and E' are oxygen, and each of R^1 , $R^{1'}$, R^3 and $R^{3'}$ are adamantan-1-yl or substituted adamantan-1-yl.
- 10 18. The process of paragraph 2, wherein M is Zr or Hf, preferably Hf, both E and E' are oxygen, both R^1 and $R^{1'}$ are C_4 - C_{20} cyclic tertiary alkyls, and both R^7 and $R^{7'}$ are C_1 - C_{20} alkyls.
19. The process of paragraph 2, wherein M is Zr or Hf, preferably Hf, both E and E' are O, both R^1 and $R^{1'}$ are C_4 - C_{20} cyclic tertiary alkyls, and both R^7 and $R^{7'}$ are C_1 - C_{20} alkyls.
20. The process of paragraph 2, wherein M is Zr or Hf, preferably Hf, both E and E' are O,
- 15 both R^1 and $R^{1'}$ are C_4 - C_{20} cyclic tertiary alkyls, and both R^7 and $R^{7'}$ are C_1 - C_3 alkyls.
21. The process of paragraph 1 wherein the catalyst compound is represented by one or more of the following formulas:

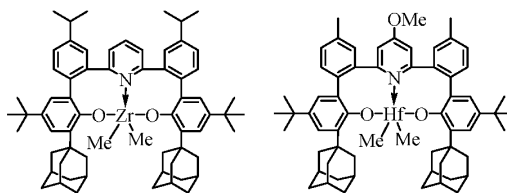




Complex 11

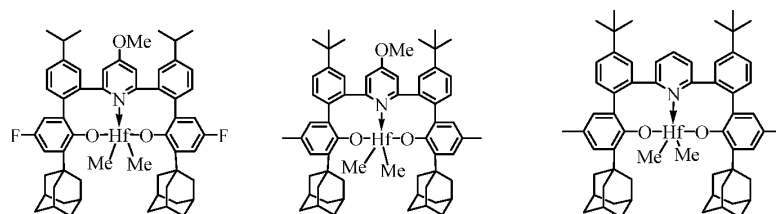
Complex 12

Complex 13



Complex 14

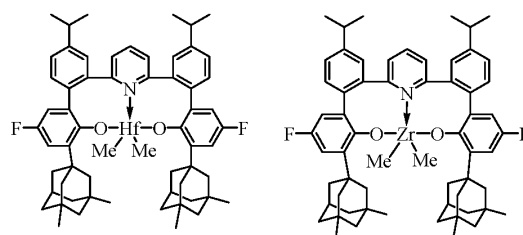
Complex 15



Complex 16

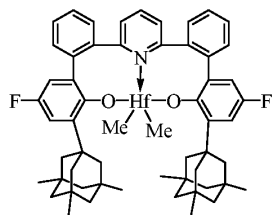
Complex 17

Complex 18

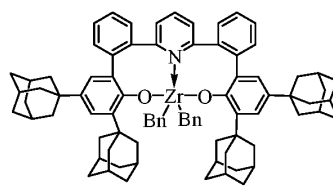


Complex 19

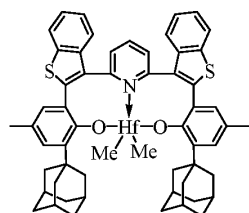
Complex 20



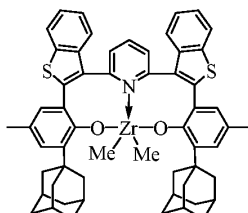
Complex 21



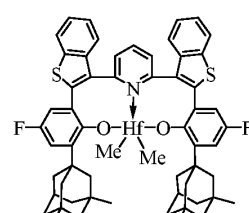
Complex 22



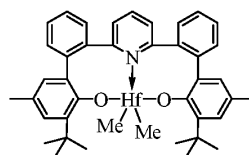
Complex 23



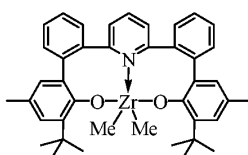
Complex 24



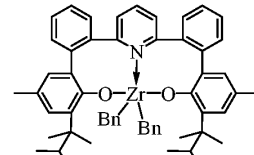
Complex 25



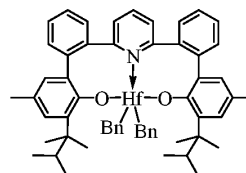
Complex 26



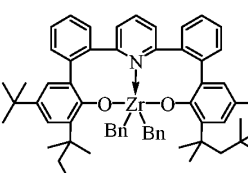
Complex 27



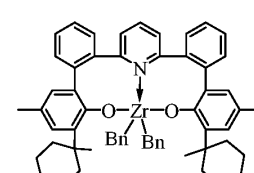
Complex 29



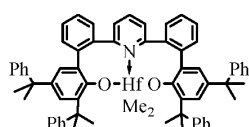
Complex 30



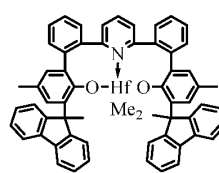
Complex 31



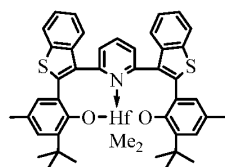
Complex 32



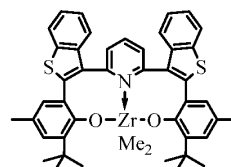
Complex 33



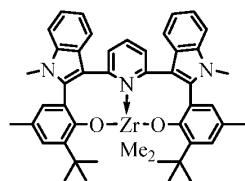
Complex 34



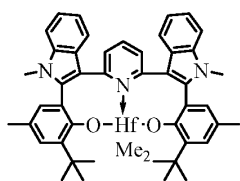
Complex 35



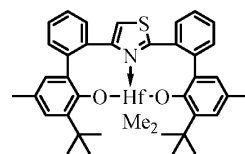
Complex 36



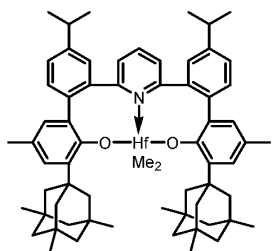
Complex 37



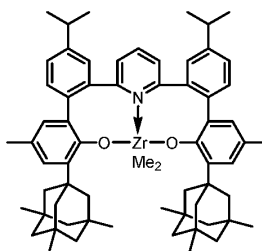
Complex 38



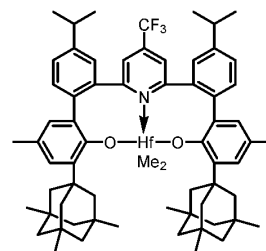
Complex 39



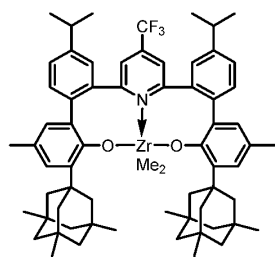
Complex 40



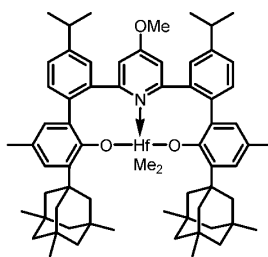
Complex 41



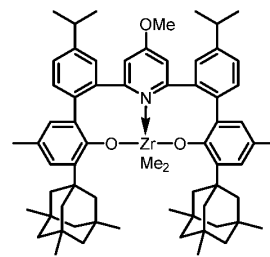
Complex 42



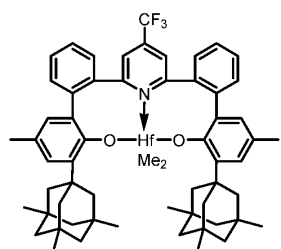
Complex 43



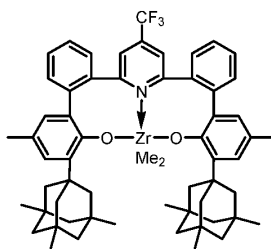
Complex 44



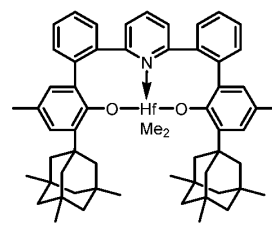
Complex 45



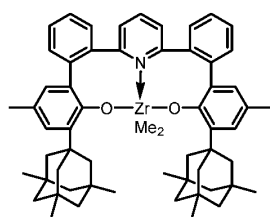
Complex 46



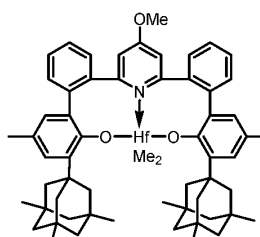
Complex 47



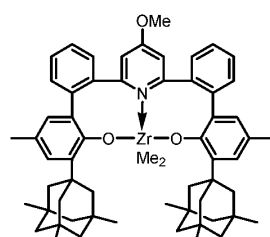
Complex 48



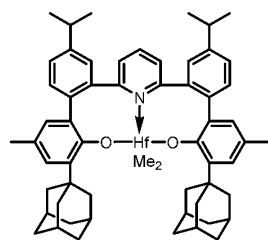
Complex 49



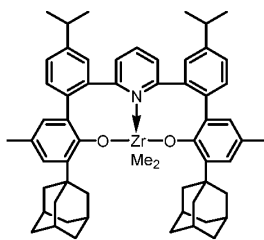
Complex 50



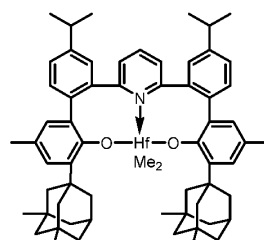
Complex 51



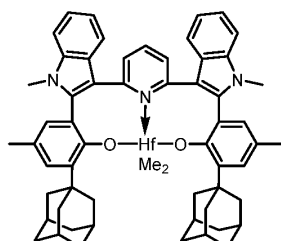
Complex 52



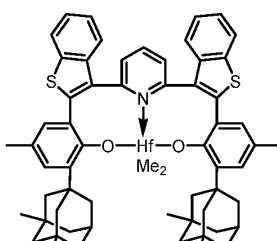
Complex 53



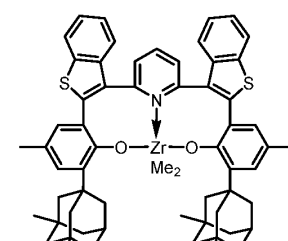
Complex 54



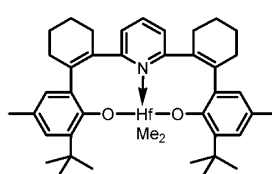
Complex 56



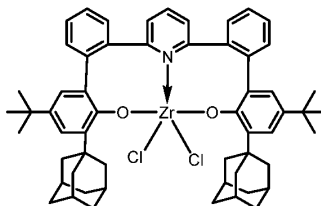
Complex 57



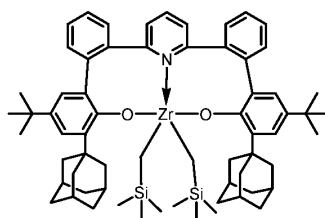
Complex 58



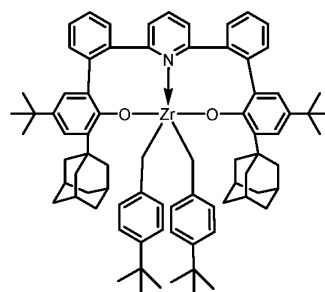
Complex 59



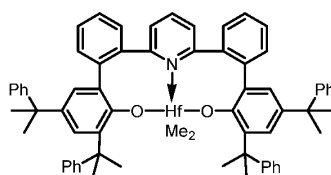
Complex 60



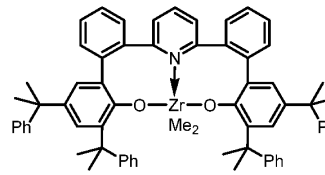
Complex 62



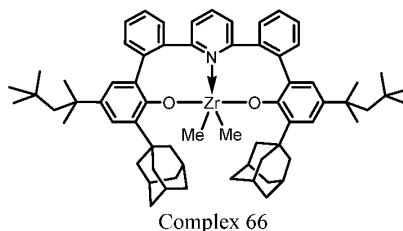
Complex 63



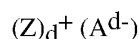
Complex 64



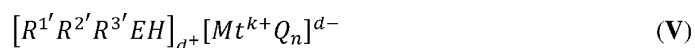
Complex 65



22. The process of paragraph 21 wherein the catalyst compound is selected from Complexes 1, 2, 5, 7, 9, 10, 11, 12, 14, 15, 16, 19, 20, 23, and 25.
- 5 23. The process of any of paragraphs 1 to 22 wherein the activator comprises an alumoxane or a non-coordinating anion.
24. The process of any of paragraphs 1 to 23, wherein the activator is soluble in non-aromatic-hydrocarbon solvent.
25. The process of any of paragraphs 1 to 24 wherein the catalyst system is free of aromatic solvent.
- 10 26. The process of any of paragraphs 1 to 25, wherein the activator is represented by the formula:



- wherein Z is (L-H) or a reducible Lewis Acid, L is an neutral Lewis base; H is hydrogen;
- 15 (L-H)⁺ is a Bronsted acid; A^{d-} is a non-coordinating anion having the charge d⁻; and d is an integer from 1 to 3.
27. The process of any of paragraphs 1 to 25 wherein the activator is represented by the formula:



- 20 wherein:

E is nitrogen or phosphorous;

d is 1, 2 or 3; *k* is 1, 2, or 3; *n* is 1, 2, 3, 4, 5, or 6; $n - k = d$;

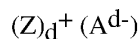
R^{1'}, *R*^{2'}, and *R*^{3'} are independently a C₁ to C₅₀ hydrocarbyl group optionally substituted with one or more alkoxy groups, silyl groups, a halogen atoms, or halogen containing groups,

- 25 wherein *R*^{1'}, *R*^{2'}, and *R*^{3'} together comprise 15 or more carbon atoms;

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

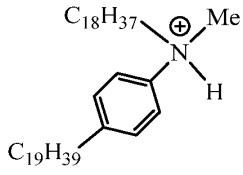
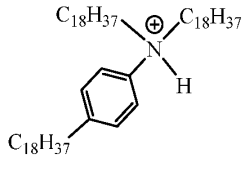
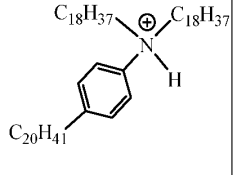
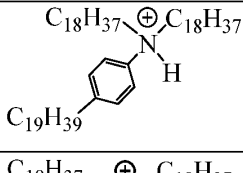
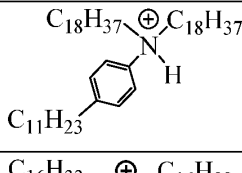
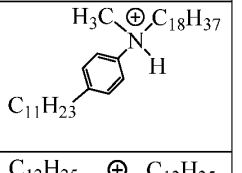
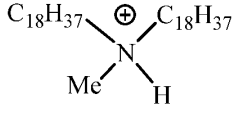
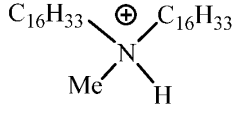
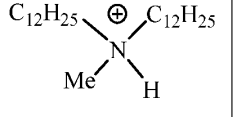
each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical.

28. The process of any of paragraphs 1 to 22 wherein the activator is represented by the formula:



wherein A^{d-} is a non-coordinating anion having the charge d^- ; and d is an integer from 1 to 3 and $(Z)_d^+$ is represented by one or more of:

10		11		12	
13		14		15	
16		17		18	
19		20		21	
22		23		24	
25		26		27	

29		28		30	
31		32		33	
34		35		36	

29. The process of any of paragraphs 1 to 25, wherein the activator is one or more of:
- N-methyl-4-nonadecyl-N-octadecylbenzenaminium tetrakis(pentafluorophenyl)borate,
N-methyl-4-nonadecyl-N-octadecylbenzenaminium tetrakis(perfluoronaphthalen-2-yl)borate,
- 5 dioctadecylmethylammonium tetrakis(pentafluorophenyl)borate,
dioctadecylmethylammonium tetrakis(perfluoronaphthalen-2-yl)borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate,
trimethylammonium tetrakis(perfluoronaphthalen-2-yl)borate,
- 10 triethylammonium tetrakis(perfluoronaphthalen-2-yl)borate,
tripropylammonium tetrakis(perfluoronaphthalen-2-yl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthalen-2-yl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthalen-2-yl)borate,
N,N-dimethylanilinium tetrakis(perfluoronaphthalen-2-yl)borate,
- 15 N,N-diethylanilinium tetrakis(perfluoronaphthalen-2-yl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthalen-2-yl)borate,
tropillium tetrakis(perfluoronaphthalen-2-yl)borate,
triphenylcarbenium tetrakis(perfluoronaphthalen-2-yl)borate,
triphenylphosphonium tetrakis(perfluoronaphthalen-2-yl)borate,
- 20 triethylsilylium tetrakis(perfluoronaphthalen-2-yl)borate,
benzene(diazonium) tetrakis(perfluoronaphthalen-2-yl)borate,
trimethylammonium tetrakis(perfluorobiphenyl)borate,
triethylammonium tetrakis(perfluorobiphenyl)borate,

- tripropylammonium tetrakis(perfluorobiphenyl)borate,
tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
tri(t-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
5 N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate,
tropillium tetrakis(perfluorobiphenyl)borate,
triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
triphenylphosphonium tetrakis(perfluorobiphenyl)borate,
10 triethylsilylium tetrakis(perfluorobiphenyl)borate,
benzene(diazonium) tetrakis(perfluorobiphenyl)borate,
[4-t-butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B],
trimethylammonium tetraphenylborate,
triethylammonium tetraphenylborate,
15 tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,
N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
20 N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate,
tropillium tetraphenylborate,
triphenylcarbenium tetraphenylborate,
triphenylphosphonium tetraphenylborate,
triethylsilylium tetraphenylborate,
25 benzene(diazonium)tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl)borate,
triethylammonium tetrakis(pentafluorophenyl)borate,
tripropylammonium tetrakis(pentafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,
30 tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate,

- tropillium tetrakis(pentafluorophenyl)borate,
 triphenylcarbenium tetrakis(pentafluorophenyl)borate,
 triphenylphosphonium tetrakis(pentafluorophenyl)borate,
 triethylsilylium tetrakis(pentafluorophenyl)borate,
 5 benzene(diazonium) tetrakis(pentafluorophenyl)borate,
 trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate,
 triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 10 dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 15 triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 20 triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 tri(t-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 25 N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 30 triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
 dicyclohexylammonium tetrakis(pentafluorophenyl)borate,
 tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate,

- tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate,
 triphenylcarbenium tetrakis(perfluorophenyl)borate,
 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium,
 tetrakis(pentafluorophenyl)borate,
- 5 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine, and
 triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).
30. The process of any of paragraphs 1 to 29 wherein the process is a solution process.
31. The process of any of paragraphs 1 to 30 wherein the process occurs at a temperature
 of from about 0°C to about 300°C, at a pressure in the range of from about 0.35 MPa to about
- 10 18 MPa, and at a time up to 300 minutes.
32. The process of any of paragraphs 1 to 31 wherein the process occurs at a temperature
 of 65°C to about 150°C.
33. The process of any of paragraphs 1 to 32 further comprising obtaining propylene
 polymer, preferably wherein the propylene polymer is isotactic and has a mmmm pentad
- 15 tacticity index of 75% or greater.
34. The process of paragraph 33 wherein the polymer has a T_m of 150°C or greater as
 measured by DSC.
35. The process of paragraph 33 or 34 wherein the polymer has a Mw of 50,000 g/mol or
 greater (as measured by GPC-DRI, relative to linear polystyrene standards).
- 20 36. The process of paragraph 33, 34 or 35 wherein the polymer has less than 200 total regio
 defects/10,000 monomer units and greater than 1 total regio defects/10,000 monomer units as
 measured by ¹³C-NMR.
37. The process of paragraph 33, 34, 35 or 36 wherein the polymer has less than 30
 1,3-regio defects/10,000 monomer units as measured by ¹³C-NMR.
- 25 38. The process of any of paragraphs 33 to 37 wherein the polymer has a percentage of total
 regio defects less than 40%.
39. The process of paragraph 33 wherein the polymer has 1) a T_m as measured by DSC of
 155°C or greater, 2) wherein the total regio defects/10,000 monomer units is less than -1.18 x
 T_m(°C) + 210, and 3) wherein the total regio defects is not less than 3 total regio defects/10,000
- 30 monomer units.
40. The process of any of paragraphs 33 to 39 wherein the polymer has greater than 0.05
 unsaturated end-groups per 1000C as determined by ¹H NMR.
41. The process of any of paragraphs 33 to 40 wherein the polymer has 1) a Mw (GPC-
 DRI, relative to linear polystyrene standards) less than (10⁻⁸)(e^{0.1962z}) where z is the T_m (°C) of

- the polymer as measured by DSC (2nd melt) and 2) a Mw greater than $(2 \times 10^{-16})(e^{0.2956z})$ where z is the Tm of the polymer as measured by DSC (2nd melt), and 3) wherein the Tm of the polymer is 155°C or greater.
42. The process of any of paragraphs 33 to 41 wherein the polymer is a propylene-alpha-olefin copolymer wherein the alpha-olefin is a C₄-C₂₀ alpha olefin and wherein the propylene-alpha-olefin copolymer contains as 20 mol% propylene or greater, with the lower limit of C₄-C₂₀ alpha-olefin being 1 mol%.
43. The process of the paragraph 42 wherein the alpha-olefin is a C₄-C₈ alpha-olefin, or mixtures thereof.
44. The process of 42 or 43 wherein the propylene-alpha-olefin copolymer has at least 50% isotactic triads as measured by ¹³C NMR.
45. An isotactic polypropylene polymer
- 1) Tm of 155°C or greater as measured by DSC (2nd melt),
 - 2) a mmmm pentad tacticity index of 90% or greater,
 - 3) a Mw of 50,000 g/mol or greater (as measured by GPC-DRI, relative to linear polystyrene standards),
 - 4) less than 35 total regio defects/10,000 monomer units and greater than 1 total regio defects/10,000 monomer units as measured by ¹³C-NMR.
46. The polymer of paragraph 45 wherein the polymer has less than 5 1,3-regio defects/10,000 monomer units as measured by ¹³C-NMR.
47. The polymer of paragraph 45 or 46 wherein the polymer has a percentage of total regio defects less than 30%.
48. The polymer of paragraph 45, 46 or 47 wherein the polymer has 1) total regio defects/10,000 monomer units of less than $-1.18 \times T_m + 210$, and 2) wherein the total regio defects is not less than 3 total regio defects/10,000 monomer units.
49. The polymer of any of paragraphs 45 to 48 wherein the polymer has greater than 0.05 unsaturated end-groups per 1000C as determined by ¹H NMR.
50. The polymer of any of paragraphs 45 to 49 wherein the polymer has 1) a Mw (GPC-DRI, relative to linear polystyrene standards) less than $(10^{-8})(e^{0.1962z})$ where z is the Tm (°C) of the polymer as measured by DSC (2nd melt) and 2) a Mw greater than $(2 \times 10^{-16})(e^{0.2956z})$ where z is the Tm of the polymer as measured by DSC (2nd melt), and 3) wherein the Tm of the polymer is 155°C or greater.
51. The polymer of any of paragraphs 45 to 50 wherein the Tm is 160°C or greater.
52. The polymer of any of paragraphs 45 to 51 wherein the Mw is 100,000 g/mol or greater.

53. The polymer of any of paragraphs 45 to 52 wherein the mmmm pentad tacticity index of 95% or greater.
54. An isotactic crystalline propylene polymer produced in a process comprising contacting in a homogeneous phase, propylene with a catalyst system comprising activator and a transition metal catalyst complex of a dianionic, tridentate ligand that features a central neutral heterocyclic Lewis base and two phenolate donors, where the tridentate ligand coordinates to the metal center to form two eight-membered rings.
55. The polymer of paragraph 54 wherein the polymer has a melting point of 120°C or higher.
56. The polymer of paragraph 54 or 55 wherein the polymer has a mmmm pentad tacticity index of 70% or greater.
57. The polymer of paragraph 54, 55, or 56 wherein the polymerization temperature is 70°C or higher.
58. The process of any paragraphs 45 to 57, wherein the propylene copolymer has a heat of fusion of greater than 100 J/g, preferably greater than 110 J/g.
59. The process of any paragraphs 1 to 44, further comprising obtaining a propylene copolymer having a heat of fusion of greater than 100 J/g, preferably greater than 110 J/g.
60. An isotactic crystalline propylene polymer produced by a polymerization process comprising contacting in a homogeneous phase propylene with a catalyst system comprising an activator and a group 4 bis(phenolate) catalyst compound, wherein the polymerization process takes place at a temperature of 90°C or higher, to produce a polymer with the following characteristics:
- a Mw (GPC-DRI, relative to linear polystyrene standards) less than $(10^{-8})(e^{0.1962z})$, where z is the T_m (°C) of the polymer as measured by DSC (2nd melt);
 - a Mw (GPC-DRI, relative to linear polystyrene standards) greater than $(2 \times 10^{-16})(e^{0.2956z})$ where z is the T_m (°C) of the polymer as measured by DSC (2nd melt).
61. The polymer of paragraph 60 wherein the T_m is 160°C or greater.
62. The polymer of paragraph 60 wherein the Mw is 100,000 g/mol or greater.
63. The polymer of paragraph 60 wherein the mmmm pentad tacticity index of 95% or greater.

Experimental

Starting materials

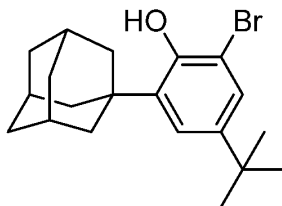
[0268] 4-Methylphenol (Merck), triphenylphosphine (Merck), 2-bromo-4-isopropylidobenzene (abcr GmbH), 2-bromopyridine (abcr GmbH), 2,6-dibromo-4-

- methoxypyridine (abcr GmbH), 2,6-dichloro-4-trifluoromethylpyridine (abcr GmbH), 3,5-dimethyladamantan-1-ol (abcr GmbH), 3,5-dimethyl-1-bromoadamantane (abcr GmbH), benzo[*b*]thiophene (Merck), N-bromosuccinimide (Merck), bis(pinacolato)diboron (Aldrich), cyclohexanone (Merck), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Aldrich),
- 5 2,6-dibromopyridine (Aldrich), 2-bromoiodobenzene (Acros), 2.5 M ⁿBuLi in hexanes (Acros), Pd(PPh₃)₄ (Aldrich), PdCl₂ (Aurat, Russia), RuCl₃ hydrate (Aurat, Russia), 1,1'-bis(di-*tert*-butylphosphino)ferrocene (Merck), methoxymethyl chloride (aka MOMCl, Aldrich), N-methylindole (Merck), N-(5-chloro-2-pyridyl)bis(trifluoromethanesulfonimide) (Aldrich), NaH, 60% wt. in mineral oil (Aldrich), ethyl acetate (Merck), methanol (Merck), toluene
- 10 (Merck), n-hexane (Merck), n-pentane (Merck), isopropanol (Merck), diethyl ether (Merck), acetonitrile (Merck), hexanes (Merck), carbon tetrachloride (Merck), 1,4-dioxane (Merck), dichloromethane (Merck), HfCl₄ (<0.05% Zr, Strem), ZrCl₄ (Merck), Cs₂CO₃ (Merck), sodium periodate (Merck), iodine (Merck), bromine (Merck), methanesulfonic acid (Merck), acetic acid (Aldrich), potassium *tert*-butoxide (Merck), sodium hydrocarbonate (Merck), sulfuric acid
- 15 98% (Merck), ammonia solution 28-30% (Merck), 12N HCl (Merck), K₂CO₃ (Merck), Na₂SO₄ (Akzo Nobel), silica gel 60, 40-63 μm (Merck), Celite 503 (Aldrich), CDCl₃ (Deutero GmbH) were used as received. Benzene-*d*₆ (Deutero GmbH) and dichloromethane-*d*₂ (Deutero GmbH) were dried over MS (mole sieves) 4A prior use. Tetrahydrofuran (aka THF, Merck), diethyl ether and 1,4-dioxane for organometallic synthesis were freshly distilled from sodium
- 20 benzophenone ketyl. Toluene, n-hexane, hexanes and n-pentane for organometallic synthesis were dried over MS 4A. 3% aqueous ammonia and 10% HCl were prepared from corresponding reagents via dilution with distilled water. Ethylaluminum dichloride (1.0M in hexane) and (trimethylsilyl)methylmagnesium chloride (1.0M in diethyl ether) were purchased from Sigma Aldrich.
- 25 **[0269]** 1-(*tert*-Butyl)-2-(methoxymethoxy)-5-methylbenzene was prepared as described in [*Chem. Commun.* **2015**, 51, pp. 16675-16678]. Tetrabenzylhafnium was prepared as described in [*J. Organomet. Chem.* **1972**, 36(1), pp. 87-92]. 2-(Adamantan-1-yl)-4-(*tert*-butyl)phenol was prepared from 4-*tert*-butylphenol (Merck) and adamantanol-1 (Aldrich) as described in [*Organic Letters*, **2015**, v.17(9), pp. 2242-2245]. 2-(Adamantan-1-yl)-4-methylphenol was
- 30 prepared as described in [*Angew. Chem., Int. Ed.*, **2002**, 41(16), pp. 3059-3061].
- [0270]** The 4-*tert*-butylbenzyl Grignard was made using a modified procedure from *Tetrahedron* 2019, v.75(32), pp. 4298-4306 using 4-*tert*-butylbenzyl bromide instead of benzyl bromide.

[0271] ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded with at least a 400 MHz spectrometer (such as a Bruker Avance-400 spectrometer) using 1–10% solutions in deuterated solvents. Chemical shifts for ^1H and ^{13}C are referenced to the residual ^1H or ^{13}C resonances of the deuterated solvents.

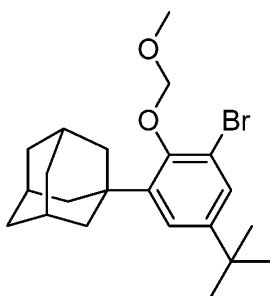
5 [0272] Transition metal complex 5 and complex 6 were prepared as follows:

[0273] **2-(Adamantan-1-yl)-6-bromo-4-(*tert*-butyl)phenol**



To a solution of 57.6 g (203 mmol) of 2-(adamantan-1-yl)-4-(*tert*-butyl)phenol in 400 mL of chloroform a solution of 10.4 mL (203 mmol) of bromine in 200 mL of chloroform was added dropwise for 30 minutes at room temperature. The resulting mixture was diluted with 400 mL of water. The obtained mixture was extracted with dichloromethane (3 x 100 mL), the combined organic extract was washed with 5% NaHCO_3 , dried over Na_2SO_4 , and then evaporated to dryness. Yield 71.6 g (97%) of a white solid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.32 (d, $J = 2.3$ Hz, 1 H), 7.19 (d, $J = 2.3$ Hz, 1 H), 5.65 (s, 1 H), 2.18 - 2.03 (m, 9 H), 1.78 (m, 6 H), 1.29 (s, 9 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.07, 143.75, 137.00, 126.04, 123.62, 112.11, 40.24, 37.67, 37.01, 34.46, 31.47, 29.03.

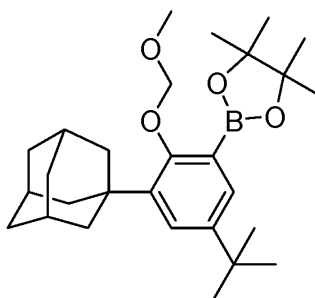
[0274] **(1-(3-Bromo-5-(*tert*-butyl)-2-(methoxymethoxy)phenyl)adamantane**



To a solution of 71.6 g (197 mmol) of 2-(adamantan-1-yl)-6-bromo-4-(*tert*-butyl)phenol in 1,000 mL of THF 8.28 g (207 mmol, 60% wt. in mineral oil) of sodium hydride was added portionwise at room temperature. To the resulting suspension 16.5 mL (217 mmol) of methoxymethyl chloride was added dropwise for 10 minutes at room temperature. The obtained mixture was stirred overnight, then poured into 1,000 mL of water. The obtained mixture was extracted with dichloromethane (3 x 300 mL), the combined organic extract was

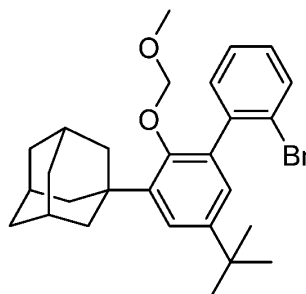
washed with 5% NaHCO₃, dried over Na₂SO₄ and then evaporated to dryness. Yield 80.3 g (~quant.) of a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.39 (d, J = 2.4 Hz, 1 H), 7.27 (d, J = 2.4 Hz, 1 H), 5.23 (s, 2 H), 3.71 (s, 3 H), 2.20 - 2.04 (m, 9 H), 1.82 - 1.74 (m, 6 H), 1.29 (s, 9 H). ¹³C NMR (CDCl₃, 100 MHz): δ 150.88, 147.47, 144.42, 128.46, 123.72, 117.46, 99.53, 57.74, 41.31, 38.05, 36.85, 34.58, 31.30, 29.08.

[0275] (2-(3-Adamantan-1-yl)-5-(tert-butyl)-2-(methoxymethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



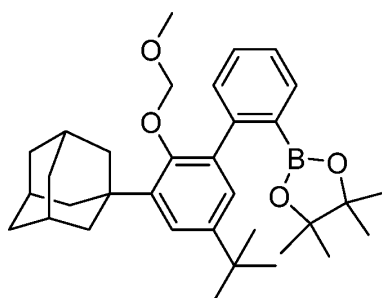
To a solution of 22.5 g (55.0 mmol) of (1-(3-bromo-5-(tert-butyl)-2-(methoxymethoxy)phenyl)adamantane in 300 mL of dry THF 23.2 mL (57.9 mmol, 2.5 M) of ⁿBuLi in hexanes was added dropwise for 20 minutes at -80°C. The reaction mixture was stirred at this temperature for 1 hour followed by addition of 14.5 mL (71.7 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred at room temperature for 1 hour, then poured into 300 mL of water. The obtained mixture was extracted with dichloromethane (3 x 300 mL), the combined organic extract was dried over Na₂SO₄, and then evaporated to dryness. Yield 25.0 g (~quant.) of a colorless viscous oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.54 (d, J = 2.5 Hz, 1 H), 7.43 (d, J = 2.6 Hz, 1 H), 5.18 (s, 2 H), 3.60 (s, 3 H), 2.24 - 2.13 (m, 6 H), 2.09 (br. s., 3 H), 1.85 - 1.75 (m, 6 H), 1.37 (s, 12 H), 1.33 (s, 9 H). ¹³C NMR (CDCl₃, 100 MHz): δ 159.64, 144.48, 140.55, 130.58, 127.47, 100.81, 83.48, 57.63, 41.24, 37.29, 37.05, 34.40, 31.50, 29.16, 24.79.

[0276] 1-(2'-Bromo-5-(tert-butyl)-2-(methoxymethoxy)-[1,1'-biphenyl]-3-yl)adamantane



To a solution of 25.0 g (55.0 mmol) of 2-(3-adamantan-1-yl)-5-(tert-butyl)-2-(methoxymethoxy)phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in 200 mL of dioxane 15.6 g (55.0 mmol) of 2-bromiodobenzene, 19.0 g (137 mmol) of potassium carbonate, and 100 mL of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 3.20 g (2.75 mmol) of $\text{Pd}(\text{PPh}_3)_4$. Thus obtained mixture was stirred for 12 hours at 100°C , then cooled to room temperature and diluted with 100 mL of water. The obtained mixture was extracted with dichloromethane (3 x 100 mL), the combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm , eluent: hexane-dichloromethane = 10:1, vol.). Yield 23.5 g (88%) of a white solid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (dd, J = 1.0, 8.0 Hz, 1 H), 7.42 (dd, J = 1.7, 7.6 Hz, 1 H), 7.37 - 7.32 (m, 2 H), 7.20 (dt, J = 1.8, 7.7 Hz, 1 H), 7.08 (d, J = 2.5 Hz, 1 H), 4.53 (d, J = 4.6 Hz, 1 H), 4.40 (d, J = 4.6 Hz, 1 H), 3.20 (s, 3 H), 2.23 - 2.14 (m, 6 H), 2.10 (br. s., 3 H), 1.86 - 1.70 (m, 6 H), 1.33 (s, 9 H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 151.28, 145.09, 142.09, 141.47, 133.90, 132.93, 132.41, 128.55, 127.06, 126.81, 124.18, 123.87, 98.83, 57.07, 41.31, 37.55, 37.01, 34.60, 31.49, 29.17.

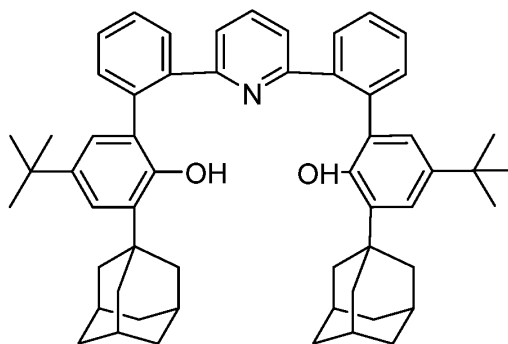
[0277] 2-(3'-(Adamantan-1-yl)-5'-(tert-butyl)-2'-(methoxymethoxy)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



To a solution of 30.0 g (62.1 mmol) of 1-(2'-bromo-5-(tert-butyl)-2-(methoxymethoxy)-[1,1'-biphenyl]-3-yl)adamantane in 500 mL of dry THF 25.6 mL (63.9 mmol, 2.5 M) of $n\text{BuLi}$ in

hexanes was added dropwise for 20 minutes at -80°C. The reaction mixture was stirred at this temperature for 1 hour followed by addition of 16.5 mL (80.7 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred at room temperature for 1 hour, then poured into 300 mL of water. The obtained mixture was extracted with dichloromethane (3 x 300 mL), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 32.9 g (~quant.) of a colorless glassy solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.75 (d, J = 7.3 Hz, 1 H), 7.44 - 7.36 (m, 1 H), 7.36 - 7.30 (m, 2 H), 7.30 - 7.26 (m, 1 H), 6.96 (d, J = 2.4 Hz, 1 H), 4.53 (d, J = 4.7 Hz, 1 H), 4.37 (d, J = 4.7 Hz, 1 H), 3.22 (s, 3 H), 2.26 - 2.14 (m, 6 H), 2.09 (br. s., 3 H), 1.85 - 1.71 (m, 6 H), 1.30 (s, 9 H), 1.15 (s, 6 H), 1.10 (s, 6 H). ¹³C NMR (CDCl₃, 100 MHz): δ 151.35, 146.48, 144.32, 141.26, 136.15, 134.38, 130.44, 129.78, 126.75, 126.04, 123.13, 98.60, 83.32, 57.08, 41.50, 37.51, 37.09, 34.49, 31.57, 29.26, 24.92, 24.21.

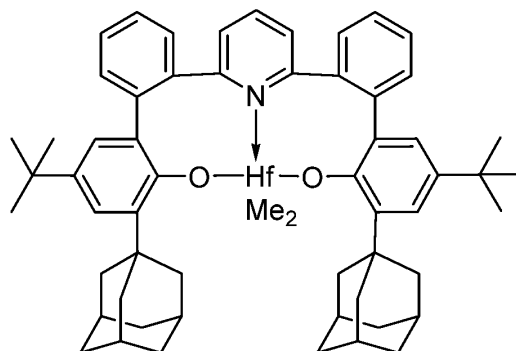
[0278] 2',2'''-(Pyridine-2,6-diyl)bis((3-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-ol) (QQ)



To a solution of 32.9 g (62.0 mmol) of 2-(3'-(adamantan-1-yl)-5'-(*tert*-butyl)-2'-(methoxymethoxy)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in 140 mL of dioxane 7.35 g (31.0 mmol) of 2,6-dibromopyridine, 50.5 g (155 mmol) of cesium carbonate and 70 mL of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 3.50 g (3.10 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature and diluted with 50 mL of water. The obtained mixture was extracted with dichloromethane (3 x 50 mL), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil 300 mL of THF, 300 mL of methanol, and 21 mL of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 500 mL of water. The obtained mixture was extracted with dichloromethane (3 x 350 mL), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. The residue

was purified by flash chromatography on silica gel 60 (40-63 μ m, eluent: hexane-ethyl acetate = 10:1, vol.). The obtained glassy solid was triturated with 70 mL of n-pentane, the precipitate obtained was filtered off, washed with 2 x 20 mL of n-pentane, and dried *in vacuo*. Yield 21.5 g (87%) of a mixture of two isomers as a white powder. ^1H NMR (CDCl_3 , 400 MHz): δ 8.10 + 6.59 (2s, 2H), 7.53 – 7.38 (m, 10H), 7.09 + 7.08 (2d, J = 2.4 Hz, 2H), 7.04 + 6.97 (2d, J = 7.8 Hz, 2H), 6.95 + 6.54 (2d, J = 2.4 Hz), 2.03 – 1.79 (m, 18H), 1.74 – 1.59 (m, 12H), 1.16 + 1.01 (2s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz, minor isomer shifts labeled with *): δ 157.86, 157.72*, 150.01, 149.23*, 141.82*, 141.77, 139.65*, 139.42, 137.92, 137.43, 137.32*, 136.80, 136.67*, 136.29*, 131.98*, 131.72, 130.81, 130.37*, 129.80, 129.09*, 128.91, 128.81*, 127.82*, 127.67, 126.40, 125.65*, 122.99*, 122.78, 122.47, 122.07*, 40.48, 40.37*, 37.04, 36.89*, 34.19*, 34.01, 31.47, 29.12, 29.07*.

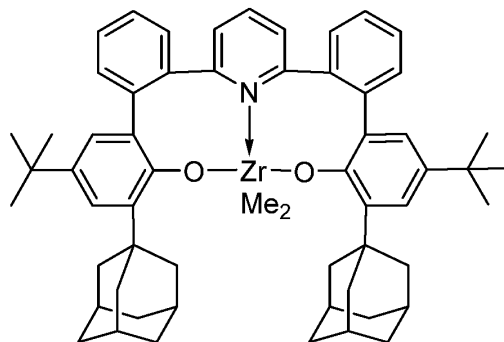
[0279] Dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis((3-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-olate))] (Complex 5)



To a suspension of 3.22 g (10.05 mmol) of hafnium tetrachloride (<0.05% Zr) in 250 mL of dry toluene 14.6 mL (42.2 mmol, 2.9 M) of MeMgBr in diethyl ether was added in one portion via syringe at 0°C. The resulting suspension was stirred for 1 minute, and 8.00 g (10.05 mmol) of 2',2'''-(pyridine-2,6-diyl)bis((3-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-ol) was added portion-wise for 1 minute. The reaction mixture was stirred for 36 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 100 mL of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 50 mL of n-hexane, the obtained precipitate was filtered off (G3), washed with 20 mL of n-hexane (2 x 20 mL), and then dried *in vacuo*. Yield 6.66 g (61%, ~1:1 solvate with n-hexane) of a light-beige solid. Anal. Calc. for $\text{C}_{59}\text{H}_{69}\text{HfNO}_2 \times 1.0(\text{C}_6\text{H}_{14})$: C, 71.70; H, 7.68; N, 1.29. Found: C 71.95; H, 7.83; N 1.18. ^1H NMR (C_6D_6 , 400 MHz): δ 7.58 (d, J = 2.6 Hz, 2 H), 7.22 - 7.17 (m, 2 H), 7.14 - 7.08 (m, 4 H), 7.07 (d, J = 2.5 Hz, 2 H), 7.00 - 6.96 (m, 2 H), 6.48 - 6.33

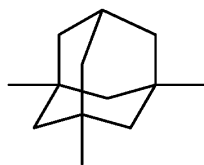
(m, 3 H), 2.62 - 2.51 (m, 6H), 2.47 - 2.35 (m, 6H), 2.19 (br.s, 6H), 2.06 - 1.95 (m, 6H), 1.92 - 1.78 (m, 6H), 1.34 (s, 18 H), -0.12 (s, 6 H). ^{13}C NMR (C_6D_6 , 100 MHz): δ 159.74, 157.86, 143.93, 140.49, 139.57, 138.58, 133.87, 133.00, 132.61, 131.60, 131.44, 127.98, 125.71, 124.99, 124.73, 51.09, 41.95, 38.49, 37.86, 34.79, 32.35, 30.03.

5 **[0280] Dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis((3-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-olate))] (Complex 6)**



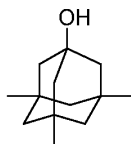
To a suspension of 2.92 g (12.56 mmol) of zirconium tetrachloride in 300 mL of dry toluene 18.2 mL (52.7 mmol, 2.9 M) of MeMgBr in diethyl ether was added in one portion via syringe
 10 at 0°C. To the resulting suspension 10.00 g (12.56 mmol) of 2',2'''-(pyridine-2,6-diyl)bis((3-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-ol)) was immediately added in one portion. The reaction mixture was stirred for 2 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 100 mL of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated
 15 to dryness. The residue was triturated with 50 mL of n-hexane, the obtained precipitate was filtered off (G3), washed with n-hexane (2 x 20 mL), and then dried *in vacuo*. Yield 8.95 g (74%, ~1:0.5 solvate with n-hexane) of a beige solid. Anal. Calc. for $\text{C}_{59}\text{H}_{69}\text{ZrNO}_2 \times 0.5(\text{C}_6\text{H}_{14})$: C, 77.69; H, 7.99; N, 1.46. Found: C 77.90; H, 8.15; N 1.36. ^1H NMR (C_6D_6 , 400 MHz): δ 7.56 (d, J = 2.6 Hz, 2 H), 7.20 - 7.17 (m, 2 H), 7.14 - 7.07
 20 (m, 4 H), 7.07 (d, J = 2.5 Hz, 2 H), 6.98 - 6.94 (m, 2 H), 6.52 - 6.34 (m, 3 H), 2.65 - 2.51 (m, 6H), 2.49 - 2.36 (m, 6H), 2.19 (br.s., 6H), 2.07 - 1.93 (m, 6H), 1.92 - 1.78 (m, 6H), 1.34 (s, 18 H), 0.09 (s, 6 H). ^{13}C NMR (C_6D_6 , 100 MHz): δ 159.20, 158.22, 143.79, 140.60, 139.55, 138.05, 133.77, 133.38, 133.04, 131.49, 131.32, 127.94, 125.78, 124.65, 124.52, 42.87, 41.99, 38.58, 37.86, 34.82, 32.34, 30.04.

25 **[0281] (1*s*,3*s*,5*s*)-1,3,5-Trimethyladamantane (A)**



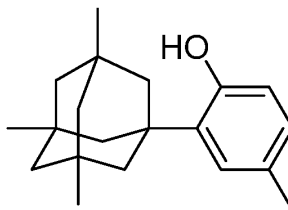
In a Parr pressure reactor, to a solution of 15.0 g (62.0 mmol) of 3,5-dimethyl-1-bromoadamantane in 80 ml of diethyl ether, 22.3 ml (64.0 mmol, 2.9 M) of MeMgBr in diethyl ether was added in one portion. The resulting solution was heated to 105°C and stirred
 5 overnight at this temperature. After that, the reactor was cooled to room temperature, and pressure was released. Further on, 100 ml of 10% HCl was carefully added. The obtained mixture was extracted with diethyl ether (3 x 30 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 11.3 g (99%) of a colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 1.98 – 2.03 (m, 1H), 1.25 – 1.28 (m, 6H), 1.00 – 1.12 (m, 6H), 0.78
 10 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 51.1, 43.2, 31.4, 30.7, 30.0.

[0282] (3*s*,5*s*,7*s*)-3,5,7-Trimethyladamantan-1-ol (B)



To a solution of 11.3 g (62.0 mmol) of (1*s*,3*s*,5*s*)-1,3,5-trimethyladamantane (A) in 70 ml of acetonitrile, 103 ml of water, 70 ml of carbon tetrachloride, 55.0 g (255 mmol) of sodium
 15 periodate, and 330 mg (1.28 mmol) of ruthenium(III) chloride (hydrate) were added. The resulting suspension was stirred for 12 hours at 60°C, then cooled to room temperature, and diluted with 50 ml of water. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified using Kugelrohr apparatus (1 mbar, 100°C). Yield 12.1 g
 20 (96%) of a white crystalline solid. ¹H NMR (CDCl₃, 400 MHz): δ 1.44 (br.s, 1H), 1.30 (s, 6H), 0.97 – 1.15 (m, 6H), 0.88 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 70.5, 50.7, 49.8, 34.1, 29.5.

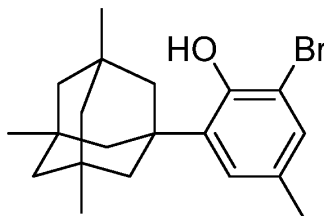
[0283] 4-Methyl-2-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)phenol (C)



To a solution of 20.8 g (192 mmol) of 4-methylphenol and 18.7 g (96.3 mmol) of (3*s*,5*s*,7*s*)-3,5,7-trimethyladamantan-1-ol (B) in 100 ml of dichloromethane, 5.8 ml of 97% sulfuric acid was added dropwise for 30 minutes at room temperature. The resulting mixture was stirred for 30 minutes at room temperature and then carefully poured into 300 ml of 3% aqueous ammonia.

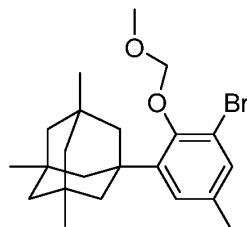
- 5 The crude product was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified using Kugelrohr apparatus (0.3 mbar, 160°C) yielding 23.1 g (84%) of the title product as a white crystalline solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.04 (d, J = 2.1 Hz, 1H), 6.86 (ddd, J = 7.9, 2.2, 0.6 Hz, 1H), 6.55 (d, J = 7.9 Hz), 4.52 (s, 1H), 2.29 (s, 3H), 1.67 (s, 6H), 1.10 – 1.18 (m, 6H), 0.90 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 151.9, 135.2, 129.7, 127.7, 127.0, 116.6, 10
- 50.4, 46.1, 39.1, 32.1, 30.6, 20.9.

[0284] 2-Bromo-4-methyl-6-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)phenol (D)



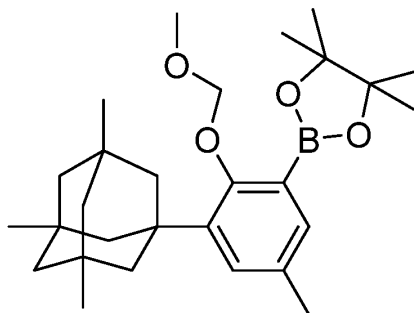
- To a solution of 8.97 g (31.5 mmol) of 4-methyl-2-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)phenol (C) in 90 ml of dichloromethane, 5.04 g (31.5 mmol) of bromine was added dropwise at room temperature. The resulting mixture was stirred for 12 hours at room temperature and then carefully poured into 200 ml of 5% NaHCO₃. The crude product was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 11.4 g (99%) of a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.17 (d, J = 2.0 Hz, 1H), 6.99 (d, J = 2.0 Hz, 1H), 5.65 (s, 1H), 2.28 (s, 3H), 1.67 (s, 6H), 1.10 – 1.21 (m, 6H), 0.91 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 148.1, 136.5, 130.3, 129.4, 127.3, 112.1, 50.3, 45.8, 39.9, 32.1, 30.5, 20.6.
- 15
- 20

[0285] (3*r*,5*r*,7*r*)-1-(3-Bromo-2-(methoxymethoxy)-5-methylphenyl)-3,5,7-trimethyladamantane (E)



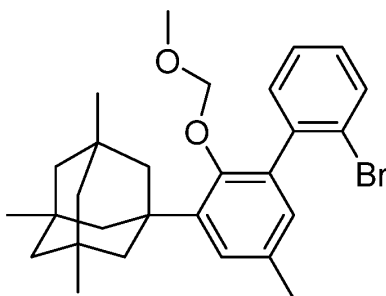
To a solution of 11.4 g (31.4 mmol) of 2-bromo-4-methyl-6-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)phenol (D) in 100 ml of dry THF, 1.06 g (34.9 mmol, 60% wt. (in mineral oil) sodium hydride was added at room temperature. After that, 2.65 ml (34.9 mmol) of MOMCl was added in one portion. The reaction mixture was heated for 24 hours at 60°C and then poured into 130 ml of cold water. The crude product was extracted with 3 x 20 ml of dichloromethane. The combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 11.9 g (91%) of a yellowish solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.25 (d, J = 2.0 Hz, 1H), 7.06 (d, J = 2.0 Hz, 1H), 5.23 (s, 2H), 3.71 (s, 3H), 2.29 (s, 3H), 1.68 (s, 6H), 1.10 – 1.21 (m, 6H), 0.92 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 151.3, 144.0, 134.4, 131.9, 127.4, 117.6, 99.9, 57.8, 50.2, 46.8, 40.3, 32.2, 30.6, 20.7.

[0286] 2-(2-(Methoxymethoxy)-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (F)



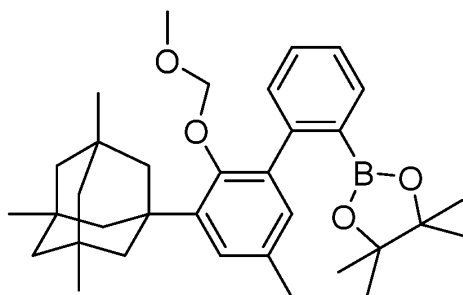
To a solution of 12.4 g (30.5 mmol) of (3*r*,5*r*,7*r*)-1-(3-bromo-2-(methoxymethoxy)-5-methylphenyl)-3,5,7-trimethyladamantane (E) in 200 ml of dry THF, 14.6 ml (30.5 mmol) of 2.5 M ⁿBuLi in hexanes was added dropwise for 20 minutes at -80°C. The reaction mixture was stirred at this temperature for 1 hour followed by addition of 9.33 ml (45.7 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 130 ml of water. The crude product was extracted with dichloromethane (3 x 40 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 12.9 g (93%) of a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.39 (d, J = 1.9 Hz, 1H), 7.22 (d, J = 1.9 Hz, 1H), 5.16 (s, 2H), 3.61 (s, 3H), 2.31 (s, 3H), 1.72 (s, 6H), 1.38 (s, 12H), 1.09 – 1.18 (m, 6H), 0.90 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 159.8, 140.4, 134.7, 131.6, 131.2, 101.2, 83.6, 57.9, 50.4, 46.7, 39.5, 32.2, 30.6, 24.74, 20.8.

[0287] (3*r*,5*r*,7*r*)-1-(2'-Bromo-2-(methoxymethoxy)-5-methyl-[1,1'-biphenyl]-3-yl)-3,5,7-trimethyladamantane (G)



To a solution of 4.50 g (9.90 mmol) of 2-(2-(methoxymethoxy)-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (F) in 20 ml of 1,4-dioxane, 2.80 g (9.90 mmol) of 2-bromoiodobenzene, 3.42 g (24.8 mmol) of potassium carbonate, and 10 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 286 mg (0.25 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 105°C, then cooled to room temperature, and diluted with 100 ml of water. The crude product was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μ m, eluent: hexane-dichloromethane = 10:1, vol.). Yield 3.90 g (82%) of a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.73 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.38 – 7.46 (m, 2H), 7.24 – 7.28 (m, 1H), 7.23 (d, *J* = 1.6 Hz, 1H), 6.97 (d, *J* = 1.6 Hz, 1H), 4.56 – 4.58 (m, 1H), 4.47 – 4.48 (m, 1H), 3.31 (s, 3H), 2.41 (s, 3H), 1.80 (s, 6H), 1.17 – 1.29 (m, 6H), 0.98 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 151.9, 141.8, 141.1, 134.5, 132.9, 132.2, 132.0, 130.0, 128.6, 127.8, 127.1, 124.0, 99.1, 57.1, 50.3, 46.8, 39.8, 32.2, 30.7, 21.1.

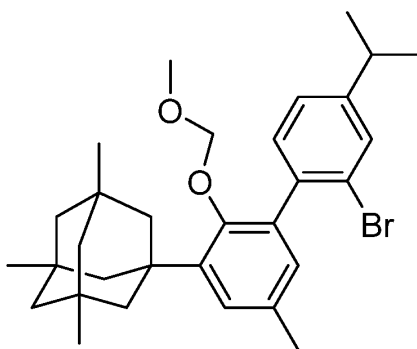
[0288] 2-(2'-(Methoxymethoxy)-5'-methyl-3'-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (H)



To a solution of 3.80 g (7.86 mmol) of (3*r*,5*r*,7*r*)-1-(2'-bromo-5-methyl-2-(methoxymethoxy)-[1,1'-biphenyl]-3-yl)-3,5,7-trimethyladamantane (G) in 40 ml of dry THF, 4.10 ml (10.2 mmol) of 2.5 M ^{*n*}BuLi in hexanes was added dropwise for 20 minutes at -80°C. The reaction mixture

was stirred for 1 hour at this temperature followed by an addition of 2.57 ml (12.6 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 100 ml of water. The crude product was extracted with dichloromethane (3 x 100 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane-diethyl ether = 10:1, vol.). Yield 3.71 g (90%) of a colorless glassy solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.78 (dd, J = 7.4, 1.0 Hz, 1H), 7.32 – 7.45 (m, 3H), 7.11 (d, J = 1.9 Hz, 1H), 6.89 (d, J = 1.9 Hz, 1H), 4.41 – 4.48 (m, 2H), 3.32 (s, 3H), 2.33 (s, 3H), 1.79 (br.s, 6H), 1.13 – 1.25 (m, 18H), 0.94 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ 151.9, 145.6, 141.1, 136.6, 134.4, 131.5, 130.5, 130.3, 129.9, 126.7, 126.1, 98.9, 83.4, 57.2, 50.4, 47.0, 39.7, 32.2, 30.7, 25.2, 24.8, 24.1, 21.0.

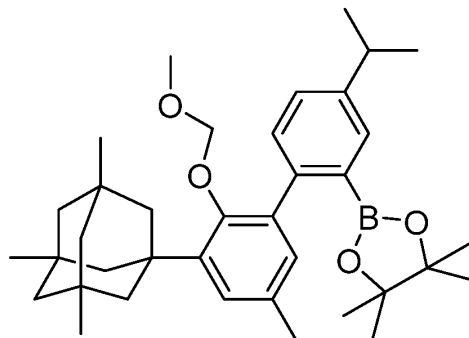
[0289] (3*r*,5*r*,7*r*)-1-(2'-Bromo-4'-isopropyl-2-(methoxymethoxy)-5-methyl-[1,1'-biphenyl]-3-yl)-3,5,7-trimethyladamantane (I)



To a solution of 4.64 g (10.2 mmol) of 2-(2-(methoxymethoxy)-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (F) in 20 ml of 1,4-dioxane, 3.32 g (10.2 mmol) of 2-bromo-4-isopropyl iodobenzene, 3.53 g (25.5 mmol) of potassium carbonate, and 10 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 295 mg (0.255 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 105°C, then cooled to room temperature, and diluted with 100 ml of water. The crude product was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane-dichloromethane = 10:1, vol.). Yield 4.37 g (81%) of a yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.56 (d, J = 1.5 Hz, 1H), 7.31 – 7.39 (m, 2H), 7.20 – 7.26 (m, 1H), 7.18 (d, J = 2.0 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 4.43 – 4.54 (m, 2H), 3.26 (s, 3H), 2.96 (sept, J = 6.9 Hz, 1H), 2.37 (s, 3H), 1.76 (s, 6H), 1.32 (d, J = 6.9 Hz, 6H), 1.14 – 1.24 (m, 6H), 0.95

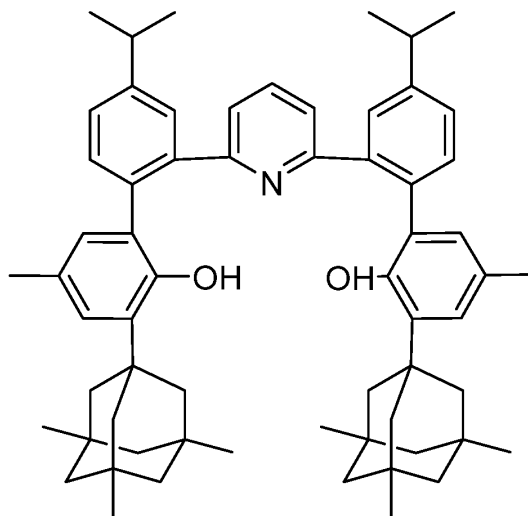
(s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 152.0, 149.9, 141.8, 138.4, 134.5, 132.1, 132.0, 130.7, 130.2, 127.6, 125.4, 123.8, 99.0, 57.0, 50.4, 46.8, 39.8, 33.6, 32.2, 30.7, 23.91, 23.88, 21.0.

[0290] 2-(4-Isopropyl-2'-(methoxymethoxy)-5'-methyl-3'-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (J)



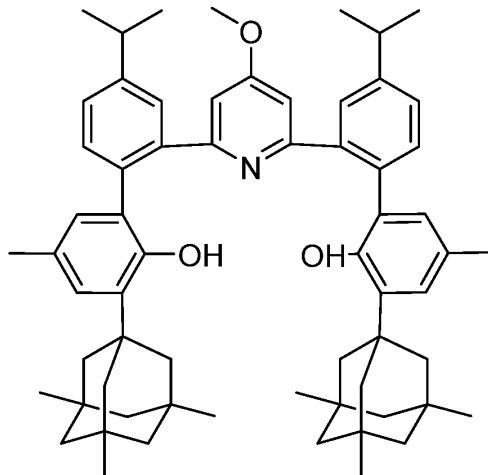
5 To a solution of 4.37 g (8.30 mmol) of (3*r*,5*r*,7*r*)-1-(2'-bromo-4'-isopropyl-2-(methoxymethoxy)-5-methyl-[1,1'-biphenyl]-3-yl)-3,5,7-trimethyladamantane (I) in 50 ml of dry THF 4.32 ml (10.8 mmol) of 2.5 M $n\text{BuLi}$ in hexanes was added dropwise for 20 minutes at -80°C . The reaction mixture was stirred for 1 hour at this temperature followed by an addition of 2.71 ml (13.3 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 100 ml of water. The crude product was extracted with dichloromethane (3 x 100 ml), the combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm , eluent: hexane-diethyl ether = 10:1, vol.). Yield 4.32 g (91%) of a colorless glassy solid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.61 (s, 1H), 7.29 – 7.37 (m, 2H), 7.08 (d, $J = 2.0$ Hz, 1H), 6.88 (d, $J = 2.0$ Hz, 1H), 4.40 – 4.47 (m, 2H), 3.30 (s, 3H), 2.99 (sept, $J = 6.9$ Hz, 1H), 2.32 (s, 3H), 1.78 (br.s, 6H), 1.32 (d, $J = 6.9$ Hz, 6H), 1.12 – 1.29 (m, 18H), 0.93 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 152.0, 146.5, 143.1, 141.0, 136.7, 132.5, 131.4, 130.6, 130.3, 127.8, 126.5, 98.9, 83.3, 57.2, 50.4, 47.0, 39.7, 33.8, 32.2, 30.7, 25.2, 24.8, 24.1, 24.0, 21.0.

[0291] 2',2'''-(Pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3'-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (K)



To a solution of 1.50 g (2.62 mmol) of 2-(4-isopropyl-2'-(methoxymethoxy)-5'-methyl-3'-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (J) in 7 ml of 1,4-dioxane, 310 mg (1.31 mmol) of 2,6-dibromopyridine, 2.13 g (6.55 mmol) of cesium carbonate, and 4 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 151 mg (0.131 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature, and diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil, 20 ml of THF, 20 ml of methanol, and 2 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 200 ml of water. The crude product was extracted with dichloromethane (3 x 70 ml), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μ m, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 770 mg (67%) of a mixture of two isomers as a white foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.24 – 7.40 (m, 7H), 7.06 (s, 1H), 6.88 – 6.96 (m, 6H), 6.37 (d, J = 1.6 Hz, 1H), 2.97 – 3.06 (m, 2H), 2.29 + 2.03 (2s, 6H), 1.24 – 1.53 (m, 24H), 0.88 – 1.07 (m, 12H), 0.78 + 0.68 (2s, 18H). ¹³C NMR (CDCl₃, 100 MHz) δ 158.4, 158.3, 150.1, 149.4, 148.7, 148.4, 140.0, 138.9, 136.5, 136.47, 136.4, 134.2, 134.1, 133.8, 133.6, 132.5, 131.3, 130.0, 129.5, 129.04, 129.01, 128.97, 128.73, 128.69, 128.5, 128.44, 128.36, 127.5, 127.2, 126.9, 126.6, 122.4, 122.1, 50.5, 50.2, 46.0, 45.9, 39.3, 39.1, 33.9, 33.88, 32.0, 31.9, 30.7, 30.5, 24.12, 24.07, 24.04, 23.96, 21.1, 20.6.

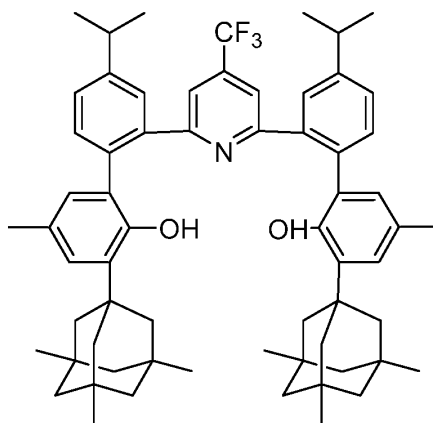
[0292] 2',2'''-(4-Methoxypyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (L)



To a solution of 1.50 g (2.62 mmol) of 2-(4-isopropyl-2'-(methoxymethoxy)-5'-methyl-3'-
 5 ((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-
 dioxaborolane (J) in 7 ml of 1,4-dioxane, 350 mg (1.31 mmol) of 2,6-dibromo-4-
 methoxypyridine, 2.13 g (6.55 mmol) of cesium carbonate, and 4 ml of water were
 subsequently added. The mixture obtained was purged with argon for 10 minutes followed by
 addition of 151 mg (0.131 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C,
 10 then cooled to room temperature, and diluted with 50 ml of water. Thus obtained mixture was
 extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over
 Na₂SO₄ and then evaporated to dryness. To the resulting oil, 20 ml of THF, 20 ml of methanol,
 and 2 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at
 60°C and then poured into 200 ml of water. The crude product was extracted with
 15 dichloromethane (3 x 70 ml), the combined organic extract was washed with 5% NaHCO₃,
 dried over Na₂SO₄, and then evaporated to dryness. The residue was purified by flash
 chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate = 10:1, vol.). Yield
 930 mg (78%) of a mixture of two isomers as a white foam. ¹H NMR (CDCl₃, 400 MHz):
 δ 7.25 – 7.50 (m, 8H), 6.93 – 6.98 + 6.37 – 6.51 (2m, 6H), 3.36 + 3.50 (2s, 3H), 3.01 – 3.08
 20 (m, 2H), 2.06 + 2.31 (2s, 6H), 1.25 – 1.60 (m, 24H), 0.91 – 1.11 (m, 12H), 0.80 + 0.70
 (2s, 18H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.63, 159.83, 159.64, 150.15, 149.57, 148.61,
 148.36, 139.91, 138.70, 136.68, 136.63, 134.29, 134.27, 132.46, 131.32, 130.37, 129.84,
 129.09, 129.04, 128.71, 128.45, 128.39, 127.63, 127.21, 126.82, 126.59, 108.71, 108.38, 55.08,

54.61, 50.42, 50.17, 46.18, 45.84, 39.34, 39.11, 33.89, 33.87, 32.02, 31.86, 30.69, 30.46, 24.10, 24.06, 23.94, 21.06, 20.59.

[0293] 2',2'''-(4-Trifluoromethylpyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (M)



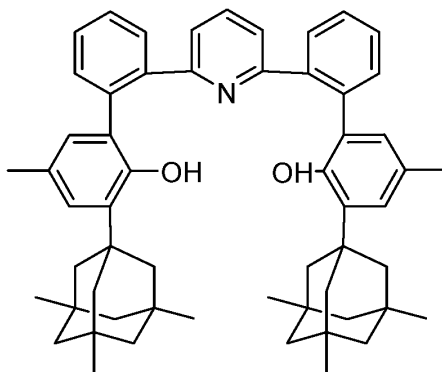
5

To a solution of 1.50 g (2.62 mmol) of 2-(4-isopropyl-2'-(methoxymethoxy)-5'-methyl-3'-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (J) in 7 ml of 1,4-dioxane, 283 mg (1.31 mmol) of 2,6-dichloro-4-trifluoromethylpyridine, 2.13 g (6.55 mmol) of cesium carbonate, and 4 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 151 mg (0.131 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature, and diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil, 20 ml of THF, 20 ml of methanol, and 2 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 200 ml of water. The crude product was extracted with dichloromethane (3 x 70 ml), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 930 mg (78%) of a mixture of two isomers as a light-yellow foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.32 – 7.46 (m, 7H), 7.07 – 7.12 (m, 2H), 6.93 – 7.00 (m, 3H), 6.47 + 6.23 + 5.88 (3m, 2H), 3.00 – 3.08 (m, 2H), 2.10 + 2.31 (2s, 6H), 1.27 – 1.56 (m, 24H), 0.90 – 1.09 (m, 12H), 0.79 + 0.73 (2s, 18H). ¹³C NMR (CDCl₃, 100 MHz) δ 159.59, 159.49, 149.54, 149.24, 149.00, 148.78, 139.14, 138.36, 136.34, 136.13, 133.90, 133.82, 133.76, 133.62, 132.36, 131.46, 129.22, 128.86, 128.84, 128.75, 128.71, 128.69, 128.66, 128.57, 128.51, 128.44,

10
15
20
25

128.37, 127.98, 127.77, 127.25, 127.03, 117.95, 117.66, 50.41, 50.22, 45.94, 45.74, 39.26, 39.07, 33.96, 33.93, 32.01, 31.89, 30.61, 30.46, 24.09, 24.04, 24.00, 23.97, 20.98, 20.60.

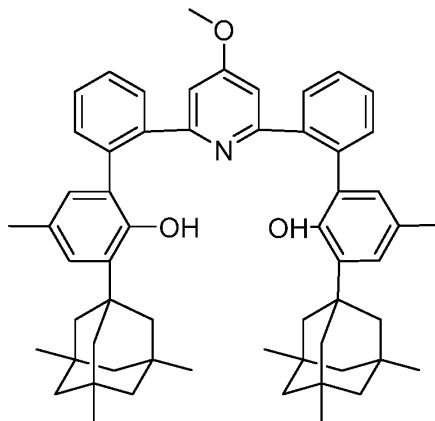
[0294] 2',2'''-(Pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (N)



5

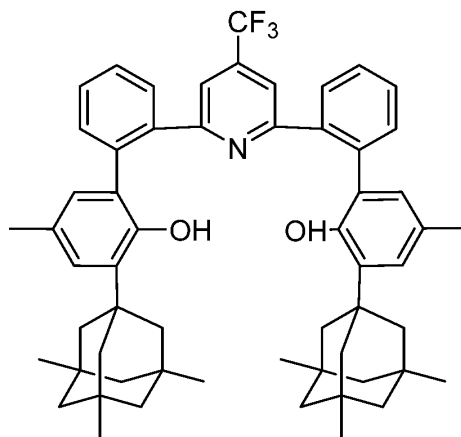
To a solution of 1.20 g (2.26 mmol) of 2-(2'-(methoxymethoxy)-5'-methyl-3'-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (H) in 7 ml of 1,4-dioxane, 241 mg (1.01 mmol) of 2,6-dibromopyridine, 1.84 g (6.55 mmol) of cesium carbonate, and 4 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 131 mg (0.113 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature, and diluted with 50 ml of water. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil, 20 ml of THF, 20 ml of methanol, and 2 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 200 ml of water. The crude product was extracted with dichloromethane (3 x 70 ml), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μ m, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 660 mg (82%) of a mixture of two isomers as a white foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.46- 7.51 (m, 6H), 7.34 – 7.40 (m, 3H), 6.89 – 6.98 (m, 5H), 6.47 – 6.60 (m, 3H), 2.12 + 2.30 (2s, 6H), 1.28 – 1.51 (m, 12H), 0.91 – 1.07 (m, 12H), 0.73 + 0.81 (2s, 18H). ¹³C NMR (CDCl₃, 100 MHz) δ 157.99, 157.84, 149.66, 149.12, 140.14, 139.26, 136.59, 136.53, 136.47, 136.39, 136.28, 136.22, 132.26, 131.43, 130.68, 130.25, 129.62, 129.49, 129.32, 129.09, 128.85, 128.81, 128.63, 128.51, 128.06, 128.03, 127.04, 126.81, 122.29, 121.99, 50.43, 50.22, 46.02, 45.88, 39.31, 39.14, 32.12, 32.04, 31.91, 30.68, 30.58, 30.50, 21.03, 20.67.

[0295] 2',2'''-(4-Methoxypyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (O)



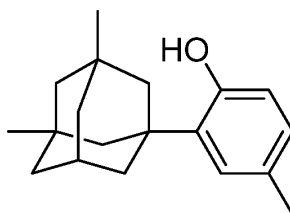
To a solution of 1.20 g (2.26 mmol) of 2-(2'-(methoxymethoxy)-5'-methyl-3'-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (H) in 7 ml of 1,4-dioxane, 272 mg (1.01 mmol) of 2,6-dibromo-4-methoxypyridine, 1.84 g (6.55 mmol) of cesium carbonate, and 4 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 131 mg (0.113 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature, and diluted with 50 ml of water. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil, 20 ml of THF, 20 ml of methanol, and 2 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 200 ml of water. The crude product was extracted with dichloromethane (3 x 70 ml), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 680 mg (80%) of a mixture of two isomers as a white foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.44 – 7.56 (m, 6H), 7.34 – 7.40 (m, 2H), 6.90 – 7.05 (m, 5H), 6.44 – 6.50 (m, 3H), 3.37 + 3.47 (2s, 3H), 2.11 + 2.30 (2s, 6H), 1.29 – 1.74 (m, 12H), 0.91 – 1.18 (m, 12H), 0.72 + 0.80 (2s, 18H). ¹³C NMR (CDCl₃, 100 MHz) δ 165.71, 165.62, 159.37, 159.22, 149.80, 149.35, 139.99, 138.99, 136.77, 136.74, 136.62, 136.59, 132.27, 131.43, 130.44, 130.15, 130.09, 129.71, 129.60, 129.12, 128.84, 128.72, 128.58, 127.96, 126.99, 126.81, 108.73, 108.35, 55.01, 54.66, 50.41, 50.19, 46.15, 46.03, 45.88, 39.36, 39.17, 32.12, 32.03, 31.89, 30.69, 30.58, 30.48, 21.02, 20.67.

[0296] 2',2'''-(4-Trifluoromethylpyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (P)



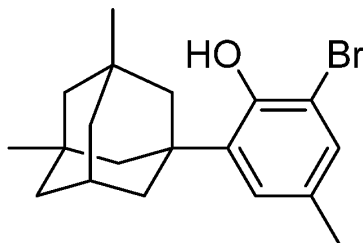
To a solution of 1.20 g (2.26 mmol) of 2-(2'-(methoxymethoxy)-5'-methyl-3'-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (H) in 7 ml of 1,4-dioxane, 220 mg (1.01 mmol) of 2,6-dichloro-4-trifluoromethylpyridine, 1.84 g (6.55 mmol) of cesium carbonate, and 4 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 131 mg (0.113 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature, and diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil 20 ml of THF, 20 ml of methanol, and 2 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 200 ml of water. The crude product was extracted with dichloromethane (3 x 70 ml), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 802 mg (93%) of a mixture of two isomers as a light-yellow foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.43 – 7.56 (m, 8H), 7.09 – 7.11 (m, 2H), 6.97 – 7.01 (m, 2H), 6.57 + 6.92 (m, 2H), 5.57 + 5.72 (2s, 2H), 2.17 + 2.32 (2s, 6H), 1.28 – 1.54 (m, 12H), 0.90 – 1.12 (m, 12H), 0.77 + 0.82 (2s, 18H). ¹³C NMR (CDCl₃, 100 MHz) δ 159.12, 159.02, 149.14, 148.61, 139.31, 138.78, 136.26, 136.21, 136.18, 136.10, 132.02, 131.48, 130.59, 130.37, 130.06, 129.81, 129.33, 129.04, 128.47, 128.40, 128.33, 128.19, 127.37, 127.24, 117.81, 117.48, 50.39, 50.25, 45.92, 45.75, 39.27, 39.13, 32.02, 31.93, 30.59, 30.47, 20.90, 20.66.

[0297] 2-((1*r*,3*R*,5*S*,7*r*)-3,5-Dimethyladamantan-1-yl)-4-methylphenol (Q)



To a solution of 8.10 g (75.0 mmol) of 4-methylphenol and 13.5 g (75.0 mmol) of 3,5-dimethyladamantan-1-ol in 150 ml of dichloromethane, a solution of 4.90 ml (75.0 mmol) of methanesulfonic acid and 5 ml of acetic acid in 100 ml of dichloromethane was added dropwise for 1 hour at room temperature. The resulting mixture was stirred at room temperature for 12 hours and then carefully poured into 300 ml of 5% NaHCO₃. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified using Kugelrohr apparatus (1 mbar, 70°C) yielding 14.2 g (70%) of a product as a light-yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.02 (s, 1H), 6.86 (dd, J = 8.0, 1.5 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 4.61 (s, 1H), 2.27 (s, 3H), 2.14 – 2.19 (m, 1H), 1.95 (br.s, 2H), 1.65 – 1.80 (m, 4H), 1.34 – 1.48 (m, 4H), 1.21 (br.s, 2H), 0.88 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 152.0, 135.5, 129.7, 127.7, 127.0, 116.6, 51.1, 46.8, 43.2, 39.0, 38.3, 31.4, 30.9, 30.0, 20.8.

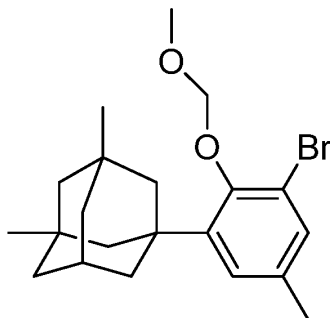
[0298] 2-Bromo-6-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-methylphenol (R)



To a solution of 14.2 g (52.5 mmol) of 2-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-methylphenol (Q) in 200 ml of dichloromethane, a solution of 2.70 ml (52.5 mmol) of bromine in 100 ml of dichloromethane was added dropwise for 1 hour at room temperature. The resulting mixture was stirred at room temperature for 12 hours and then carefully poured into 200 ml of 5% NaHCO₃. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 17.0 g (92%) of a light-yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.16 (d, J = 2.0 Hz, 1H), 6.97 (d, J = 1.8 Hz, 1H), 5.64 (s, 1H), 2.27 (s, 3H), 2.14 – 2.20 (m, 1H), 1.94 (br.s, 2H), 1.67 – 1.79 (m, 4H), 1.35 – 1.47 (m, 4H), 1.21 (br.s, 2H), 0.88 (s, 6H). ¹³C NMR (CDCl₃, 100

MHz): δ 148.2, 136.8, 130.3, 129.4, 127.3, 112.1, 51.0, 46.4, 43.1, 39.1, 38.7, 31.4, 30.9, 30.0, 20.6.

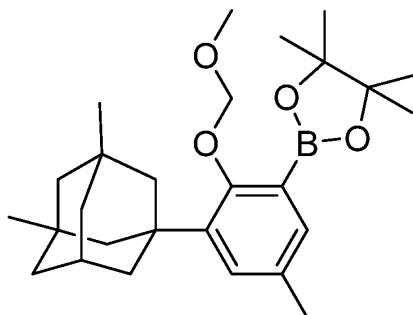
[0299] (1*r*,3*R*,5*S*,7*r*)-1-(3-Bromo-2-(methoxymethoxy)-5-methylphenyl)-3,5-dimethyladamantane (S)



5

To a solution of 17.0 g (48.7 mmol) of 2-bromo-6-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-methylphenol (R) in 200 ml of dry THF, 1.95 g (50.0 mmol, 60% wt. in mineral oil) of sodium hydride was added portionwise at room temperature. After that, 4.00 ml (53.0 mmol) of MOMCl was added dropwise for 1 hour. The reaction mixture was heated at 60°C for 24
 10 hours and then poured into 300 ml of cold water. The crude product was extracted with 3 x 200 ml of dichloromethane. The combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 17.2 g (90%) of a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.22 (d, J = 1.5 Hz, 1H), 7.04 (d, J = 1.5 Hz, 1H), 5.21 (s, 2H), 3.69 (s, 3H), 2.26 (s, 3H), 2.11 – 2.19 (m, 1H), 1.92 (br.s, 2H), 1.65 – 1.80 (m, 4H), 1.34 – 1.43 (m, 4H), 1.20 (s, 2H),
 15 0.87 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 151.21, 144.4, 134.4, 131.9, 127.5, 117.6, 99.8, 57.9, 50.9, 47.5, 43.0, 39.8, 39.5, 31.5, 31.0, 30.0, 20.7.

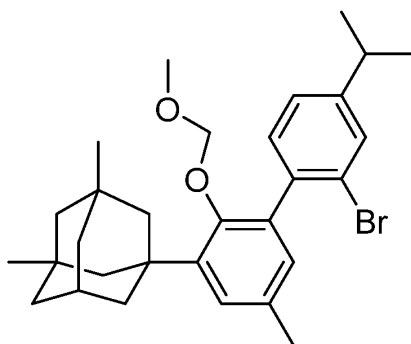
[0300] 2-(3-((1*r*,3*R*,5*S*,7*r*)-3,5-Dimethyladamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (T)



20 To a solution of 12.8 g (32.4 mmol) of (1*r*,3*R*,5*S*,7*r*)-1-(3-bromo-2-(methoxymethoxy)-5-methyl-phenyl)-3,5-dimethyladamantane (S) in 200 ml of dry THF, 14.3 ml (35.6 mmol) of

- 2.5 M ⁿBuLi in hexanes was added dropwise for 20 minutes at -80°C. The reaction mixture was stirred at this temperature for 1 hour followed by addition of 10.0 ml (48.7 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 300 ml of water. The crude product was
- 5 extracted with dichloromethane (3 x 100 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was recrystallized from isopropanol. Yield 11.1 g (78%) of a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.37 (d, J = 1.8 Hz, 1H), 7.20 (d, J = 2.0 Hz, 1H), 5.14 (s, 2H), 3.60 (s, 3H), 2.29 (s, 3H), 2.11 – 2.18 (m, 1H), 1.97 (br.s, 2H), 1.69 – 1.84 (m, 4H), 1.34 – 1.47 (m, 4H), 1.36 (s, 12H), 1.20 (s, 2H), 0.87 (s, 6H).
- 10 ¹³C NMR (CDCl₃, 100 MHz): δ 159.8, 140.7, 134.7, 131.7, 131.2, 101.1, 83.7, 57.9, 51.1, 47.4, 43.2, 39.7, 38.7, 31.5, 31.0, 30.1, 24.8, 20.8.

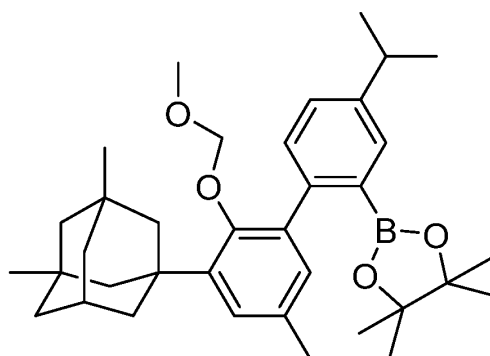
[0301] (1*r*,3*R*,5*S*,7*r*)-1-(2'-Bromo-4'-isopropyl-2-(methoxymethoxy)-5-methyl-[1,1'-biphenyl]-3-yl)-3,5-dimethyladamantane (U)



- 15 To a solution of 4.00 g (9.09 mmol) of 2-(3-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (T) in 20 ml of 1,4-dioxane, 3.55 g (10.9 mmol) of 2-bromo-4-isopropyl iodobenzene, 7.40 g (22.7 mmol) of cesium carbonate, and 10 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 525 mg (0.454 mmol) of Pd(PPh₃)₄.
- 20 This mixture was stirred for 12 hours at 105°C, then cooled to room temperature, and diluted with 100 ml of water. The crude product was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-dichloromethane = 10:1, vol.). Yield 3.16 g (68%) of a yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.50 (d, J = 1.7 Hz, 1H), 7.24 – 7.25 (m, 1H), 7.18 (dd, J = 8.0, 1.7 Hz, 1H), 7.11 (d, J = 2.0 Hz, 1H), 6.88 (d, J = 1.7 Hz, 1H), 4.38 – 4.48 (m, 2H), 3.18 (s, 3H), 2.91 (sept, J = 6.9 Hz, 1H), 2.31 (s, 3H), 2.13 – 2.19 (m, 1H), 1.94 – 2.01 (m, 2H), 1.78 – 1.86 (m, 2H), 1.66
- 25

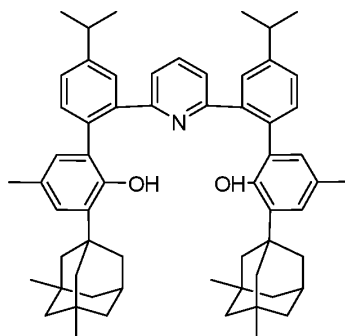
– 1.72 (m, 2H), 1.34 – 1.46 (m, 4H), 1.27 (d, $J = 6.9$ Hz, 6H), 1.19 (s, 2H), 0.87 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 151.9, 149.9, 142.1, 138.4, 134.6, 132.0, 130.7, 130.2, 127.6, 125.4, 123.9, 99.0, 57.0, 51.0, 47.53, 47.49, 43.2, 39.7, 39.0, 33.6, 31.5, 31.1, 30.1, 23.90, 23.88, 21.0.

- 5 **[0302]** 2-(3'-((1*r*,3*R*,5*S*,7*r*)-3,5-Dimethyladamantan-1-yl)-4-isopropyl-2'-(methoxymethoxy)-5'-methyl-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (V)



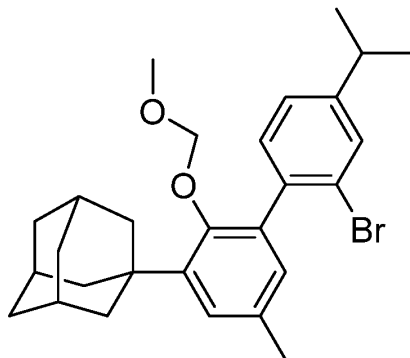
- To a solution of 3.15 g (6.16 mmol) of (1*r*,3*R*,5*S*,7*r*)-1-(2'-bromo-4'-isopropyl-2-(methoxymethoxy)-5'-methyl-[1,1'-biphenyl]-3-yl)-3,5-dimethyladamantane (U) in 50 ml of dry THF, 2.51 ml (6.28 mmol) of 2.5 M $n\text{BuLi}$ in hexanes was added dropwise for 20 minutes at -80°C . The reaction mixture was stirred for 1 hour at this temperature followed by an addition of 1.90 ml (9.24 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 100 ml of water. The crude product was extracted with dichloromethane (3 x 100 ml), the combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm , eluent: hexane-diethyl ether = 10:1, vol.). Yield 2.96 g (84%) of a colorless glassy solid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.58 (s, 1H), 7.28 – 7.30 (m, 2H), 7.06 (d, $J = 2.0$ Hz, 1H), 6.85 (d, $J = 1.7$ Hz, 1H), 4.39 – 4.47 (m, 2H), 3.27 (s, 3H), 2.96 (sept, $J = 6.9$ Hz, 1H), 2.29 (s, 3H), 2.15 – 2.21 (m, 1H), 1.73 – 2.05 (m, 6H), 1.34 – 1.52 (m, 4H), 1.30 (d, $J = 6.9$ Hz, 6H), 1.16 – 1.23 (m, 14H), 0.90 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 151.8, 146.5, 143.1, 141.3, 136.7, 132.4, 131.4, 130.6, 130.3, 127.8, 126.5, 98.8, 83.3, 57.2, 51.0, 43.2, 39.9, 38.9, 33.8, 31.5, 31.0, 30.2, 25.2, 24.2, 24.1, 24.05, 21.0.

- 25 **[0303]** 2',2'''-(Pyridine-2,6-diyl)bis(3-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4'-isopropyl-5-methyl-[1,1'-biphenyl]-2-ol) (W)



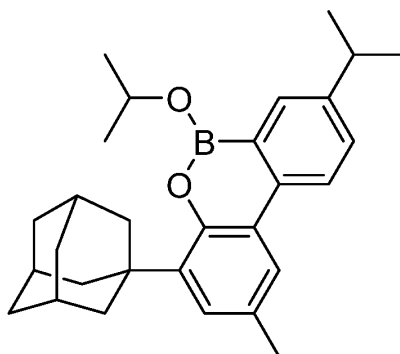
To a solution of 2.90 g (5.30 mmol) of 2-(3'-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-isopropyl-2'-(methoxymethoxy)-5'-methyl-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (V) in 20 ml of 1,4-dioxane, 625 mg (2.65 mmol) of 2,6-dibromopyridine, 5.13 g (15.4 mmol) of cesium carbonate, and 10 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 355 mg (0.300 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature, and diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil 20 ml of THF, 20 ml of methanol, and 2 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 200 ml of water. The crude product was extracted with dichloromethane (3 x 70 ml), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 1.30 g (57%) of a mixture of two isomers as a white foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.42 – 7.50 + 7.67 – 7.75 (m, 2H), 7.25 – 7.40 (m, 5H), 7.10 – 7.24 (m, 2H), 6.81 – 7.01 (m, 5H), 6.18 (br.s, 1H), 2.96 – 3.04 (m, 2H), 1.96 + 2.25 (2s, 6H), 1.46 – 1.91 (m, 8H), 0.97 – 1.37 (m, 28H), 0.80 + 0.71 (2s, 3H), 0.77 + 0.68 (2s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 150.44, 149.62, 148.52, 148.29, 136.86, 134.84, 134.61, 132.37, 131.35, 129.28, 129.03, 128.66, 128.42, 127.58, 126.79, 122.13, 51.23, 50.89, 47.46, 47.02, 46.48, 43.29, 43.04, 42.88, 38.36, 38.17, 33.85, 33.74, 31.47, 31.25, 31.16, 31.13, 31.00, 30.92, 30.81, 30.14, 30.06, 23.99, 23.94, 21.03, 20.57.

[0304] (3*r*,5*r*,7*r*)-1-(2'-Bromo-4'-isopropyl-2-(methoxymethoxy)-5-methyl-[1,1'-biphenyl]-3-yl)adamantane (X)



To a solution of 8.00 g (19.4 mmol) of 2-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (LL) in 40 ml of 1,4-dioxane, 6.92 g (21.3 mmol) of 2-bromo-4-isopropylidobenzene, 6.70 g (48.5 mmol) of potassium carbonate, and 20 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 1.15 g (1.00 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 105°C, then cooled to room temperature, and diluted with 100 ml of water. The crude product was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane-dichloromethane = 10:1, vol.). Yield 7.03 g (75%) of a colorless oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.57 (d, J = 1.7 Hz, 1H), 7.31 – 7.33 (m, 1H), 7.23 (dd, J = 7.9, 1.7 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 6.94 (d, J = 1.7 Hz, 1H), 4.48 – 4.54 (m, 2H), 3.22 (s, 3H), 2.96 (sept, J = 6.9 Hz, 1H), 2.37 (s, 3H), 2.20 – 2.24 (m, 6H), 2.14 (br.s, 3H), 1.80 – 1.88 (m, 6H), 1.32 (d, J = 6.9 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 151.6, 149.9, 142.8, 138.4, 134.7, 132.1, 132.0, 130.7, 130.0, 127.6, 125.3, 123.9, 98.8, 56.9, 41.3, 37.2, 37.0, 33.6, 29.2, 23.88, 23.87, 21.0.

[0305] 4-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-6-isopropoxy-8-isopropyl-2-methyl-6*H*-dibenzo[*c,e*][1,2]oxaborinine (Y)

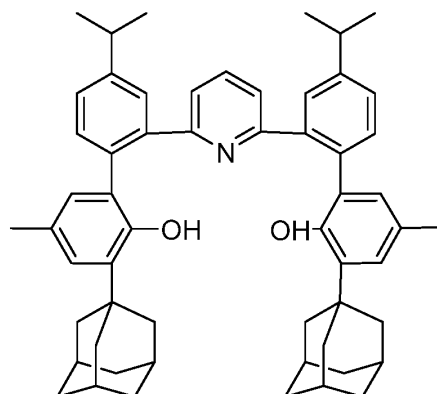


To a solution of 7.00 g (14.5 mmol) of (3*r*,5*r*,7*r*)-1-(2'-bromo-4'-isopropyl-2-(methoxymethoxy)-5-methyl-[1,1'-biphenyl]-3-yl)adamantane (X) in 150 ml of dry THF, 8.71 ml (21.7 mmol) of 2.5 M ⁿBuLi in hexanes was added dropwise for 20 minutes at -80°C. The reaction mixture was stirred for 1 hour at this temperature followed by an addition of

5 7.40 ml (36.3 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 100 ml of water. The crude product was extracted with dichloromethane (3 x 100 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was recrystallized from isopropanol. Yield 3.01 g (48%) of a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.06 (d, J =

10 8.4 Hz, 1H), 7.89 (d, J = 1.8 Hz, 1H), 7.81 (s, 1H), 7.51 (dd, J = 8.4, 2.0 Hz, 1H), 7.12 (d, J = 1.6 Hz, 1H), 5.24 (sept, J = 6.1 Hz, 1H), 3.02 (sept, J = 6.9 Hz, 1H), 2.42 (s, 3H), 2.25 – 2.29 (m, 6H), 2.14 (br.s, 3H), 1.83 (br.s, 6H), 1.41 (d, J = 6.1 Hz, 6H), 1.32 (d, J = 6.9 Hz, 6H).

[0306] 2',2'''-(Pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4'-isopropyl-5-methyl-[1,1'-biphenyl]-2-ol) (Z)



15

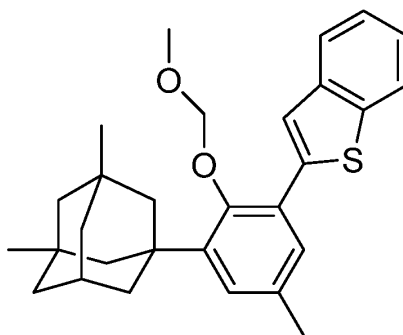
To a solution of 2.90 g (6.77 mmol) of 4-((3*r*,5*r*,7*r*)-adamantan-1-yl)-6-isopropoxy-8-isopropyl-2-methyl-6*H*-dibenzo[*c,e*][1,2]oxaborinine (Y) in 20 ml of 1,4-dioxane, 786 mg (3.32 mmol) of 2,6-dibromopyridine, 5.52 g (16.9 mmol) of cesium carbonate, and 10 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes

20 followed by addition of 313 mg (0.271 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature, and diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate = 10:1, vol.). Yield

25 1.60 g (61%) of a mixture of two isomers as a white foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.14 – 7.17 + 7.25 – 7.47 + 7.70 – 7.74 (3m, 9H), 6.97 – 7.04 (m, 2H), 6.85 – 6.90 + 6.15 (2m, 4H),

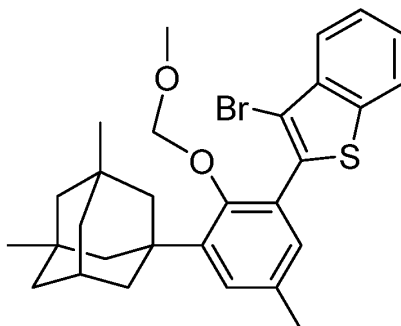
3.00 – 3.10 (m, 2H), 1.90 – 1.98 + 2.26 (2m, 18H), 1.56 – 1.84 (m, 18H), 1.35 – 1.38 (m, 12H).
¹³C NMR (CDCl₃, 100 MHz) δ 158.36, 158.29, 150.47, 149.79, 148.39, 139.71, 138.46,
 137.87, 137.49, 136.93, 136.64, 134.88, 134.73, 132.29, 131.09, 130.62, 130.01, 129.33,
 129.03, 128.59, 128.39, 128.27, 127.51, 126.93, 126.74, 126.35, 122.25, 122.00, 40.37, 40.22,
 5 37.03, 36.85, 36.67, 36.48, 33.82, 33.65, 29.11, 28.99, 23.98, 23.94, 23.92, 20.87, 20.52.

[0307] 2-(3-((1*r*,3*R*,5*S*,7*r*)-3,5-Dimethyladamantan-1-yl)-2-(methoxymethoxy)-5-methyl phenyl)benzo[*b*]thiophene (AA)



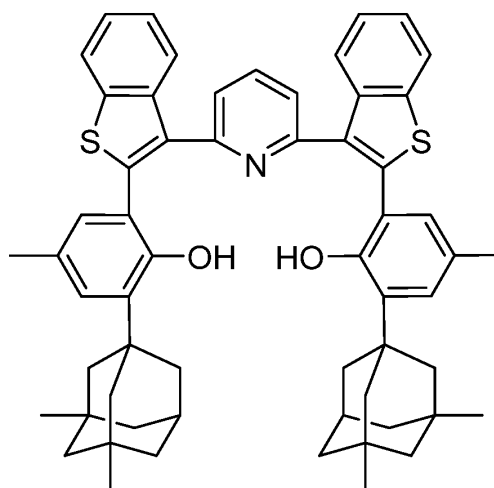
To a solution of 6.14 g (45.8 mmol) of benzo[*b*]thiophene in 200 ml of dry THF, 17.4 ml
 10 (43.5 mmol, 2.5 M) of ⁿBuLi in hexanes was added dropwise at -10°C. The reaction mixture
 was stirred for 2 hours at 0°C, followed by an addition of 5.94 g (43.5 mmol) of ZnCl₂. Next,
 the obtained solution was warmed to room temperature, 9.00 g (22.9 mmol) of (1*r*,3*R*,5*S*,7*r*)-
 1-(3-bromo-2-(methoxymethoxy)-5-methylphenyl)-3,5-dimethyladamantane (S) and 1.17 g
 (2.29 mmol) of Pd[P^{*i*}Bu₃]₂ were subsequently added. The resulting mixture was stirred
 15 overnight at 60°C, then poured into 250 ml of water. The crude product was extracted with
 3 x 150 ml of dichloromethane. The combined organic extract was dried over Na₂SO₄ and then
 evaporated to dryness. The residue was purified by flash chromatography on silica gel 60
 (40-63 μm; eluent: hexane-ethyl acetate = 10:1, vol.). Yield 8.30 g (81%) of a light-yellow
 solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.86 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.52
 20 (s, 1H), 7.32 – 7.40 (m, 2H), 7.17 – 7.20 (m, 2H), 4.76 (s, 2H), 3.48 (s, 3H), 2.37 (s, 3H), 2.19
 – 2.26 (m, 1H), 2.04 (br.s, 2H), 1.76 – 1.90 (m, 4H), 1.40 – 1.52 (m, 4H), 1.25 (s, 2H), 0.93 (s,
 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 152.1, 142.9, 141.9, 140.2, 140.1, 133.0, 130.0, 128.5,
 124.3, 124.1, 123.4, 122.1, 99.1, 57.7, 50.1, 47.5, 43.1, 39.8, 39.1, 31.5, 31.0, 30.1, 21.0.

[0308] 3-Bromo-2-(3-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-2-(methoxymethoxy)-5-methyl phenyl)benzo[*b*]thiophene (BB)

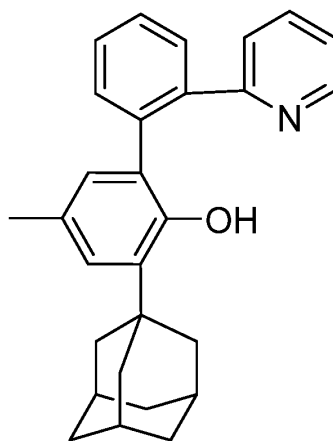


To a solution of 8.25 g (18.5 mmol) of 2-(3-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)benzo[*b*]thiophene (AA) in 150 ml of dichloromethane, 3.29 g (18.5 mmol) of N-bromosuccinimide was added at room temperature. The reaction mixture was stirred for 12 hours at this temperature, then poured into 100 ml of water. The crude product was extracted with 3 x 50 ml of dichloromethane. The combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was recrystallized from 120 ml of n-hexane. Yield 9.03 g (93%) of a beige solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.92 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.27 (s, 1H), 7.15 (s, 1H), 4.68 (s, 2H), 3.38 (s, 3H), 2.41 (s, 3H), 2.21 – 2.28 (m, 1H), 2.08 (br.s, 2H), 1.79 – 1.96 (m, 4H), 1.40 – 1.56 (m, 4H), 1.28 (s, 2H), 0.96 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 153.4, 142.4, 138.6, 138.2, 137.4, 132.4, 130.8, 129.3, 125.9, 125.4, 125.0, 123.4, 122.2, 107.7, 99.4, 57.4, 51.0, 47.4, 43.1, 39.6, 39.0, 31.5, 31.0, 30.1, 21.0.

[0309] 6,6'-(Pyridine-2,6-diylbis(benzo[*b*]thiophene-3,2-diyl))bis(2-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-methylphenol) (CC)



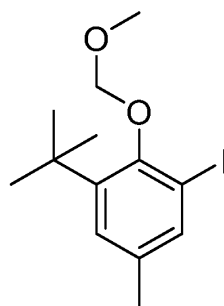
- To a solution of 4.00 g (7.55 mmol) of 3-bromo-2-(3-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)benzo[*b*]thiophene (BB) in 50 ml of dry THF, 3.08 ml (7.70 mmol, 2.5M) of ⁿBuLi in hexanes was added dropwise at -80°C. The reaction mixture was stirred for 30 minutes at this temperature, then 1.03 g (7.70 mmol) of ZnCl₂ was added. The obtained mixture was warmed to room temperature, then 0.86 g (3.63 mmol) of 2,6-dibromopyridine and 194 mg (0.38 mmol) of Pd[P^tBu₃]₂ were subsequently added. The obtained mixture was stirred overnight at 60°C and then poured into 100 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil, 50 ml of THF, 50 ml of methanol and 2 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 200 ml of water. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm; eluent: hexane-ethyl acetate-triethylamine = 100:10:1, vol.). Yield 1.12 g (35%) of a light-yellow foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.87 – 7.93 (m, 5H), 7.66 (t, J = 7.8 Hz, 1H), 7.39 – 7.46 (m, 5H), 7.23 (d, J = 7.8 Hz, 2H), 6.90 – 6.98 (m, 4H), 2.24 (s, 6H), 1.78 – 1.82 (m, 2H), 1.50 – 1.56 (m, 4H), 0.97 – 1.34 (m, 18H), 0.70 (s, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ 153.5, 150.6, 140.3, 140.0, 138.9, 137.9, 137.8, 131.9, 129.5, 128.7, 128.5, 124.9, 124.8, 123.9, 122.9, 122.1, 50.9, 46.6, 42.9, 38.3, 37.8, 31.2, 30.9, 30.2, 20.9.
- [0310] 3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-5-methyl-2'-(pyridin-2-yl)-[1,1'-biphenyl]-2-ol (DD)**



- To a solution of 2.42 g (6.27 mmol) of 4-((3*r*,5*r*,7*r*)-adamantan-1-yl)-6-isopropoxy-2-methyl-6*H*-dibenzo[*c,e*][1,2]oxaborinine (NN) in 20 ml of 1,4-dioxane, 1.04 g (6.58 mmol) of 2-bromopyridine, 5.11 g (15.7 mmol) of cesium carbonate, and 10 ml of water were

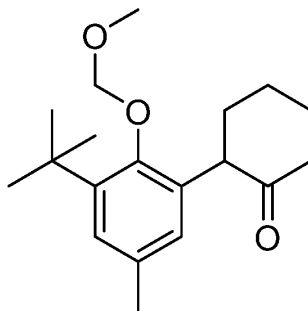
subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 362 mg (0.310 mmol) of $\text{Pd}(\text{PPh}_3)_4$. This mixture was stirred for 12 hours at 100°C , then cooled to room temperature, and diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm , eluent: hexane-ethyl acetate = 10:1, vol.). Yield 1.83 g (74%) as a white solid. ^1H NMR (CDCl_3 , 400 MHz): δ 9.62 (s, 1H), 8.41 – 8.44 (m, 1H), 7.67 (td, J = 7.8, 1.8 Hz, 1H), 7.44 – 7.49 (m, 3H), 7.31 – 7.36 (m, 2H), 7.18 (ddd, J = 7.6, 5.0, 1.1 Hz, 1H), 6.97 (d, J = 1.9 Hz, 1H), 6.68 (d, J = 2.1 Hz, 1H), 2.16 – 2.27 (m, 6H), 2.21 (s, 3H), 2.10 (br.s, 3H), 1.75 – 1.86 (m, 6H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.2, 151.4, 147.0, 139.5, 139.0, 138.6, 137.3, 133.3, 132.3, 129.5, 129.0, 128.9, 128.6, 127.5, 126.7, 123.9, 122.2, 40.6, 37.2, 36.9, 29.2, 20.9.

[0311] 1-(*tert*-Butyl)-3-iodo-2-(methoxymethoxy)-5-methylbenzene (EE)



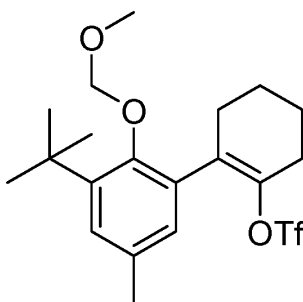
To a solution of 20.0 g (96.1 mmol) of 1-(*tert*-butyl)-2-(methoxymethoxy)-5-methylbenzene in 500 ml of diethyl ether, 77.1 ml (192 mmol, 2.5 M) of $n\text{BuLi}$ in hexanes was added dropwise at 0°C . The resulting solution was stirred overnight at room temperature. Further on, the reaction mixture was cooled to -80°C , and 51.2 g (202 mmol) of iodine was added in one portion. The obtained mixture was stirred overnight at room temperature and then poured into 100 ml of water. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was washed twice with saturated Na_2SO_3 , dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by vacuum distillation (1 mbar, bp. 127°C). Yield 26.7 g (83%) of a yellow oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.52 (d, J = 2.1 Hz, 1H), 7.14 (d, J = 1.5 Hz, 1H), 5.19 (s, 2H), 3.72 (s, 3H), 2.27 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.1, 144.5, 138.5, 135.9, 135.1, 128.9, 99.5, 57.8, 35.6, 30.9, 20.4.

[0312] 2-(3-(*tert*-Butyl)-2-(methoxymethoxy)-5-methylphenyl)cyclohexan-1-one (FF)



To a solution of 21.0 g (62.9 mmol) of 1-(*tert*-butyl)-3-iodo-2-(methoxymethoxy)-5-methylbenzene (EE) in 60 ml of dry 1,4-dioxane, 51.2 g (157 mmol) of cesium carbonate, 1.00 g of Pd₂(dba)₃, 1.70 g of 1,1'-bis(di-*tert*-butylphosphino)ferrocene, and 12.3 g (126 mmol) of cyclohexanone were subsequently added. The resulting suspension was stirred at 80°C overnight, then cooled to room temperature, and diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified using Kugelrohr apparatus (0.4 mbar, 210°C). Yield 13.0 g (68%) of a red solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.05 (d, J = 2.2 Hz, 1H), 6.86 (d, J = 2.2 Hz, 1H), 4.92 – 4.93 (m, 1H), 4.63 – 4.64 (m, 1H), 4.32 (dd, J = 12.0, 5.0 Hz, 1H), 3.58 (s, 3H), 2.52 – 2.57 (m, 2H), 2.31 (s, 3H), 2.14 – 2.20 (m, 2H), 1.82 – 2.04 (m, 4H), 1.38 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 211.6, 153.6, 142.2, 132.8, 132.7, 128.3, 126.7, 100.7, 56.6, 51.6, 42.3, 35.6, 34.8, 31.1, 28.0, 26.1, 21.3.

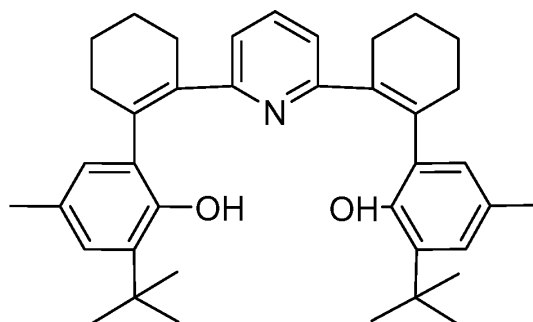
[0313] 3'-(*tert*-Butyl)-2'-(methoxymethoxy)-5'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (GG)



To a solution of 9.54 g (31.4 mmol) of 2-(3-(*tert*-butyl)-2-(methoxymethoxy)-5-methylphenyl)cyclohexan-1-one (FF) in 100 ml of THF, 4.22 g (37.7 mmol) of potassium *tert*-butoxide was added at 0°C. The resulting suspension was stirred at room temperature for 2 hours and then cooled to -30°C. Further on, 14.8 g (37.7 mmol) of N-(5-chloro-2-pyridyl)bis(trifluoromethanesulfonimide) was added in one portion. The resulting mixture was

stirred for 30 minutes at room temperature and then diluted with 50 ml of water. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μ m, eluent: dichloromethane). Yield 13.0 g (95%) as an yellow oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.11 (d, J = 2.2 Hz, 1H), 6.83 (d, J = 2.2 Hz, 1H), 4.95 – 4.96 (m, 1H), 4.89 – 4.90 (m, 1H), 3.60 (s, 3H), 2.60 – 2.70 (m, 1H), 2.49 – 2.54 (m, 2H), 2.35 – 2.43 (m, 1H), 2.30 (s, 3H), 1.87 – 1.94 (m, 2H), 1.76 – 1.82 (m, 2H), 1.42 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz) δ 151.7, 144.1, 142.8, 132.4, 130.0, 129.5, 128.5, 127.9, 119.6, 99.4, 57.2, 35.0, 30.7, 30.6, 28.0, 22.9, 22.0, 20.9.

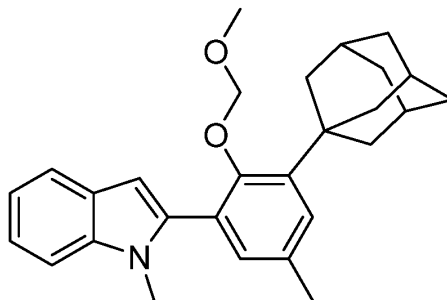
10 [0314] 6',6'''-(Pyridine-2,6-diyl)bis(3-(*tert*-butyl)-5-methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-ol) (HH)



To a solution of 1.13 g (4.30 mmol) of triphenylphosphine in 50 ml of 1,4-dioxane, 380 mg (2.15 mmol) of PdCl₂ was added at room temperature. The reaction mixture was heated at 90°C for 10 minutes and then cooled to room temperature. After that, 11.7 g (26.9 mmol) of 3'-(*tert*-butyl)-2'-(methoxymethoxy)-5'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl trifluoromethanesulfonate (GG), 7.50 g (29.5 mmol) of bis(pinacolato)diboron, and 11.2 g (80.5 mmol) of potassium carbonate were subsequently added. The resulting mixture was stirred at 90°C for 2 days, then diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness yielding 11.2 g of the crude product. To 3.90 g (9.28 mmol) of this product, 1.00 g (4.22 mmol) of 2,6-dibromopyridine, 8.25 g (25.3 mmol) of cesium carbonate, 490 mg (0.42 mmol) of Pd(PPh₃)₄, 20 ml of 1,4-dioxane, and 10 ml of water were added. The resulting mixture was stirred at 90°C for 7 days, then diluted with 50 ml of water. Thus obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by preparative HPLC (eluent: acetonitrile). Yield 290 mg (10%) of a white foam.

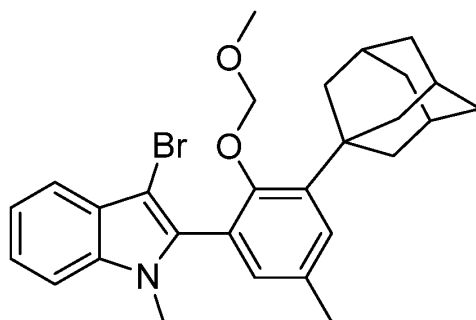
^1H NMR (CDCl_3 , 400 MHz): δ 6.49 – 7.16 (m, 7H), 2.32 – 2.71 (m, 6H), 2.11 + 2.21 (2s, 8H), 1.78 – 1.89 (m, 8H), 1.27 + 1.14 (2s, 18H). ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.7, 148.0, 140.7, 137.9, 136.9, 136.2, 135.0, 130.2, 128.3, 126.6, 126.3, 125.8, 122.1, 74.1, 58.3, 34.5, 32.7, 32.2, 29.6, 29.54, 29.49, 27.7, 23.1, 22.9, 22.7, 22.6, 20.9.

5 **[0315] 2-(3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-1-methyl-1*H*-indole (II)**



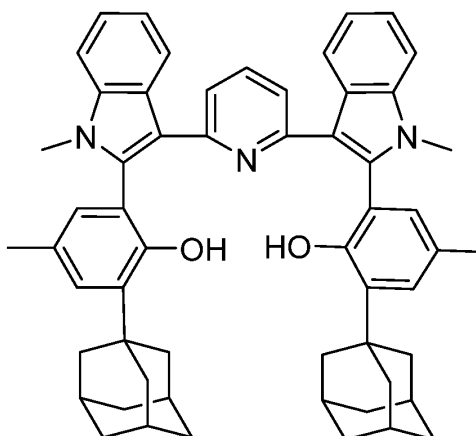
To a solution of 3.52 g (26.9 mmol) of N-methylindole in 250 ml of dry THF, 10.0 ml (25.0 mmol, 2.5 M) of $n\text{BuLi}$ in hexanes was added dropwise at -10°C . The reaction mixture was stirred for 1 hour at 0°C followed by an addition of 3.40 g (25.0 mmol) of ZnCl_2 . Next, the obtained solution was warmed to room temperature, 7.00 g (19.2 mmol) of (3*r*,5*r*,7*r*)-1-(3-bromo-2-(methoxymethoxy)-5-methylphenyl)adamantane and 447 mg (0.876 mmol) of $\text{Pd}[\text{P}^t\text{Bu}_3]_2$ were subsequently added. The resulting mixture was stirred overnight at 60°C , then poured into 250 ml of water. The crude product was extracted with 3 x 50 ml of dichloromethane. The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexane-ethyl acetate = 10:1, vol.). Yield 4.04 g (51%) of a yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.65–7.68 (m, 1H), 7.37–7.41 (m, 1H), 7.13–7.28 (m, 3H), 7.08–7.10 (m, 1H), 6.55–6.56 (m, 1H), 4.42–4.53 (m, 2H), 3.64 (s, 3H), 3.23 (s, 3H), 2.38 (s, 3H), 2.21 (s, 6H), 2.14 (br.s, 3H), 1.82 (br.s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 152.4, 143.0, 139.9, 137.5, 132.8, 131.0, 128.6, 128.1, 126.1, 121.4, 120.4, 119.6, 109.4, 101.6, 98.6, 57.4, 41.2, 37.2, 37.0, 30.7, 29.1, 21.0.

[0316] 2-(3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-3-bromo-1-methyl-1*H*-indole (JJ)



To a solution of 3.15 g (7.58 mmol) of 2-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-1-methyl-1*H*-indole (II) in 80 ml of chloroform, 1.38 g (7.73 mmol) of N-bromosuccinimide was added at room temperature. The reaction mixture was stirred for 2 hours at this temperature, then poured into 100 ml of water. The crude product was extracted with 3 x 50 ml of dichloromethane. The combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was triturated with 5 ml of n-hexane and dried *in vacuo*. Yield 3.66 g (98%) of a light-yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.64 (d, J = 7.8 Hz, 1H), 7.35 – 7.40 (m, 1H), 7.30 – 7.35 (m, 1H), 7.23 – 7.28 (m, 2H), 7.09 (m, 1H), 4.66 – 4.67 (m, 1H), 4.24 – 4.26 (m, 1H), 3.61 (s, 3H), 3.15 (s, 3H), 2.40 (s, 3H), 2.13 – 2.23 (m, 9H), 1.83 (br.s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 153.2, 143.0, 136.8, 136.3, 132.7, 131.4, 129.3, 127.0, 123.7, 122.6, 120.3, 119.2, 109.5, 99.0, 90.2, 57.3, 41.2, 37.2, 37.0, 31.1, 29.1, 21.0.

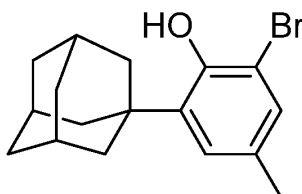
[0317] **6,6'-(Pyridine-2,6-diylbis(1-methyl-1*H*-indole-3,2-diyl))bis(2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methylphenol) (KK)**



To a solution of 3.61 g (7.30 mmol) of 2-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-3-bromo-1-methyl-1*H*-indole (JJ) in 100 ml of dry THF, 3.02 ml (7.45 mmol,

2.5 M) of n BuLi in hexanes was added dropwise at -80°C . The reaction mixture was stirred for 30 minutes at this temperature, then 1.01 g (7.45 mmol) of ZnCl_2 was added. The obtained mixture was warmed to room temperature, then 822 mg (3.47 mmol) of 2,6-dibromopyridine and 311 mg (0.61 mmol) of $\text{Pd}[\text{P}^t\text{Bu}_3]_2$ were subsequently added. The obtained mixture was stirred overnight at 60°C and then poured into 100 ml of water. The crude product was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. To the resulting oil, 50 ml of THF, 50 ml of methanol and 4 ml of 12 N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 200 ml of water. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexane-ethyl acetate-triethylamine = 100:10:1, vol.). Yield 1.92 g (67%) of a mixture of two isomers as a yellow foam. ^1H NMR (CDCl_3 , 400 MHz): δ 8.91 + 8.52 (2br.s, 2H), 7.83 – 7.85 + 7.89 – 7.91 (2m, 2H), 7.54 + 7.60 (2t, J = 7.6 Hz, 1H), 7.42 – 7.44 (m, 2H), 7.33 – 7.36 (m, 2H), 7.13 – 7.27 (m, 4H), 6.98 (s, 2H), 6.60 + 6.91 (2s, 2H), 3.61 + 3.57 (2s, 6H), 2.30 + 2.18 (2s, 6H), 1.39 – 1.93 (m, 30H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 154.0, 153.7, 152.5, 152.0, 139.4, 138.8, 137.7, 137.4, 137.3, 135.7, 135.5, 129.6, 129.1, 128.7, 128.5, 128.3, 128.1, 126.8, 126.6, 122.5, 122.4, 121.8, 121.6, 121.1, 120.7, 120.5, 119.5, 119.3, 115.2, 114.7, 109.62, 109.58, 40.3, 40.0, 36.9, 36.8, 36.7, 36.6, 30.9, 30.7, 29.0, 28.95, 20.9, 20.8.

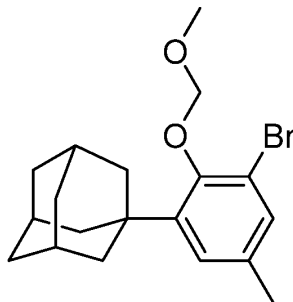
[0318] 2-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-6-bromo-4-methylphenol (OO)



To a solution of 21.2 g (87.0 mmol) of 2-(adamantan-1-yl)-4-methylphenol in 200 ml of dichloromethane, a solution of 4.50 ml (87.0 mmol) of bromine in 100 ml of dichloromethane was added dropwise for 10 minutes at room temperature. The resulting mixture was diluted with 400 ml of water. The crude product was extracted with dichloromethane (3 x 70 ml), the combined organic extract was washed with 5% NaHCO_3 , dried over Na_2SO_4 and then evaporated to dryness. Yield 21.5 g (77%) of a white solid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.17 (s, 1H), 6.98 (s, 1H), 5.65 (s, 1H), 2.27 (s, 3H), 2.10 – 2.13 (m, 9H), 1.80 (m, 6H),

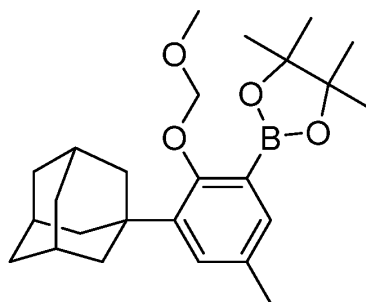
^{13}C NMR (CDCl_3 , 100 MHz): δ 148.18, 137.38, 130.24, 129.32, 127.26, 112.08, 40.18, 37.32, 36.98, 28.99, 20.55.

[0319] (3*r*,5*r*,7*r*)-1-(3-Bromo-2-(methoxymethoxy)-5-methylphenyl)adamantine (PP)



- 5 To a solution of 21.3 g (66.4 mmol) of 2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-6-bromo-4-methylphenol (OO) in 400 ml of THF, 2.79 g (69.7 mmol, 60% wt. in mineral oil) of sodium hydride was added portionwise at room temperature. To the resulting suspension 5.55 ml (73.0 mmol) of methoxymethyl chloride was added dropwise for 10 minutes at room temperature. The obtained mixture was stirred overnight, then poured into 200 ml of water. Thus obtained
- 10 mixture was extracted with dichloromethane (3 x 200 ml), the combined organic extract was washed with 5% NaHCO_3 , dried over Na_2SO_4 , and then evaporated to dryness. Yield 24.3 g (quant.) of a white solid. ^1H NMR (CDCl_3 , 400 MHz): δ 7.24 (d, J = 1.5 Hz, 1H), 7.05 (d, J = 1.8 Hz, 1H), 5.22 (s, 2H), 3.71 (s, 3H), 2.27 (s, 3H), 2.05 – 2.12 (m, 9H), 1.78 (m, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 151.01, 144.92, 134.34, 131.80, 127.44, 117.57, 99.56, 57.75,
- 15 41.27, 37.71, 36.82, 29.03, 20.68.

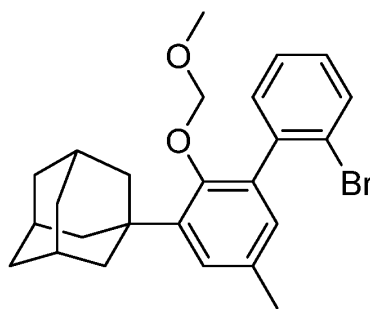
[0320] 2-(3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (LL)



- To a solution of 20.0 g (55.0 mmol) of (3*r*,5*r*,7*r*)-1-(3-bromo-2-(methoxymethoxy)-5-methylphenyl)adamantine (PP) in 400 ml of dry THF, 22.5 ml (56.4 mmol) of 2.5 M $n\text{BuLi}$ in hexanes was added dropwise for 20 minutes at -80°C . The reaction mixture was stirred at this

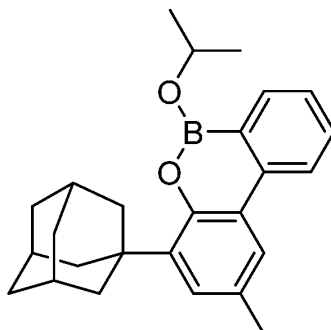
temperature for 1 hour followed by addition of 16.7 ml (82.2 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 300 ml of water. The crude product was extracted with dichloromethane (3 x 300 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 22.4 g (99%) of a colorless viscous oil. ¹H NMR (CDCl₃, 400 MHz): δ 7.35 (d, J = 2.3 Hz, 1H), 7.18 (d, J = 2.3 Hz, 1H), 5.14 (s, 2H), 3.58 (s, 3H), 2.28 (s, 3H), 2.14 (m, 6H), 2.06 (m, 3H), 1.76 (m, 6H), 1.35 (s, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ 159.68, 141.34, 134.58, 131.69, 131.14, 100.96, 83.61, 57.75, 41.25, 37.04, 29.14, 24.79, 20.83.

- 10 **[0321] (3*r*,5*r*,7*r*)-1-(2'-Bromo-2-(methoxymethoxy)-5-methyl-[1,1'-biphenyl]-3-yl)adamantane (MM)**



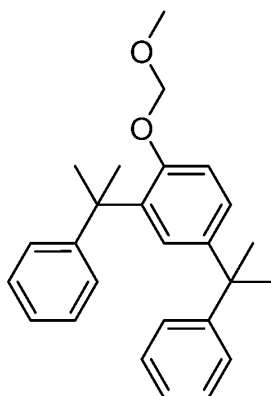
- To a solution of 10.0 g (24.3 mmol) of 2-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-2-(methoxymethoxy)-5-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (LL) in 100 ml of 1,4-dioxane, 7.22 g (25.5 mmol) of 2-bromiodobenzene, 8.38 g (60.6 mmol) of potassium carbonate, and 50 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 1.40 g (1.21 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature and diluted with 100 ml of water. The crude product was extracted with dichloromethane (3 x 150 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μ m, eluent: hexane-dichloromethane = 10:1, vol.). Yield 10.7 g (quant.) of a white solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.72 (d, J = 7.9 Hz, 1H), 7.35 – 7.44 (m, 3H), 7.19 – 7.26 (m, 1H), 6.94 (m, 1H), 4.53 (dd, J = 20.0, 4.6 Hz, 2H), 3.24 (s, 3H), 2.38 (s, 3H), 2.23 (m, 6H), 2.15 (m, 3H), 1.84 (m, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 151.51, 142.78, 141.11, 134.63, 132.76, 132.16, 132.13, 129.83, 128.57, 127.76, 127.03, 124.05, 98.85, 56.95, 41.21, 37.18, 36.94, 29.07, 21.00.

[0322] 4-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-6-isopropoxy-2-methyl-6*H*-
dibenzo[*c,e*][1,2]oxaborinine (NN)



To a solution of 10.0 g (22.7 mmol) of 1-(2'-bromo -2-(methoxymethoxy)-5-methyl -[1,1'-
5 biphenyl]-3-yl)adamantine (MM) in 120 ml of dry THF, 10.9 ml (27.2 mmol) of 2.5 M ⁿBuLi
in hexanes was added dropwise for 20 minutes at -80°C. The reaction mixture was stirred for
1 hour at this temperature followed by addition of 6.93 ml (40.0 mmol) of 2-isopropoxy-
4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred at room
temperature for 1 hour, then poured into 300 ml of water. The crude product was extracted
10 with dichloromethane (3 x 300 ml), the combined organic extract was dried over Na₂SO₄ and
then evaporated to dryness. The residue was recrystallized from 30 ml of isopropanol. Yield
6.48 g (74%) of a white crystals. ¹H NMR (CDCl₃, 400 MHz): δ 8.16 (d, J = 8.3 Hz, 1H), 8.09
(dd, J = 7.4, 1.0 Hz, 1H), 7.86 (d, J = 1.2 Hz, 1H), 7.63 – 7.68 (m, 1H), 7.43 (td, J = 7.3, 1.0
Hz), 7.19 (d, J = 1.8 Hz, 1H), 5.27 (sept, J = 6.1 Hz, 1H), 2.46 (s, 3H), 2.30 – 2.32 (m, 6H),
15 2.17 (br.s, 3H), 1.86 (br.s, 6H), 1.44 (d, J = 6.1 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 148.4,
140.6, 139.3, 133.0, 131.8, 130.7, 127.5, 126.6, 122.8, 121.9, 121.6, 65.7, 40.7, 37.2, 29.1,
24.7, 21.4.

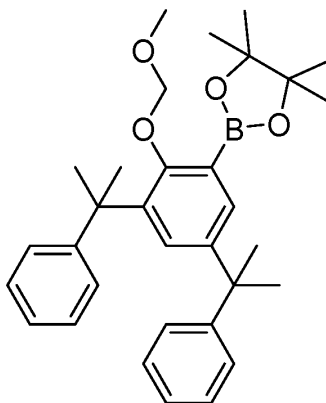
[0323] ((4-(Methoxymethoxy)-1,3-phenylene)bis(propane-2,2-diyl))dibenzene (RR)



To a solution of 30.0 g (90.8 mmol) of 2,4-bis(2-phenylpropan-2-yl)phenol in 500 ml of THF, 3.81 g (95.3 mmol, 60% wt. in mineral oil) of sodium hydride was added portionwise at room temperature. To the resulting suspension, 7.60 ml (99.9 mmol) of methoxymethyl chloride was added dropwise for 10 minutes at room temperature. The obtained mixture was stirred overnight, then poured into 500 ml of water. The obtained mixture was extracted with dichloromethane (3 x 300 ml), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. Yield 34.0 g (quant.) of a light-yellow oil.

¹H NMR (CDCl₃, 400 MHz): δ 7.49 (d, J = 2.3 Hz, 1H), 7.37 – 7.42 (m, 4H), 7.25 – 7.32 (m, 5H), 7.15 – 7.19 (m, 2H), 7.00 (d, J = 8.5 Hz, 1H), 4.68 (s, 2H), 3.06 (s, 3H), 1.84 (s, 6H), 1.74 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 153.09, 151.59, 150.96, 143.14, 137.65, 127.90, 127.58, 126.72, 125.63, 125.49, 125.41, 124.75, 114.23, 93.75, 55.28, 42.59, 42.04, 30.99, 29.55.

[0324] 2-(2-(Methoxymethoxy)-3,5-bis(2-phenylpropan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SS)



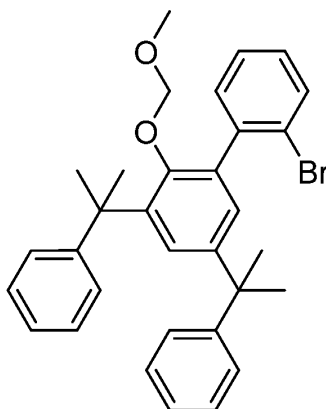
To a solution of 15.0 g (40.1 mmol) of ((4-(methoxymethoxy)-1,3-phenylene)bis(propane-2,2-diyl))dibenzene (RR) in 400 ml of dry diethyl ether, 32.0 ml (80.2 mmol) of 2.5 M ⁿBuLi in hexanes was added dropwise for 20 minutes at 0°C. The reaction mixture was stirred for 3 hours at room temperature, then cooled to -80°C, followed by an addition of 24.5 ml (120 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 400 ml of water. The obtained mixture was extracted with dichloromethane (3 x 300 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. Yield 20.0 g (quant.) of a colorless viscous oil.

¹H NMR (CDCl₃, 400 MHz): δ 7.49 (d, J = 2.4 Hz, 1H), 7.34 (d, J = 2.5 Hz, 1H), 7.29 (d, J = 4.7 Hz, 4H), 7.06 – 7.22 (m, 6H), 4.13 (s, 2H), 3.10 (s, 3H), 1.74 (s, 6H), 1.61 (s, 6H),

1.32 (s, 12H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 156.94, 151.72, 150.92, 143.88, 140.51, 131.17, 129.39, 127.81, 127.70, 126.74, 125.82, 125.41, 124.95, 98.10, 83.57, 82.74, 56.52, 42.66, 42.22, 30.88, 30.11, 26.15, 25.36, 24.76, 13.85.

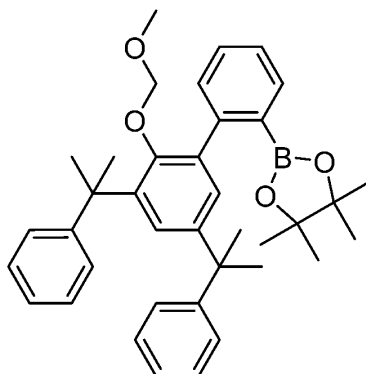
[0325] 2'-Bromo-2-(methoxymethoxy)-3,5-bis(2-phenylpropan-2-yl)-1,1'-biphenyl

5 (TT)



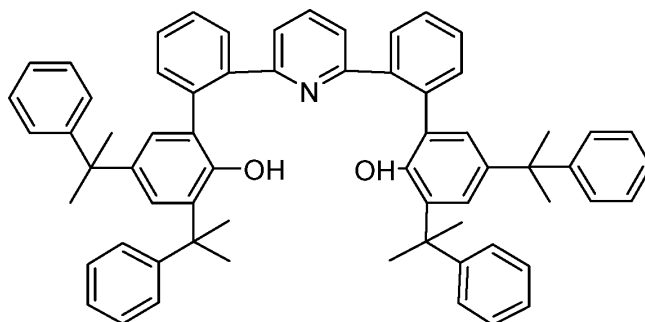
To a solution of 20.0 g (40.0 mmol) of 2-(2-(methoxymethoxy)-3,5-bis(2-phenylpropan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (SS) in 200 ml of dioxane, 12.5 g (44.0 mmol) of 2-bromoiodobenzene, 13.8 g (100 mmol) of potassium carbonate, and 100 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 2.30 g (2.00 mmol) of $\text{Pd}(\text{PPh}_3)_4$. This mixture was stirred for 12 hours at 100°C , cooled to room temperature, and then diluted with 100 ml of water. The obtained mixture was extracted with dichloromethane (3 x 200 ml), the combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm , eluent: hexane-dichloromethane = 10:1, vol.). Yield 15.6 g (74%) of a yellow viscous oil. ^1H NMR (CDCl_3 , 400 MHz): δ 7.62 (dd, J = 7.9, 1.1 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.35 – 7.39 (m, 7H), 7.30 (d, J = 4.4 Hz, 4H), 7.22 – 7.26 (m, 1H), 7.13 – 7.18 (m, 1 H), 7.08 (d, J = 2.4 Hz, 1H), 3.51 (d, J = 4.7 Hz, 1H), 3.44 (d, J = 4.7 Hz, 1H), 2.73 (s, 3H), 1.82 (s, 3H), 1.80 (s, 3H), 1.76 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 151.47, 150.67, 150.48, 144.76, 142.49, 140.96, 134.66, 132.53, 132.15, 128.72, 128.45, 127.93, 127.89, 126.75, 125.94, 125.58, 125.53, 125.23, 124.33, 97.59, 56.12, 42.82, 42.41, 31.08, 30.85, 30.22, 30.06.

[0326] 2-(2'-(Methoxymethoxy)-3',5'-bis(2-phenylpropan-2-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (UU)



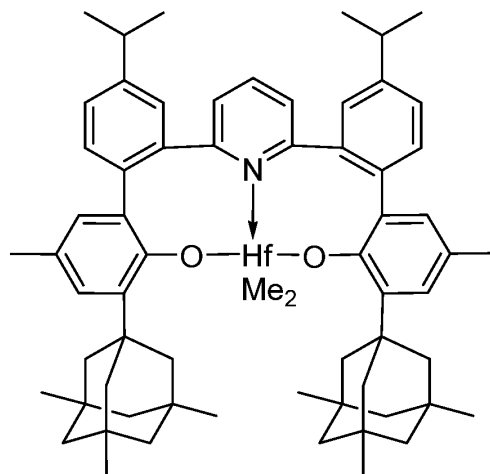
To a solution of 15.6 g (29.5 mmol) of 2'-bromo-2-(methoxymethoxy)-3,5-bis(2-phenylpropan-2-yl)-1,1'-biphenyl (TT) in 250 ml of dry THF, 15.4 ml (38.4 mmol) of 2.5 M ⁿBuLi in hexanes was added dropwise for 20 minutes at -80°C. The reaction mixture was stirred for 1 hour at this temperature followed by an addition of 10.8 ml (53.1 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The obtained suspension was stirred for 1 hour at room temperature, then poured into 300 ml of water. The obtained mixture was extracted with dichloromethane (3 x 300 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 um, eluent: hexane-diethyl ether = 10:1, vol.) Yield 9.90 g (58%) of a colorless glassy solid. ¹H NMR (CDCl₃, 400 MHz): δ 7.82 (d, J = 7.2 Hz, 1H), 7.30 – 7.43 (m, 8H), 7.20 – 7.27 (m, 5H), 7.12 – 7.17 (m, 1H), 7.08 (d, J = 2.4 Hz, 1H), 3.57 (d, J = 4.1 Hz, 1H), 3.27 (d, J = 4.1 Hz, 1H), 2.70 (s, 3H), 1.81 (s, 3H), 1.79 (s, 3H), 1.78 (s, 3H), 1.69 (s, 3H), 1.22 (s, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ 152.03, 151.10, 149.74, 146.07, 143.65, 141.71, 137.16, 134.63, 130.40, 129.69, 128.49, 127.79, 127.69, 126.73, 126.05, 125.99, 125.41, 125.31, 125.12, 96.52, 83.13, 56.13, 42.70, 42.38, 31.27, 31.02, 29.42, 24.80, 24.58.

[0327] 2',2'''-(Pyridine-2,6-diyl)bis(3,5-bis(2-phenylpropan-2-yl)-[1,1'-biphenyl]-2-ol) (VV)



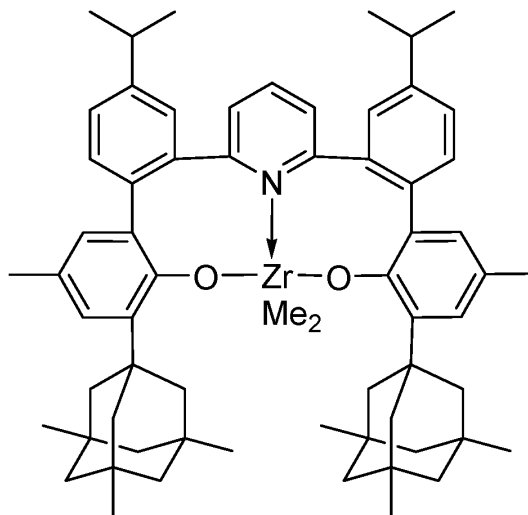
To a solution of 3.63 g (6.30 mmol) of 2-(2'-(methoxymethoxy)-3',5'-bis(2-phenylpropan-2-yl)-[1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (UU) in 14 ml of 1,4-dioxane, 745 mg (3.15 mmol) of 2,6-dibromopyridine, 5.13 g (15.8 mmol) of cesium carbonate, and 7 ml of water were subsequently added. The mixture obtained was purged with argon for 10 minutes followed by addition of 315 mg (0.315 mmol) of Pd(PPh₃)₄. This mixture was stirred for 12 hours at 100°C, then cooled to room temperature, and diluted with 50 ml of water. The obtained mixture was extracted with dichloromethane (3 x 50 ml), the combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. To the resulting oil 30 ml of THF, 30 ml of methanol, and 2 ml of 12N HCl were subsequently added. The reaction mixture was stirred overnight at 60°C and then poured into 500 ml of water. The obtained mixture was extracted with dichloromethane (3 x 35 ml), the combined organic extract was washed with 5% NaHCO₃, dried over Na₂SO₄, and then evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μ m, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 2.22 g (79%) of a mixture of two isomers as a white foam. ¹H NMR (CDCl₃, 400 MHz): δ 7.05 – 7.40 (m, 29H), 6.82 – 6.90 (m, 2H), 6.73 (d, J = 7.8 Hz, 2H), 4.85 + 5.52 (s, 2H), 1.31 – 1.65 (m, 24H). ¹³C NMR (CDCl₃, 100 MHz) δ 158.02, 151.02 (broad), 149.77 (broad), 148.46 (broad), 141.56, 140.17 (broad), 136.75 (broad), 134.89 (broad), 131.31 (broad), 130.62 (broad), 128.32, 128.23, 127.78, 127.72, 126.57, 125.71, 125.61, 125.33, 124.68 (broad), 122.22 (broad), 42.39 (broad), 41.99, 30.97 (broad), 30.77 (broad), 29.53 (broad), 29.34 (broad).

[0328] Dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 40)



To a suspension of 120 mg (0.375 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 530 μ l (1.54 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 330 mg (0.375 mmol) of 2',2'''-(pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (K) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 272 mg (67%) of a white-beige solid. Anal. Calc. for C₆₅H₈₁HfNO₂: C, 71.83; H, 7.51; N, 1.29. Found: C 72.08; H, 7.82; N 1.15. ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.77 (t, J = 7.8 Hz, 1H), 7.42 (dd, J = 8.1, 1.7 Hz, 2H), 7.17 (d, J = 8.1, 2H), 7.16 (d, J = 7.8 Hz, 2H), 7.02 (d, J = 1.9 Hz, 2H), 6.80 (d, J = 1.5 Hz, 2H), 6.58 (d, J = 1.6 Hz, 2H), 3.30 (sept, J = 6.9 Hz, 2H), 2.20 (s, 6H), 1.64 – 1.71 (m, 6H), 1.50 – 1.57 (m, 6H), 1.30 (d, J = 6.9 Hz, 6H), 1.20 (d, J = 6.9 Hz, 6H), 1.14 – 1.21 (m, 6H), 0.97 – 1.04 (m, 6H), 0.83 (s, 18H), -0.59 (s, 6H). ¹³C NMR (CD₂Cl₂, 100 MHz) δ 159.7, 159.2, 148.8, 140.2, 140.1, 137.6, 133.8, 133.3, 132.4, 129.2, 129.0, 128.7, 127.8, 126.7, 124.8, 51.9, 50.9, 46.5, 40.3, 33.4, 32.5, 30.1, 24.3, 23.5, 21.0.

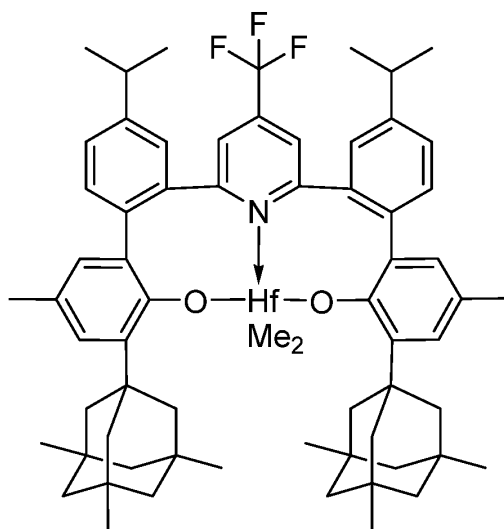
[0329] Dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 41)



To a suspension of 88 mg (0.375 mmol) of zirconium tetrachloride in 50 ml of dry toluene, 530 μ l (1.54 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe

at -30°C. To the resulting suspension, 330 mg (0.375 mmol) of 2',2'''-(pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (K) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 217 mg (58%) of a beige solid. Anal. Calc. for C₆₅H₈₁ZrNO₂: C, 78.10; H, 8.17; N, 1.40. Found: C 78.42; H, 8.35; N 1.23. ¹H NMR (CD₂Cl₂, 400 MHz): 7.77 (t, J = 7.8 Hz, 1H), 7.41 (dd, J = 8.1, 1.7 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 2.0 Hz, 2H), 6.78 (d, J = 1.6 Hz, 2H), 6.58 (d, J = 1.6 Hz, 2H), 3.02 (sept, J = 6.8 Hz, 2H), 2.20 (s, 6H), 1.67 – 1.74 (m, 6H), 1.53 – 1.60 (m, 6H), 1.29 (d, J = 6.8 Hz, 6H), 1.19 (d, J = 6.8 Hz, 6H), 1.13 – 1.19 (m, 6H), 0.97 – 1.04 (m, 6H), 0.83 (s, 18H), -0.36 (s, 6H). ¹³C NMR (CD₂Cl₂, 100 MHz) δ 159.4, 159.3, 148.8, 140.2, 140.0, 137.1, 134.1, 133.2, 132.7, 129.3, 128.9, 128.6, 127.7, 126.8, 124.4, 50.9, 46.6, 43.8, 40.4, 33.3, 32.5, 31.0, 24.4, 23.4, 21.0.

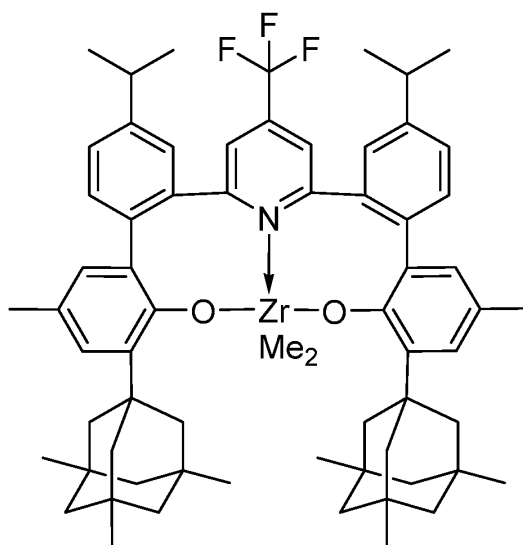
[0330] Dimethylhafnium[2',2'''-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 42)



20

To a suspension of 135 mg (0.422 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 600 µl (1.73 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 400 mg (0.422 mmol) of 2',2'''-(4-

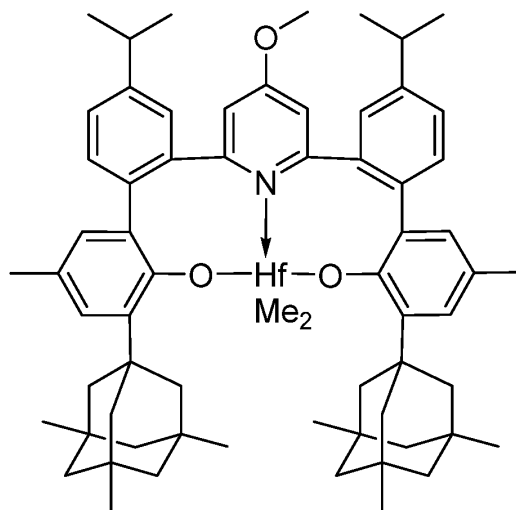
- (trifluoromethyl)pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (M) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 317 mg (65%) of a yellow solid. Anal. Calc. for C₆₆H₈₀F₃HfNO₂: C, 68.64; H, 6.98; N, 1.21. Found: C 68.87; H, 7.13; N 1.05. ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.19 – 7.29 (m, 6H), 7.11 (s, 2H), 6.98 (d, J = 1.5 Hz, 2H), 6.71 (d, J = 1.6 Hz, 2H), 3.06 (sept, J = 6.9 Hz, 2H), 2.20 (s, 6H), 1.91 – 1.97 (m, 6H), 1.76 – 1.82 (m, 6H), 1.27 – 1.34 (m, 6H), 1.28 (d, J = 6.9 Hz, 6H), 1.18 (d, J = 6.9 Hz, 6H), 1.05 – 1.10 (m, 6H), 0.98 (s, 18H), 0.04 (s, 6H). ¹³C NMR (C₆D₆, 100 MHz) δ 161.4, 160.1, 149.1, 140.7, 138.1, 134.1, 133.4, 132.3, 129.9, 129.4, 128.5, 127.4, 120.4 (q, J_{C,F} = 3.3 Hz), 53.5, 51.0, 46.9, 40.7, 33.7, 32.7, 31.4, 24.7, 23.7, 21.4.
- [0331] Dimethylzirconium[2',2'''-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 43)**



- To a suspension of 98 mg (0.422 mmol) of zirconium tetrachloride in 50 ml of dry toluene, 600 µl (1.73 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at -30°C. To the resulting suspension, 400 mg (0.422 mmol) of 2',2'''-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-

trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (M) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 390 mg (86%) of a yellow solid. Anal. Calc. for $C_{66}H_{80}F_3ZrNO_2$: C, 74.25; H, 7.55; N, 1.31. Found: C 74.46; H, 7.71; N 1.13. 1H NMR (C_6D_6 , 400 MHz): δ 7.22 – 7.35 (m, 8H), 7.02 (d, J = 1.7 Hz, 2H), 6.76 (d, J = 1.7 Hz, 2H), 3.12 (sept, J = 6.9 Hz, 2H), 2.26 (s, 6H), 2.00 – 2.07 (m, 6H), 1.84 – 1.91 (m, 6H), 1.34 – 1.40 (m, 6H), 1.33 (d, J = 6.9 Hz, 6H), 1.24 (d, J = 6.9 Hz, 6H), 1.10 – 1.17 (m, 6H), 1.04 (s, 18H), 0.33 (s, 6H). ^{13}C NMR (C_6D_6 , 100 MHz) δ 161.6, 159.7, 149.1, 140.6, 137.6, 134.0, 133.7, 132.6, 129.7, 129.5, 128.5, 127.5, 120.0 (q, $J_{C,F}$ = 3.5 Hz), 51.0, 46.9, 45.7, 40.8, 33.7, 32.7, 31.4, 24.7, 23.6, 21.4.

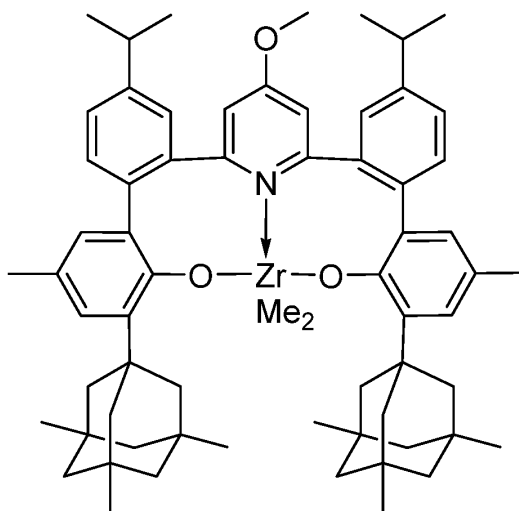
[0332] Dimethylhafnium[2',2'''-(4-(methoxy)pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 44)



To a suspension of 123 mg (0.384 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 540 μ l (1.58 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 350 mg (0.384 mmol) of 2',2'''-(4-(methoxy)pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (L) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined

organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 332 mg (77%) of a beige solid. Anal. Calc. for $C_{66}H_{83}HfNO_3$: C, 70.98; H, 7.49; N, 1.25. Found: C 71.28; H, 7.72; N 1.07. 1H NMR (C_6D_6 , 400 MHz): δ 7.28 – 7.32 (m, 4H), 7.22 (dd, J = 8.1, 1.9 Hz, 2H), 7.06 (d, J = 1.9 Hz, 2H), 6.78 (d, J = 2.0 Hz, 2H), 6.32 (s, 2H), 3.13 (sept, J = 6.9 Hz, 2H), 2.44 (s, 3H), 2.24 (s, 6H), 2.01 – 2.08 (m, 6H), 1.88 – 1.95 (m, 6H), 1.33 – 1.39 (m, 6H), 1.29 (d, J = 6.9 Hz, 6H), 1.22 (d, J = 6.9 Hz, 6H), 1.06 – 1.13 (m, 6H), 1.01 (s, 18H), 0.06 (s, 6H). ^{13}C NMR (C_6D_6 , 100 MHz) δ 168.0, 161.0, 160.5, 148.6, 138.1, 134.4, 134.1, 132.9, 129.6, 129.2, 128.3, 126.7, 111.0, 55.0, 52.8, 51.1, 47.0, 40.8, 33.6, 32.8, 31.4, 24.8, 23.7, 21.5.

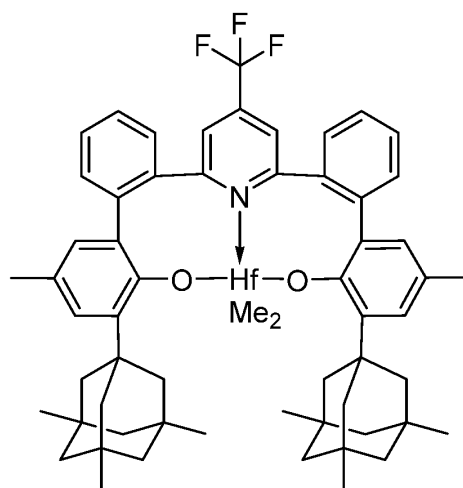
[0333] Dimethylzirconium[2',2'''-(4-(methoxy)pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 45)



To a suspension of 102 mg (0.439 mmol) of zirconium tetrachloride in 50 ml of dry toluene, 620 μ l (1.58 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at -30°C . To the resulting suspension, 400 mg (0.439 mmol) of 2',2'''-(4-(methoxy)pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (L) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of

n-hexane, and then dried *in vacuo*. Yield 334 mg (74%) of a beige solid. Anal. Calc. for $C_{66}H_{83}ZrNO_3$: C, 76.99; H, 8.13; N, 1.36. Found: C 77.28; H, 8.27; N 1.24. 1H NMR (C_6D_6 , 400 MHz): δ 7.28 – 7.32 (m, 4H), 7.19 – 7.24 (m, 2H), 7.04 (m, 2H), 6.78 (m, 2H), 6.32 (s, 2H), 3.12 (sept, $J = 6.8$ Hz, 2H), 2.45 (s, 3H), 2.23 (s, 6H), 2.04 – 2.13 (m, 6H), 1.90 – 1.99 (m, 6H), 1.32 – 1.41 (m, 6H), 1.28 (d, $J = 6.8$ Hz, 6H), 1.23 (d, $J = 6.8$ Hz, 6H), 1.07 – 1.13 (m, 6H), 1.01 (s, 18H), 0.29 (s, 6H). ^{13}C NMR (C_6D_6 , 100 MHz) δ 168.0, 161.2, 160.0, 148.6, 140.8, 137.6, 134.7, 134.0, 133.2, 129.7, 129.0, 128.3, 126.8, 110.6, 55.0, 51.1, 47.0, 44.5, 40.9, 33.6, 32.8, 31.4, 24.8, 23.6, 21.5.

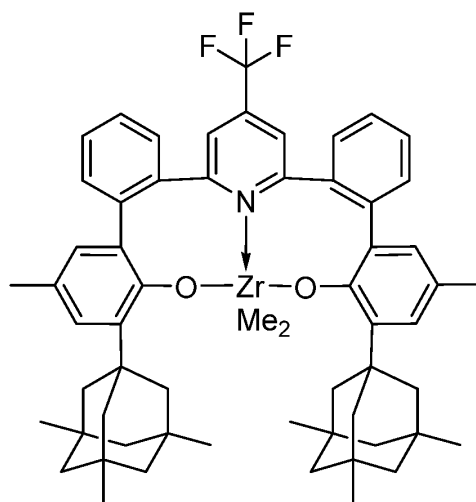
[0334] Dimethylhafnium[2',2'''-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 46)



To a suspension of 111 mg (0.347 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 490 μ l (1.43 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 300 mg (0.347 mmol) of 2',2'''-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (P) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 272 mg (73%) of a yellow solid. Anal. Calc. for $C_{60}H_{68}F_3HfNO_2$: C, 67.31; H, 6.40; N, 1.31. Found: C 67.66; H, 6.58; N 1.19. 1H NMR (CD_2Cl_2 , 400 MHz): 7.58 (td, $J = 7.6, 1.3$ Hz, 2H), 7.50 (td, $J = 7.5, 1.2$ Hz, 2H), 7.40

(s, 2H), 7.22 – 7.28 (m, 2H), 7.10 – 7.14 (m, 2H), 7.08 (d, J = 2.1 Hz, 2H), 6.63 (d, J = 1.8 Hz, 2H), 2.21 (s, 6H), 1.77 – 1.85 (m, 6H), 1.59 – 1.68 (m, 6H), 1.19 – 1.27 (m, 6H), 1.00 – 1.09 (m, 6H), 0.90 (s, 18H), -0.70 (s, 6H). δ ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 159.6, 159.4, 143.0, 138.0, 133.4, 132.2, 131.6, 129.9, 129.8, 128.9, 128.6, 127.2, 121.5, 50.9, 50.8, 47.0, 40.5, 32.7, 31.2, 21.0.

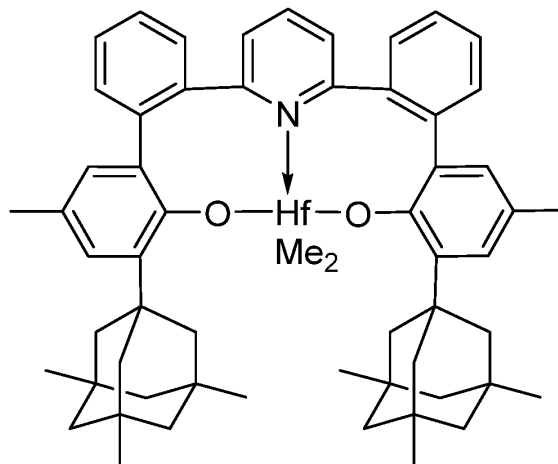
[0335] Dimethylzirconium[2',2'''-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 47)



To a suspension of 76 mg (0.324 mmol) of zirconium tetrachloride in 50 ml of dry toluene, 460 μl (1.33 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at -30°C . To the resulting suspension, 280 mg (0.324 mmol) of 2',2'''-(4-(trifluoromethyl)pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (P) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 256 mg (80%) of a yellow solid. Anal. Calc. for $\text{C}_{60}\text{H}_{68}\text{F}_3\text{ZrNO}_2$: C, 73.28; H, 6.97; N, 1.42. Found: C 73.62; H, 7.17; N 1.19. ^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.56 (td, J = 7.6, 1.3 Hz, 2H), 7.48 (td, J = 7.5, 1.2 Hz, 2H), 7.38 (s, 2H), 7.24 – 7.29 (m, 2H), 7.05 – 7.12 (m, 4H), 6.63 (d, J = 2.0 Hz, 2H), 2.21 (s, 6H), 1.79 – 1.86 (m, 6H), 1.62 – 1.69 (m, 6H), 1.19 – 1.27 (m, 6H), 1.00 – 1.09 (m, 6H), 0.89 (s, 18H), -0.45

(s, 6H). ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 160.0, 158.9, 142.9, 137.4, 133.3, 132.6, 132.4, 131.5, 129.8, 129.7, 128.9, 128.6, 127.3, 121.0, 50.9, 47.0, 42.9, 40.6, 32.7, 31.2, 21.0.

[0336] Dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 48)

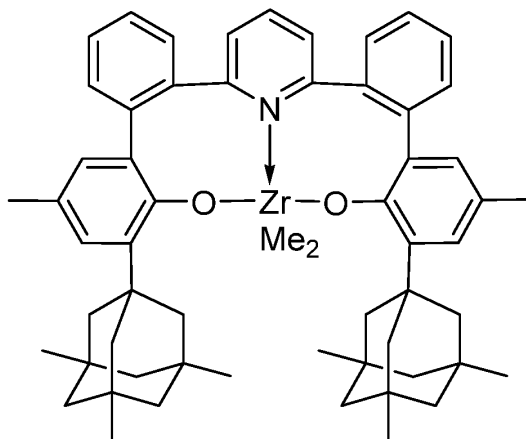


5

To a suspension of 121 mg (0.377 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 530 μl (1.54 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C . To the resulting suspension, 300 mg (0.377 mmol) of 2',2'''-(pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (N) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 254 mg (67%) of a white-beige solid. Anal. Calc. for $\text{C}_{59}\text{H}_{69}\text{HfNO}_2$: C, 70.67; H, 6.94; N, 1.40. Found: C 70.83; H, 7.12; N 1.31. ^1H NMR (C_6D_6 , 400 MHz): δ 7.36 (td, $J = 7.3, 2.0$ Hz, 2H), 7.30 (d, $J = 2.2$ Hz, 2H), 7.15 – 7.25 (m, 4H), 7.10 (d, $J = 7.8$ Hz, 2H), 6.73 (d, $J = 2.3$ Hz, 2H), 6.38 – 6.48 (m, 3H), 2.21 (s, 6H), 2.02 – 2.09 (m, 6H), 1.85 – 1.92 (m, 6H), 1.30 – 1.39 (m, 6H), 1.03 – 1.10 (m, 6H), 1.01 (s, 18H), -0.13 (s, 6H).

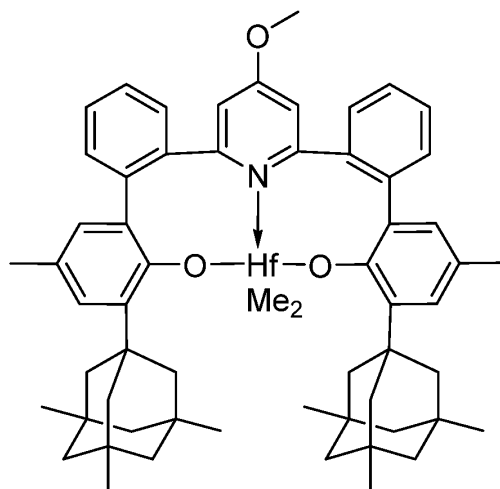
20

[0337] Dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 49)



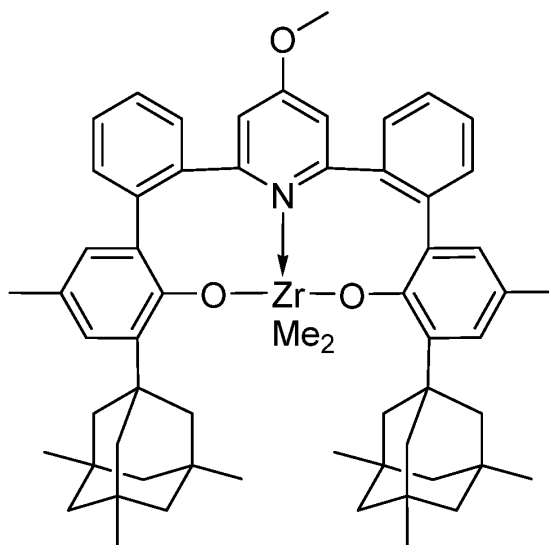
To a suspension of 88 mg (0.375 mmol) of zirconium tetrachloride in 50 ml of dry toluene, 530 μ l (1.54 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at -30°C . To the resulting suspension, 330 mg (0.375 mmol) of 2',2'''-(pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (N) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 217 mg (58%) of a beige solid. Anal. Calc. for $\text{C}_{59}\text{H}_{69}\text{ZrNO}_2$: C, 77.41; H, 7.60; N, 1.53. Found: C 77.75; H, 7.73; N 1.38. ^1H NMR (C_6D_6 , 400 MHz): δ 7.34 (td, $J = 7.5, 1.5$ Hz, 2H), 7.29 (d, $J = 2.3$ Hz, 2H), 7.13 – 7.24 (m, 4H), 7.04– 7.09 (m, 2H), 6.73 (d, $J = 2.3$ Hz, 2H), 6.38 – 6.50 (m, 3H), 2.21 (s, 6H), 2.04 – 2.12 (m, 6H), 1.87 – 1.94 (m, 6H), 1.31 – 1.38 (m, 6H), 1.04 – 1.10 (m, 6H), 1.01 (s, 18H), 0.11 (s, 6H). ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 159.1, 158.2, 142.9, 140.1, 137.4, 133.4, 133.1, 132.9, 130.9, 129.9, 129.6, 128.9, 128.2, 126.8, 124.9, 50.9, 47.0, 42.1, 40.5, 32.7, 31.2, 21.0.

[0338] Dimethylhafnium[2',2'''-(4-(methoxy)pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 50)



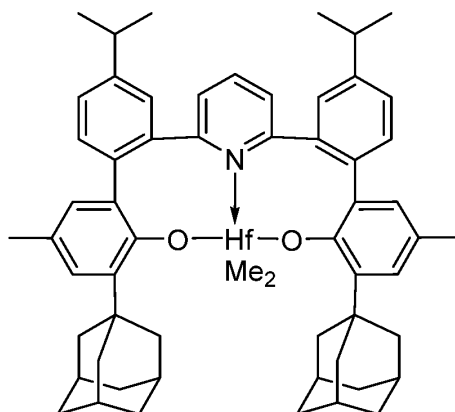
To a suspension of 97 mg (0.302 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 430 μ l (1.24 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 250 mg (0.302 mmol) of 2',2'''-(4-(methoxy)pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (O) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 247 mg (80%) of a beige solid. Anal. Calc. for C₆₀H₇₁HfNO₃: C, 69.78; H, 6.93; N, 1.36. Found: C 69.97; H, 7.06; N 1.25. ¹H NMR (C₆D₆, 400 MHz): δ 7.38 (td, J = 7.6, 1.5 Hz, 2H), 7.31 (d, J = 2.6 Hz, 2H), 7.15 – 7.25 (m, 6H), 6.78 (d, J = 2.2 Hz, 2H), 6.13 (s, 2H), 2.45 (s, 3H), 2.22 (s, 6H), 2.05 – 2.13 (m, 6H), 1.87 – 1.97 (m, 6H), 1.33 – 1.40 (m, 6H), 1.05 – 1.11 (m, 6H), 1.02 (s, 18H), -0.11 (s, 6H).

[0339] Dimethylzirconium[2',2'''-(4-(methoxy)pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-olate)] (Complex 51)



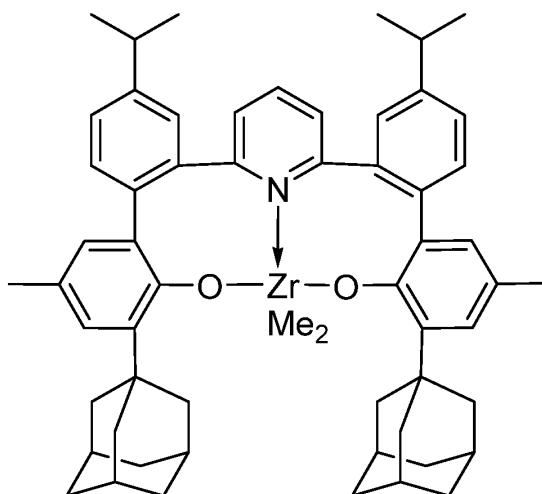
To a suspension of 102 mg (0.439 mmol) of zirconium tetrachloride in 50 ml of dry toluene, 620 μ l (1.58 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at -30°C . To the resulting suspension, 400 mg (0.439 mmol) of 2',2'''-(4-(methoxy)pyridine-2,6-diyl)bis(5-methyl-3-((3*r*,5*r*,7*r*)-3,5,7-trimethyladamantan-1-yl)-[1,1'-biphenyl]-2-ol) (O) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 334 mg (74%) of a beige solid. Anal. Calc. for $\text{C}_{60}\text{H}_{71}\text{ZrNO}_3$: C, 76.22; H, 7.57; N, 1.48. Found: C 76.51; H, 7.78; N 1.23. ^1H NMR (C_6D_6 , 400 MHz): δ 7.37 (td, $J = 7.5, 1.4$ Hz, 2H), 7.29 (d, $J = 2.3$ Hz, 2H), 7.12 – 7.20 (m, 6H), 6.78 (d, $J = 2.0$ Hz, 2H), 6.13 (s, 2H), 2.46 (s, 3H), 2.22 (s, 6H), 2.08 – 2.15 (m, 6H), 1.90 – 1.98 (m, 6H), 1.33 – 1.40 (m, 6H), 1.05 – 1.11 (m, 6H) < 1.02 (s, 18H), 0.13 (s, 6H).

[0340] Dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4'-isopropyl-5-methyl-[1,1'-biphenyl]-2-olate)] (Complex 52)



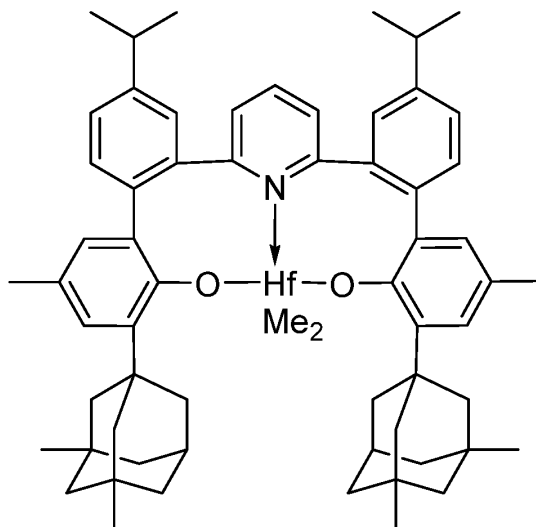
To a suspension of 161 mg (0.502 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 710 μ l (2.06 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 400 mg (0.502 mmol) of 2',2'''-(pyridine-2,6-diyl)bis(4'-isopropyl-5-methyl-3-((3*r*,5*r*,7*r*-adamantan-1-yl)-[1,1'-biphenyl]-2-ol) (Z) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 380 mg (76%) of a white solid. Anal. Calc. for C₅₉H₆₉HfNO₂: C, 70.67; H, 6.94; N, 1.40. Found: C 70.85; H, 7.05; N 1.31. ¹H NMR (C₆D₆, 400 MHz): δ 7.75 (t, J = 7.8 Hz, 1H), 7.45 (dd, J = 8.1, 1.8 Hz, 2H), 7.13-7.18 (m, 4H), 6.98 (d, J = 2.1 Hz, 2H), 6.92 (d, J = 1.7 Hz, 2H), 6.59 (d, J = 2.1 Hz, 2H), 2.96 (sept, J = 6.9 Hz, 2H), 2.19 (s, 6H), 2.17 – 2.22 (m, 6H), 2.04 – 2.13 (m, 6H), 1.95 – 2.05 (m, 6H), 1.75 – 1.84 (m, 6H), 1.65 – 1.74 (m, 6H), 1.33 (d, J = 6.9 Hz, 6H), 1.21 (d, J = 6.9 Hz, 6H), -0.71 (s, 6H). ¹³C NMR (C₆D₆, 100 MHz) δ 159.4, 158.2, 149.0, 140.7, 140.0, 138.7, 133.4, 132.81, 132.78, 129.6, 129.4, 128.0, 127.7, 126.8, 125.9, 50.0, 41.2, 37.6, 37.5, 33.7, 29.7, 26.3, 22.1, 21.0.

[0341] Dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*-adamantan-1-yl)-4'-isopropyl-5-methyl-[1,1'-biphenyl]-2-olate)] (Complex 53)

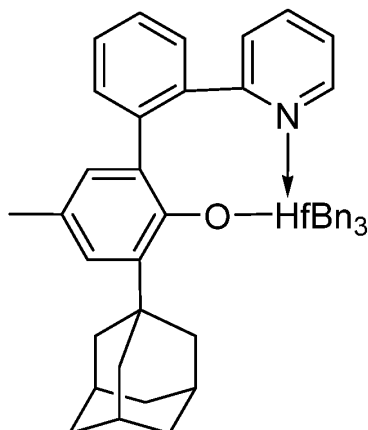


To a suspension of 102 mg (0.439 mmol) of zirconium tetrachloride in 50 ml of dry toluene, 620 μ l (1.58 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at -30°C . To the resulting suspension, 400 mg (0.439 mmol) of 2',2'''-(pyridine-2,6-diyl)bis(3-
 5 ((3*r*,5*r*,7*r*)-adamantan-1-yl)-4'-isopropyl-5-methyl-[1,1'-biphenyl]-2-ol) (Z) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained
 10 precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 334 mg (74%) of a beige solid. Anal. Calc. for $\text{C}_{59}\text{H}_{69}\text{ZrNO}_2$: C, 77.41; H, 7.60; N, 1.53. Found: C 77.74; H, 7.78; N 1.32. ^1H NMR (C_6D_6 , 400 MHz): δ 7.74 (t, $J = 7.8$ Hz, 1H), 7.44 (dd, $J = 8.1, 1.8$ Hz, 2H), 7.11 – 7.18 (m, 4H), 6.98 (d, $J = 2.0$ Hz, 2H), 6.90 (d, $J = 1.8$ Hz, 2H), 6.59 (d, $J = 1.7$ Hz, 2H), 2.94 (sept, $J = 6.9$ Hz, 2H), 2.19 (s, 6H), 2.18 – 2.27 (m, 6H),
 15 2.07 – 2.14 (m, 6H), 1.96 – 2.06 (m, 6H), 1.76 – 1.84 (m, 6H), 1.67 – 1.75 (m, 6H), 1.32 (d, $J = 6.9$ Hz, 6H), 1.20 (d, $J = 6.9$ Hz, 6H), -0.47 (s, 6H). ^{13}C NMR (C_6D_6 , 100 MHz) δ 158.9, 158.5, 148.9, 140.6, 140.0, 138.1, 133.3, 133.2, 133.1, 129.5, 129.46, 127.9, 127.6, 126.9, 125.4, 41.7, 41.2, 37.7, 37.5, 33.7, 29.7, 26.3, 22.1, 21.0.

[0342] Dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3-((1*r*,3*R*,5*S*,7*r*)-3,5-
 20 dimethyladamantan-1-yl)-4'-isopropyl-5-methyl-[1,1'-biphenyl]-2-olate)] (Complex 54)

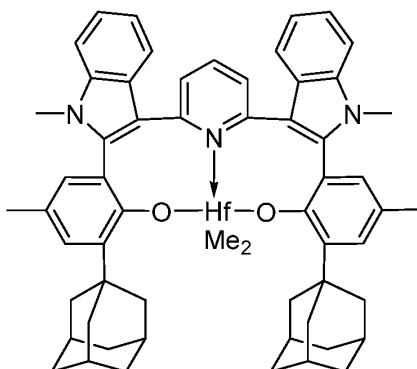


- To a suspension of 150 mg (0.469 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 663 μ l (1.92 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 400 mg (0.469 mmol) of 2',2''-(pyridine-2,6-diyl)bis(3-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4'-isopropyl-5-methyl-[1,1'-biphenyl]-2-ol) (W) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 375 mg (76%) of a white solid. Anal. Calc. for C₆₃H₇₇HfNO₂: C, 71.47; H, 7.33; N, 1.32. Found: C 71.74; H, 7.48; N 1.14. ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.75 (t, J = 7.8 Hz, 1H), 7.45 (dd, J = 8.1, 1.8 Hz, 2H), 7.14 – 7.18 (m, 4H), 7.00 (d, J = 2.1 Hz, 2H), 6.91 (d, J = 1.8 Hz, 2H), 6.59 (d, J = 1.7 Hz, 2H), 2.98 (sept, J = 6.9 Hz, 2H), 2.65 – 2.73 (m, 2H), 2.50 – 2.58 (m, 2H), 2.19 (s, 6H), 1.97 – 2.08 (m, 2H), 1.28 – 1.45 (m, 6H), 1.33 (d, J = 6.9 Hz, 6H), 1.21 (d, J = 6.9 Hz, 6H), 1.10 – 1.23 (m, 6H), 1.00 – 1.05 (m, 2H), 0.92 (s, 6H), 0.77 (s, 6H), -0.69 (s, 6H). ¹³C NMR (C₆D₆, 100 MHz) δ 159.4, 158.3, 149.0, 140.7, 140.0, 138.1, 133.4, 132.9, 132.7, 129.45, 129.43, 128.2, 127.7, 126.8, 125.8, 52.0, 50.4, 49.9, 45.9, 44.1, 42.6, 39.3, 38.6, 33.7, 32.2, 31.8, 31.6, 31.0, 30.5, 26.0, 22.4, 21.0.
- [0343] Tribenzylhafnium[3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5-methyl-2'-(pyridin-2-yl)-[1,1'-biphenyl]-2-olate] (Complex 55)**



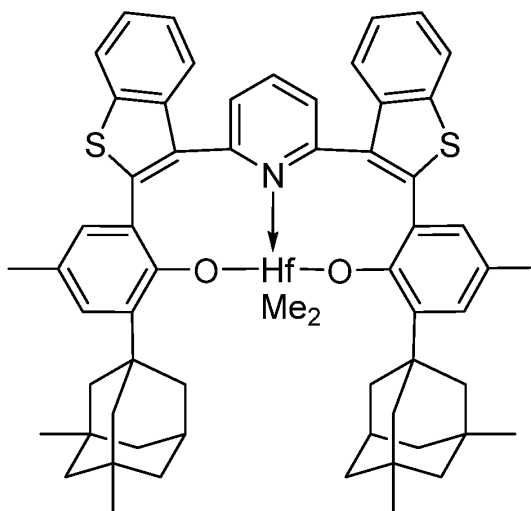
To a solution of 200 mg (0.505 mmol) of 3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5-methyl-2'-(pyridin-2-yl)-[1,1'-biphenyl]-2-ol (DD) in 50 ml of toluene, 274 mg (0.505 mmol) of tetrabenzylhafnium was added at room temperature. The resulting mixture was stirred overnight and then evaporated to dryness. The residue was triturated with 5 ml of n-pentane, the obtained precipitate was filtered off (G4), washed with 3 ml of n-pentane, and then dried *in vacuo*. Yield 288 mg (67%) of a light-yellow solid. Anal. Calc. for C₄₉H₄₉HfNO: C, 69.53; H, 5.84; N, 1.65. Found: C 69.78; H, 5.99; N 1.48. ¹H NMR (CD₂Cl₂, 400 MHz): δ 7.69 (d, J = 5.4 Hz, 1H), 7.12 – 7.19 (m, 6H), 7.11 (td, J = 7.6, 1.5 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 7.00 (td, J = 7.6, 1.5 Hz, 1H), 6.84 – 6.93 (m, 9H), 6.68 (d, J = 2.2 Hz, 1H), 6.35 – 6.47 (m, 2H), 6.20 – 6.27 (m, 1H), 6.05 (dd, J = 7.6, 1.0 Hz, 1H), 2.19 – 2.30 (m, 6H), 2.10 – 2.18 (m, 9H), 1.86 – 1.96 (m, 6H), 1.70 – 1.78 (m, 6H). ¹³C NMR (C₆D₆, 100 MHz) δ 159.4, 157.3, 148.1, 144.0, 143.8, 139.4, 138.8, 133.4, 132.8, 132.1, 132.0, 131.7, 129.1, 129.0, 128.7, 128.5, 127.9, 127.4, 123.9, 122.4, 82.6, 41.4, 37.8, 37.7, 29.9, 21.3.

[0344] Dimethylhafnium[6,6'-(pyridine-2,6-diylbis(1-methyl-1*H*-indole-3,2-diyl))bis(2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methylphenolate)] (Complex 56)



- To a suspension of 195 mg (0.611 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 860 μ l (2.50 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at -80°C. To the resulting suspension, 500 mg (0.611 mmol) of 6,6'-(pyridine-2,6-diylbis(1-methyl-1*H*-indole-3,2-diyl))bis(2-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methylphenol) (KK) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 394 mg (63%, ca. 80% purity) of a white solid. ¹H NMR (C₆D₆, 400 MHz): δ 7.20 – 7.30 (m, 6H), 7.09 – 7.15 (m, 4H), 6.75 – 6.81 (m, 3H), 6.48 (d, *J* = 2.2 Hz, 2H), 3.13 (s, 6H), 2.28 – 2.36 (m, 6H), 2.19 (s, 6H), 2.04 – 2.13 (m, 6H), 1.88 – 1.94 (m, 6H), 1.78 – 1.85 (m, 6H), 1.68 – 1.74 (m, 6H), -0.21 (s, 6H). ¹³C NMR (CD₂Cl₂, 100 MHz) δ 161.0, 154.3, 141.7, 140.3, 138.9, 129.8, 129.3, 128.1, 126.9, 126.6, 123.2, 122.2, 121.5, 119.0, 110.1, 107.0, 48.3, 40.8, 37.6, 37.3, 31.5, 29.4, 21.0.

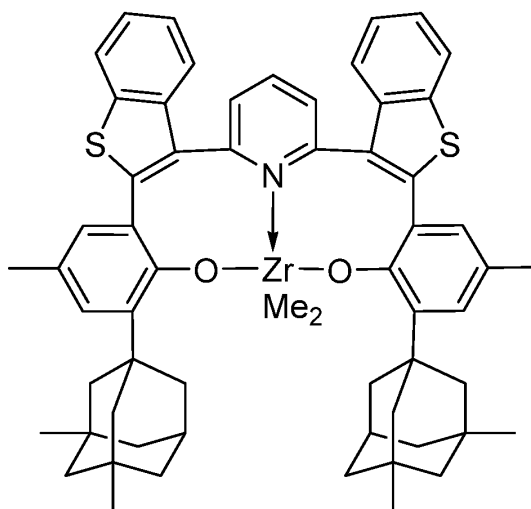
[0345] Dimethylhafnium[6,6'-(pyridine-2,6-diylbis(benzo[*b*]thiophene-3,2-diyl))bis(2-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-methylphenolate)] (Complex 57)



- To a suspension of 145 mg (0.454 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 640 μ l (1.86 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 400 mg (0.454 mmol) of 6,6'-(pyridine-2,6-diylbis(benzo[*b*]thiophene-3,2-diyl))bis(2-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-

methylphenol) (CC) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 337 mg (68%) of a beige solid. Anal. Calc. for $C_{61}H_{65}HfNO_2S_2$: C, 67.42; H, 6.03; N, 1.29. Found: C 67.64; H, 6.25; N 1.07. 1H NMR (C_6D_6 , 400 MHz): δ 7.34 – 7.38 (m, 2H), 7.28 (d, J = 2.2 Hz, 2H), 7.05 – 7.15 (m, 6H), 6.90 (d, J = 7.2 Hz, 2H), 6.67 (t, J = 7.6 Hz, 1H), 6.40 – 6.45 (m, 2H), 2.54 – 2.60 (m, 2H), 2.20 (s, 6H), 2.18 – 2.27 (m, 2H), 1.63 – 1.75 (m, 6H), 1.54 – 1.59 (m, 2H), 1.45 – 1.49 (m, 2H), 1.28 – 1.39 (m, 6H), 1.07 – 1.17 (m, 6H), 0.91 (s, 6H), 0.82 (s, 6H), 0.18 (s, 6H). ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 160.1, 154.5, 149.0, 141.3, 140.9, 140.3, 139.3, 134.4, 134.2, 130.7, 129.9, 127.0, 125.9, 125.7, 124.0, 122.8, 122.6, 51.8, 48.9, 45.7, 43.8, 42.4, 39.4, 38.4, 31.9, 31.6, 31.5, 30.9, 30.0, 21.0.

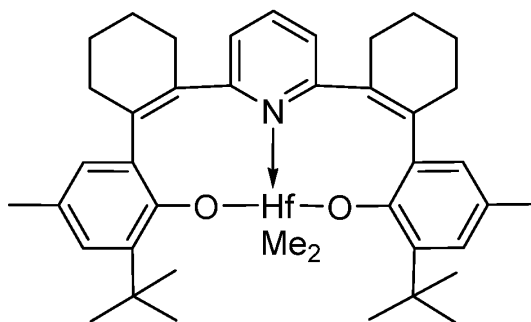
[0346] Dimethylzirconium[6,6'-(pyridine-2,6-diylbis(benzo[b]thiophene-3,2-diyl))bis(2-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-methylphenolate)] (Complex 58)



To a suspension of 80 mg (0.340 mmol) of zirconium tetrachloride in 50 ml of dry toluene, 480 μ l (1.40 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at $-30^\circ C$. To the resulting suspension, 300 mg (0.340 mmol) of 6,6'-(pyridine-2,6-diylbis(benzo[b]thiophene-3,2-diyl))bis(2-((1*r*,3*R*,5*S*,7*r*)-3,5-dimethyladamantan-1-yl)-4-methylphenol) (CC) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was

- extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 214 mg (63%) of a beige solid. Anal. Calc. for $C_{61}H_{65}ZrNO_2S_2$: C, 73.30; H, 6.56; N, 1.40. Found: C 73.54; H, 6.70; N 1.24. 1H NMR (C_6D_6 , 400 MHz): δ 7.32 – 7.37 (m, 2H), 7.28 (m, 2H), 7.08 – 7.16 (m, 6H), 6.87 – 6.92 (m, 2H), 6.67 (t, J = 8.0 Hz, 1H), 6.40 – 6.44 (m, 2H), 2.56 – 2.63 (m, 2H), 2.23 – 2.29 (m, 2H), 2.20 (s, 6H), 1.65 – 1.78 (m, 6H), 1.54 – 1.60 (m, 2H), 1.44 – 1.50 (m, 2H), 1.30 – 1.40 (m, 6H), 1.06 – 1.18 (m, 6H), 0.91 (s, 6H), 0.82 (s, 6H), 0.41 (s, 6H). ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 159.5, 154.7, 148.7, 141.3, 140.9, 140.2, 138.7, 134.3, 134.2, 130.7, 129.8, 127.2, 126.6, 125.9, 125.6, 122.8, 122.6, 51.8, 48.8, 45.8, 43.8, 42.4, 39.5, 38.5, 31.9, 31.6, 31.5, 30.9, 30.0, 21.0.

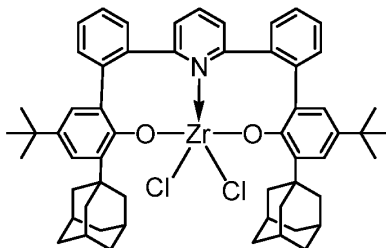
[0347] Dimethylhafnium[6',6'''-(pyridine-2,6-diyl)bis(3-(*tert*-butyl)-5-methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-olate)] (Complex 59)



- To a suspension of 91 mg (0.283 mmol) of hafnium tetrachloride (<0.05% Zr) in 50 ml of dry toluene, 400 μ l (1.17 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 160 mg (0.283 mmol) of 6',6'''-(pyridine-2,6-diyl)bis(3-(*tert*-butyl)-5-methyl-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-ol) (HH) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off (G4), washed with 2 x 5 ml of n-hexane, and then dried *in vacuo*. Yield 146 mg (67%, ca. 90% purity) of a white solid. 1H NMR (C_6D_6 , 400 MHz): δ 7.07 (d, J = 1.9 Hz, 2H), 6.62 (d, J = 2.2 Hz, 2H), 6.47 (t, J = 7.8 Hz, 1H), 6.19 (d, J = 7.8 Hz, 2H), 2.32 – 2.48 (m, 4H), 2.18 – 2.28 (m, 2H), 2.14 (s, 6H), 1.73 – 1.89 (m, 6H), 1.70 (s, 18H), 1.47 – 1.58 (m, 4H), 0.86 (s, 6H). ^{13}C NMR (CD_2Cl_2 , 100 MHz) δ 160.7, 158.2,

143.9, 140.5, 138.1, 134.3, 129.4, 126.9, 126.8, 123.6, 50.0, 35.4, 34.8, 31.6, 30.4, 22.8, 22.7, 21.0.

[0348] Dichlorozirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-olate)] (Complex 60)



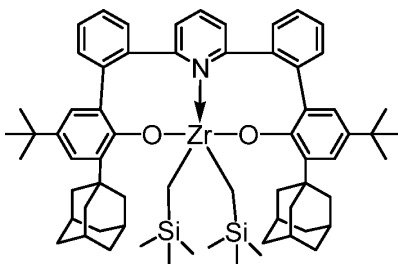
5

To a stirring suspension of dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-olate)] (Complex 6) (1.00 g, 1.09 mmol) in toluene (10 mL), ethylaluminum dichloride (2.4 mL, 1.0 M in hexane, 2.4 mmol, 2.2 equiv.) was added dropwise. The reaction was then stirred and heated to 60°C for 1 hour. Then, after removing from heat, the reaction was concentrated under a stream of nitrogen and then under high vacuum. The residue was stirred in hexane (10 mL). The resulting suspension was filtered over a plastic, fritted funnel. The filtered solid was washed with additional hexane (10 mL). The filtered solid was collected and concentrated under high vacuum to afford the product as a grey solid (0.99g, 95% yield). ¹H NMR (400 MHz, CD₂Cl₂): δ 7.86 (t, 1H, *J* = 7.8 Hz), 7.65 (td, 2H, *J* = 7.6, 1.4 Hz), 7.46 (td, 2H, *J* = 7.6, 1.3 Hz), 7.35 (dd, 2H, *J* = 7.8, 1.2 Hz), 7.27 (d, 2H, *J* = 7.8 Hz), 7.25-7.20 (m, 4H), 6.91 (d, 2H, *J* = 2.5 Hz), 2.18-2.08 (m, 6H), 2.09-1.97 (m, 12H), 1.86 (br d, 6H, *J* = 12.0 Hz), 1.71 (br d, 6H, *J* = 12.0 Hz), 1.25 (s, 18H).

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[0349] Bis([trimethylsilyl]methyl)zirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-olate)] (Complex 61)

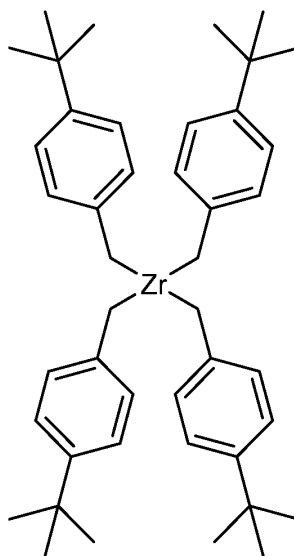


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To a stirring suspension of dichlorozirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-olate)] (Complex 60) (0.208 g, 0.218 mmol) in toluene (5mL), (trimethylsilyl)methylmagnesium chloride (1.1 mL, 1.0M in diethyl ether, 1.1 mmol, 5.1 equiv.) was added. The reaction was stirred at room temperature for 24 hours.

The reaction was then heated to 90°C and stirred for an additional 1.5 hours. The reaction was removed from heat, and the contents were subsequently concentrated under a stream of nitrogen and then under high vacuum. The residue was washed with hexane (10mL) and filtered over Celite. The filtered solid was extracted with toluene (3 × 3mL). The combined toluene filtrates were concentrated under a stream of nitrogen at 90°C and then under high vacuum to afford a fraction of the product as an off-white foam (0.150g, 65% yield). The original hexane filtrate was concentrated under a stream of nitrogen and then under high vacuum. The residue, a brown oil, was mixed with hexane (2mL) and cooled to −35°C. The resulting precipitate was filtered, while cold, on a plastic, fritted funnel. The filtered solid was collected and concentrated under high vacuum to afford a separate fraction of the product (0.030g, 13% yield). ¹H NMR (400 MHz, C₆D₆): δ 7.54 (d, 2H, *J* = 2.6 Hz), 7.46 (dd, 2H, *J* = 7.7, 1.2 Hz), 7.27 (td, 2H, *J* = 7.6, 1.4 Hz), 7.14-6.99 (m, 4H), 6.97 (dd, 2H, *J* = 7.6, 1.4 Hz), 6.45 (dd, 1H, *J* = 8.3, 7.1 Hz), 6.35-6.30 (m, 2H), 2.57 (br d, 6H, *J* = 12.1 Hz), 2.39 (br d, 6H, *J* = 12.1 Hz), 2.22 (br s, 6H), 2.02 (br d, 6H, *J* = 12.1 Hz), 1.85 (br d, 6H, *J* = 12.1 Hz), 1.29 (s, 18H), 1.17 (d, 2H, *J* = 11.8 Hz), 0.21 (s, 18H), −1.57 (d, 2H, *J* = 11.8 Hz).

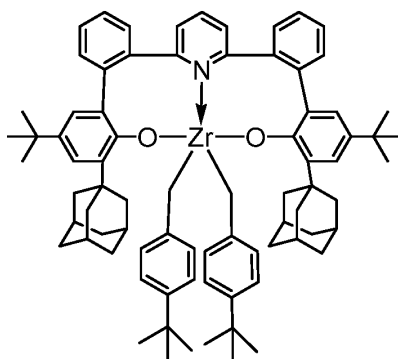
[0350] Tetrakis(4-*tert*-butylbenzyl)zirconium (Complex 62)



To a stirring suspension of zirconium chloride (0.290 g, 1.25 mmol) in dichloromethane (5mL) cooled to −70°C, a solution of 4-*tert*-butylbenzylmagnesium bromide (2.31 g, containing diethyl ether, 56.6% purity by mass, in 5 mL dichloromethane, approximately 1.04 M, 5.20 mmol, 4.18 equiv.) was added dropwise via addition funnel. The addition funnel was then removed, the reaction vessel was covered in foil to avoid light, and the reaction was stirred for

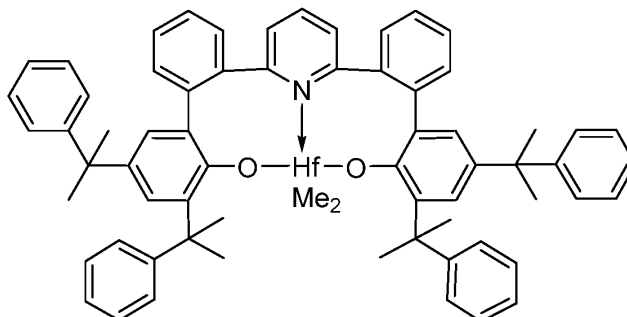
2 hours while slowly warming to room temperature. The reaction was filtered over Celite. The filtrate was concentrated under a stream of nitrogen and then under high vacuum. The residue was stirred in pentane. The resulting suspension was filtered on a plastic, fritted funnel. The filtered solid was collected and concentrated under high vacuum to afford the product as an orange-yellow solid, containing diethyl ether (1.74 equiv.) (0.973g, 96% yield).

[0351] Bis(4-*tert*-butylbenzyl)zirconium[2',2'''-(pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-olate)] (Complex 63)



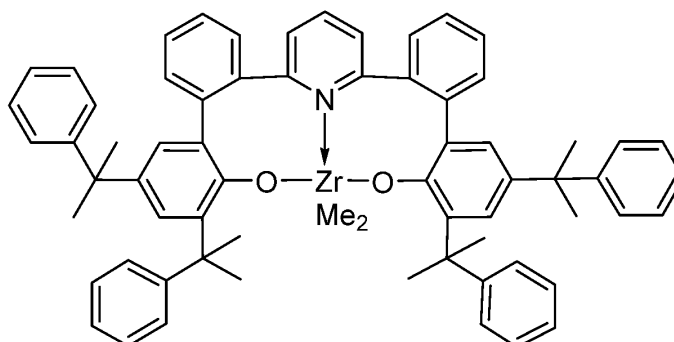
To a stirring solution of tetrakis(4-*tert*-butylbenzyl)zirconium (Complex 62) (0.171g, 0.251 mmol, 1 equiv.) in toluene (10mL), a solution of 2',2'''-(pyridine-2,6-diyl)bis(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-5-(*tert*-butyl)-[1,1'-biphenyl]-2-ol) (QQ) (0.200g, 0.251 mmol) in toluene (5mL) was added slowly. The reaction was stirred at room temperature for 4 hours. The reaction was filtered over Celite. The filtrate was concentrated under a stream of nitrogen and then under high vacuum. The residue was washed with pentane (5mL) and concentrated under high vacuum. The resulting solid was washed with minimal toluene and concentrated under high vacuum to afford the product as an off-white solid (0.108g, 36% yield). ¹H NMR (400 MHz, C₆D₆): δ 7.64 (d, 2H, *J* = 2.6 Hz), 7.53-7.47 (m, 2H), 7.15-6.95 (m, 12H), 6.78 (d, 4H, *J* = 8.2 Hz), 6.48 (dd, 1H, *J* = 8.4, 7.1 Hz), 6.38-6.34 (m, 2H), 2.53 (br d, 6H, *J* = 12.3 Hz), 2.45-2.35 (m, 8H), 2.22 (br s, 6H), 2.06 (br d 6H, *J* = 11.9 Hz), 1.86 (br d, 6H, *J* = 12.1 Hz), 1.32 (s, 18H), 1.29 (s, 18H), 0.19 (d, 2H, *J* = 11.2 Hz).

[0352] Dimethylhafnium[2',2'''-(pyridine-2,6-diyl)bis(3,5-bis(2-phenylpropan-2-yl)-[1,1'-biphenyl]-2-olate)] (Catalyst 64)

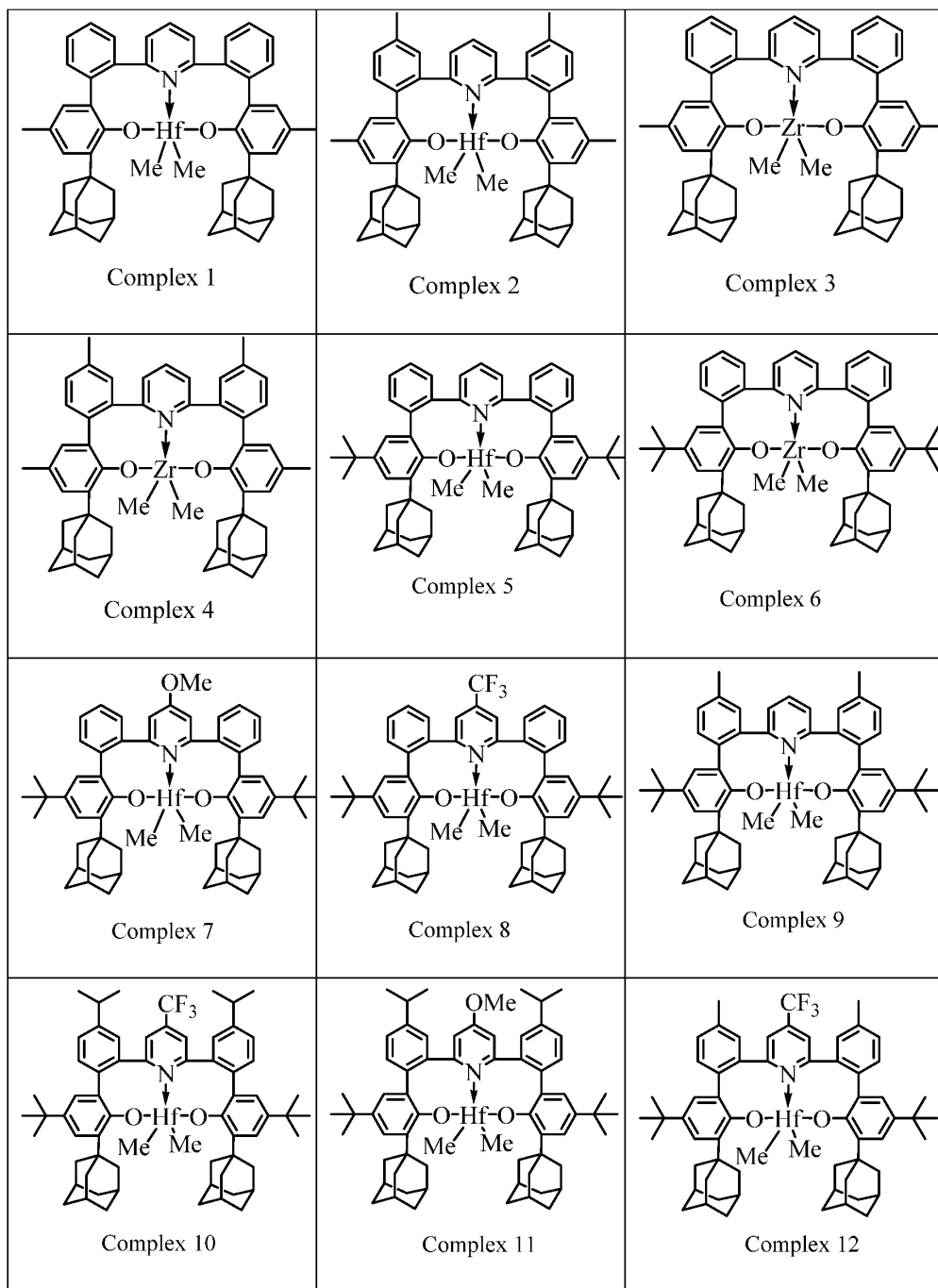


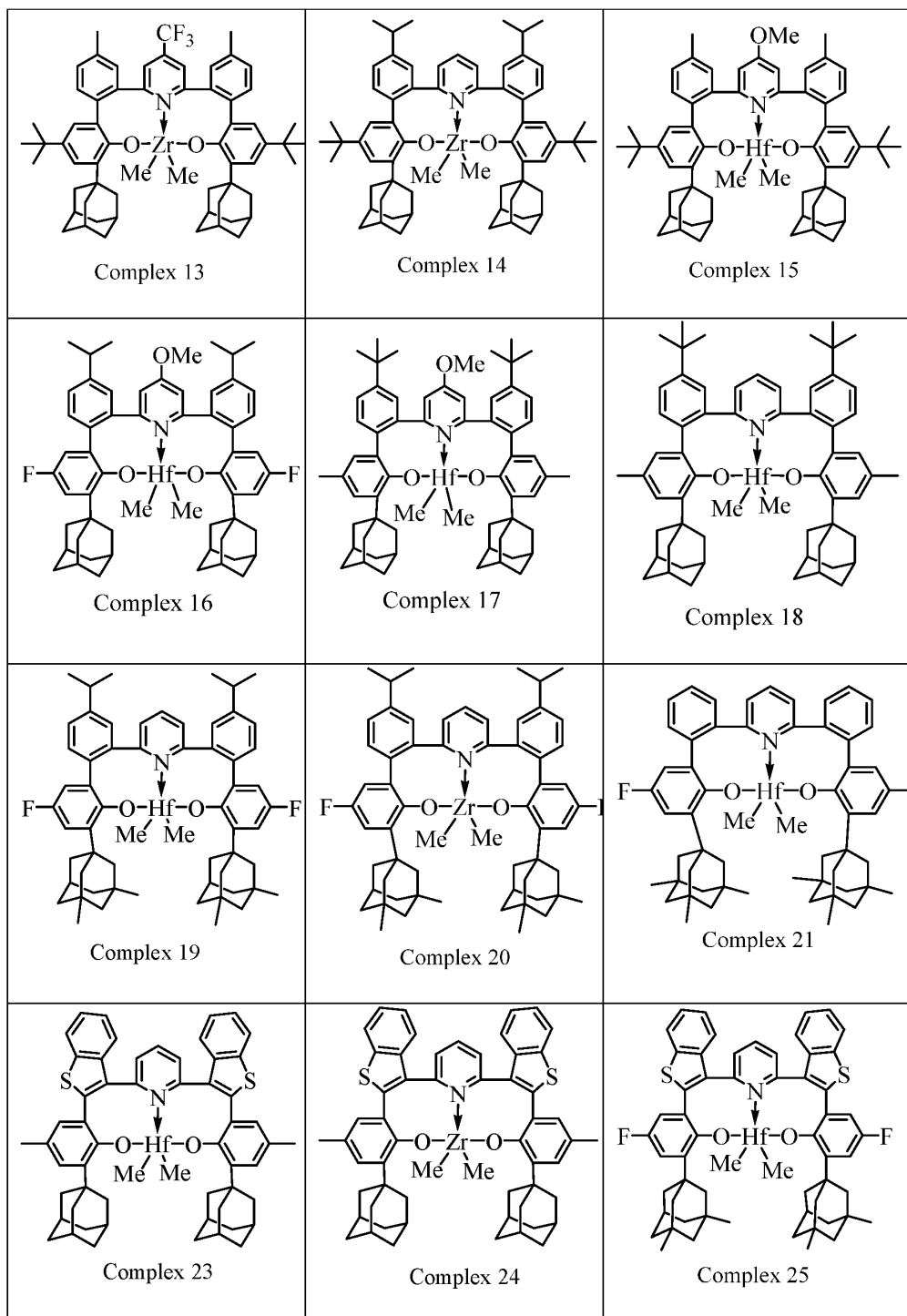
To a suspension of 144 mg (0.450 mmol) of hafnium tetrachloride in 50 mL of dry toluene, 698 μ L (2.03 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at 0°C. To the resulting suspension, 400 mg (0.450 mmol) of 2',2'''-(pyridine-2,6-diyl)bis(3,5-bis(2-phenylpropan-2-yl)-[1,1'-biphenyl]-2-ol) (VV) was immediately added in one portion. The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solid obtained was extracted with 2 x 20 mL of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 mL of n-hexane, the obtained precipitate was filtered off, washed with 2 x 5 mL of n-hexane, and then dried *in vacuo*. Yield 335 mg (68%) of a white-beige solid. Anal. Calc. for C₆₇H₆₅HfNO₂: C, 73.51; H, 5.98; N, 1.28. Found: C 73.85; H, 6.12; N 1.13. ¹H NMR (C₆D₆, 400 MHz): δ 7.33 – 7.35 (m, 6H), 7.23-7.24 (m, 4H), 7.03 – 7.20 (m, 15H), 6.98 (t, J = 7.2 Hz, 2H), 6.86 (d, J = 7.4 Hz, 2H), 6.58 (t, J = 7.6 Hz, 1H), 6.33 (d, J = 7.8 Hz, 2H), 1.96 (s, 6H), 1.76 (s, 6H), 1.61 (s, 6H), 1.60 (s, 6H), -0.74 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz) δ 158.12, 157.62, 151.61, 150.77, 142.27, 138.95, 138.69, 136.28, 132.75, 132.18, 131.68, 130.74, 127.67, 127.40, 126.91, 126.83, 126.65, 126.20, 125.21, 124.88, 48.42, 42.89, 42.32, 32.58, 30.96, 30.84, 28.46.

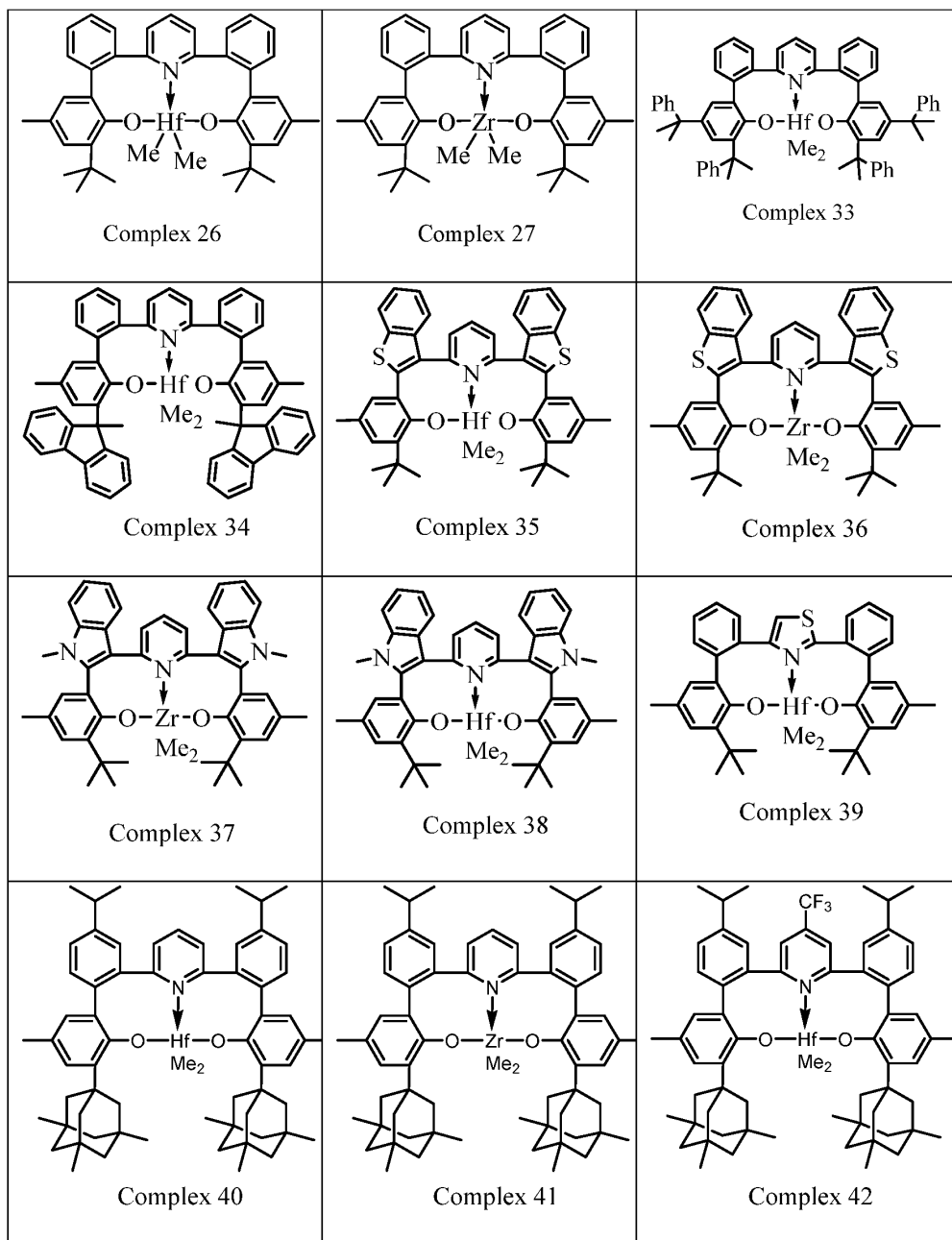
[0353] Dimethylzirconium[2',2'''-(pyridine-2,6-diyl)bis(3,5-bis(2-phenylpropan-2-yl)-[1,1'-biphenyl]-2-olate)] (Complex 65)

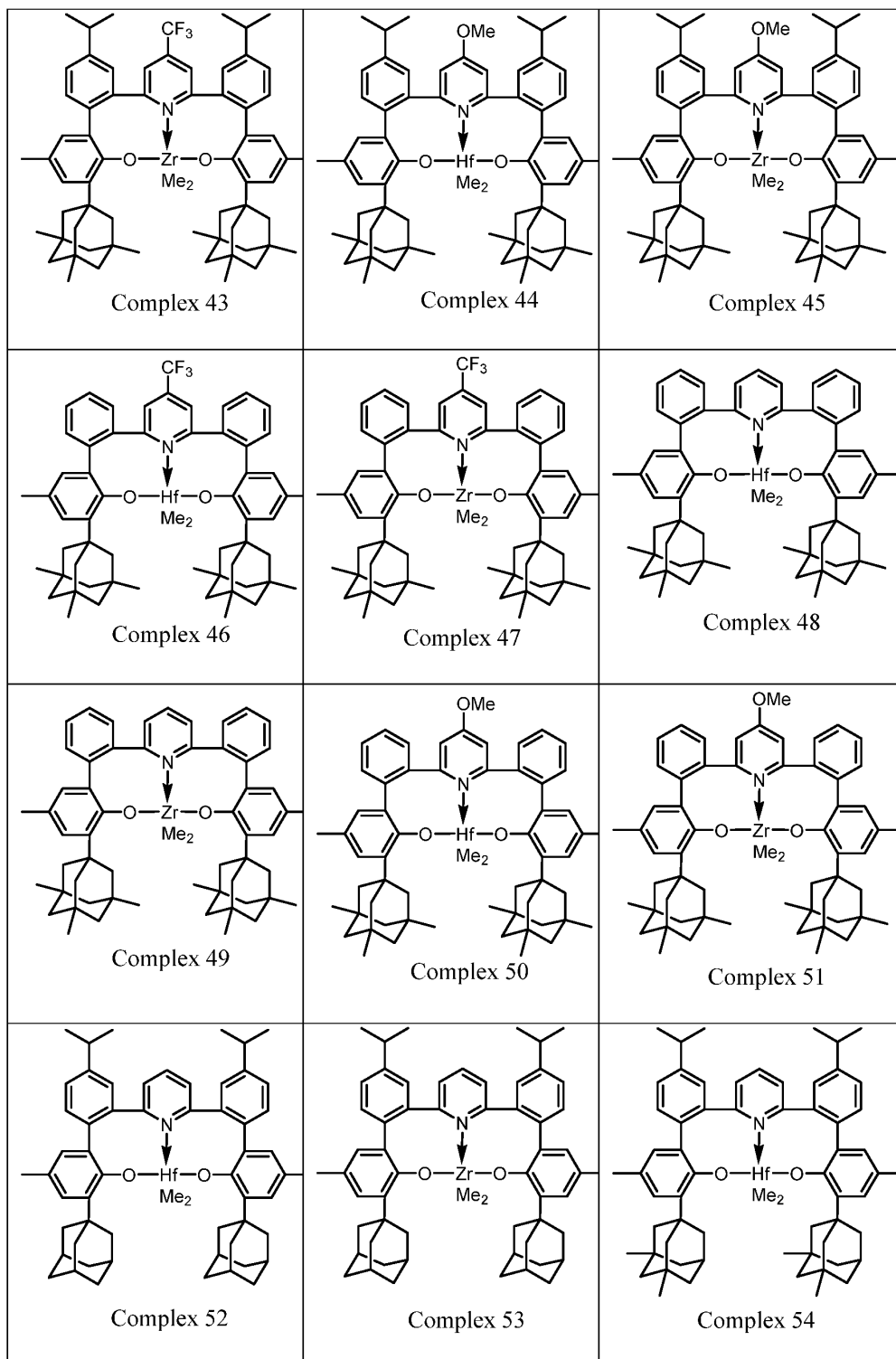


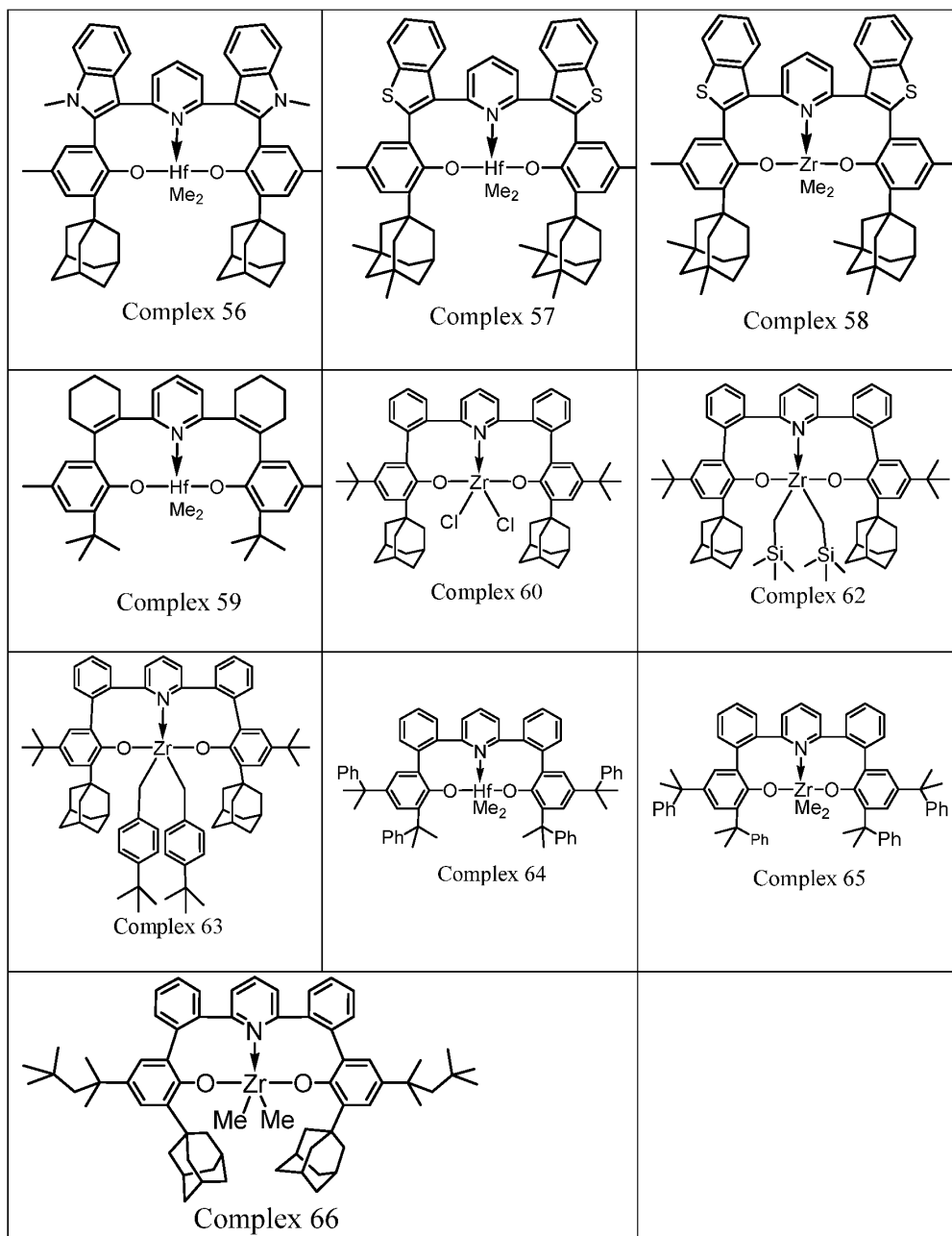
- To a suspension of 584 mg (2.50 mmol) of zirconium tetrachloride in 100 ml of dry toluene, 3.50 ml (10.2 mmol) of 2.9 M MeMgBr in diethyl ether was added in one portion via syringe at -40°C. To the resulting suspension, 2.22 g (2.50 mmol) of 2',2'''-(pyridine-2,6-diyl)bis(3,5-bis(2-phenylpropan-2-yl)-[1,1'-biphenyl]-2-ol) (VV) was immediately added in one portion.
- 5 The reaction mixture was stirred for 4 hours at room temperature and then evaporated to near dryness. The solids obtained were extracted with 2 x 30 ml of hot toluene, and the combined organic extract was filtered through a thin pad of Celite 503. Next, the filtrate was evaporated to dryness. The residue was triturated with 5 ml of n-hexane, the obtained precipitate was filtered off, washed two times with 5 ml of n-hexane, and then dried *in vacuo*. Yield 2.37 g
- 10 (94%) of a white-beige solid. Anal. Calc. for C₆₇H₆₅ZrNO₂: C, 79.88; H, 6.50; N, 1.39. Found: C 80.17; H, 6.71; N 1.34. ¹H NMR (C₆D₆, 400 MHz): δ 7.34 – 7.37 (m, 6H), 7.24 – 7.26 (m, 4H), 7.20 (dd, J = 7.7, 1.1 Hz, 2H), 7.12 – 7.19 (m, 8H), 7.02 – 7.10 (m, 8H), 6.97 (t, J = 7.3 Hz, 2H), 6.84 (dd, J = 7.4, 1.3 Hz, 2H), 6.59 (t, J = 7.7 Hz, 1H), 6.32 (d, J = 7.8 Hz, 2H), 1.97 (s, 6H), 1.75 (s, 6H), 1.62 (s, 6H), 1.61 (s, 6H), -0.49 (s, 6H).
- 15 **[0354]** The following transition metal complexes were used in polymerization experiments. Detailed synthetic procedures for some of the complexes can be found in following co-pending applications:
- 1) USSN 16/788,022, filed February 11, 2020;
 - 2) USSN 16/788,088, filed February 11, 2020;
 - 20 3) USSN 16/788,124, filed February 11, 2020;
 - 4) USSN 16/787,708, filed February 11, 2020; and
 - 5) concurrently filed PCT application number_____ entitled “Propylene Copolymers Obtained Using Transition Metal Bis(Phenolate) Catalyst Complexes and Homogeneous Process for Production Thereof” (attorney docket number **2020EM048**), which
- 25 claims priority to USSN 62/972,962, filed February 11, 2020.



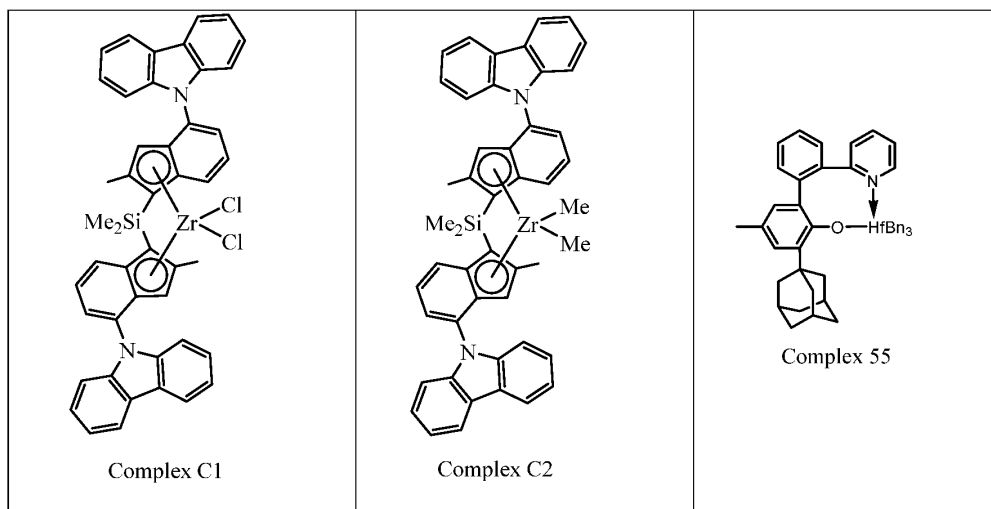








[0355] The following comparative complexes were used:



Small Scale Polymerizations:

[0356] Polymerization Reagents. Pre-catalyst solutions were made using a given transition metal complex dissolved in toluene (ExxonMobil Chemical-anhydrous, stored under N₂) (98%), typically at a concentration of 0.5 mmol/L. When noted, some complexes were pre-alkylated using methylalumoxane (MAO, 10 wt% in toluene available from Albemarle Corp.). Prealkylation was performed by first dissolving the metallocene complex in the appropriate amount of toluene, and then adding 20 equivalents of MAO to give final pre-catalyst solution concentrations of 0.5 mmol complex/L and 10 mmol MAO/L.

[0357] Activation of the complexes was performed using either methylalumoxane (Activator D, MAO, 10 wt% in toluene, Albemarle Corp.), dimethylanilinium tetrakis(perfluorophenyl)borate (Activator A, Boulder Scientific or W.R. Grace), triphenylcarbonium tetrakis(perfluorophenyl)borate (Activator B, Strem Chemical Co.), or dimethylanilinium tetrakis(perfluoronaphthalen-2-yl)borate (Activator C, W.R. Grace). MAO was typically used as a 0.5 wt% or 1.0 wt% toluene solution. Micromoles of MAO reported below are based on the micromoles of aluminum in MAO, which has a formula weight of 58.0 grams/mole. N,N-Dimethylanilinium tetrakis(perfluorophenyl)borate (A), triphenylcarbonium tetrakis(perfluorophenyl)borate (B), and N,N-dimethylanilinium tetrakis(perfluoronaphthalen-2-yl)borate (C) were typically used as a 5 mmol/L solution in toluene.

[0358] For polymerization runs using borate activators (A, B or C), tri-n-octylaluminum (TNOAL, neat, AkzoNobel) was also used as a scavenger prior to introduction of the activator

and metallocene complex into the reactor. TNOAL was typically used as a 5 mmol/L solution in toluene.

[0359] Solvents, polymerization grade toluene and/or isohexanes were supplied by ExxonMobil Chemical Co. and were purified by passage through a series of columns: two
5 500 cc OXYCLEAR cylinders in series from Labclear (Oakland, Calif.), followed by two 500 cc columns in series packed with dried 3 Å molecular sieves (8-12 mesh; Aldrich Chemical Company), and two 500 cc columns in series packed with dried 5 Å molecular sieves (8-12 mesh; Aldrich Chemical Company).

[0360] Polymerization grade propylene was purified by passage through a series of
10 columns: 2,250 cc OXICLEAR cylinder from Labclear followed by a 2,250 cc column packed with 3 Å molecular sieves (8-12 mesh; Aldrich Chemical Company), then two 500 cc columns in series packed with 5 Å molecular sieves (8-12 mesh; Aldrich Chemical Company), then a 500 cc column packed with SELEXSORB CD (BASF), and finally a 500 cc column packed with SELEXSORB COS (BASF).

15 [0361] 1-octene (C₈), 1-decene (C₁₀), 1-tetradecene (C₁₄) and 4-methyl-1-pentene (4MP1) were purified by degassing with nitrogen, stirring over Na/K, filtering through dry Celite, followed by column purification using Brockman basic alumina.

[0362] **Reactor Description and Preparation:** Polymerizations were conducted in an inert atmosphere (N₂) drybox using autoclaves equipped with an external heater for
20 temperature control, glass inserts (internal volume of reactor ~ 22.5 ml), septum inlets, a regulated supply of nitrogen, ethylene and propylene, and disposable PEEK mechanical stirrers (800 RPM). The autoclaves were prepared by purging with dry nitrogen at 110°C or 115°C for 5 hours and then at 25°C for 5 hours.

Propylene Polymerizations (PP):

25 [0363] The reactor was prepared as described above, heated to 40°C, and then purged with propylene gas at atmospheric pressure. For MAO-activated runs, toluene, MAO, propylene (1.0 ml unless otherwise listed in the tables) and comonomer (if used) were added via syringe. The reactor was then heated to process temperature (typically 70°C or 100°C unless otherwise mentioned) while stirring at 800 RPM. The pre-catalyst solution was added via syringe with
30 the reactor at process conditions. The reactor temperature was monitored and typically maintained within $\pm 1^\circ\text{C}$. Polymerizations were halted by addition of approximately 50 psi O₂/Ar (5 mole % O₂) or an air gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched based on a predetermined pressure loss of approximately 8 psi unless specified differently (max quench value in psi) or for a maximum of 30 minutes

polymerization time unless specified differently. The reactors were then cooled and vented. The polymers were isolated after solvent removal *in vacuo*. Actual quench times are reported. Quench times less than maximum reaction times indicate the reaction quenched with uptake. Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol metallocene complex per hour of reaction time (gP/mmol cat•hr). Propylene homopolymerization examples including characterization are summarized in Tables 1 to 4, and 9 below. Propylene copolymerization examples including characterization are summarized in Tables 9 and 10 below.

[0364] Small Scale Polymer Characterization. For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, Sigma-Aldrich, 99%) at 165°C in a shaker oven for approximately 3 hours. The typical concentration of polymer in solution was from 0.1 to 0.9 mg/ml with a BHT concentration of 1.25 mg BHT/ml of TCB. Samples were cooled to 135°C for testing.

[0365] High temperature size exclusion chromatography was performed using an automated "Rapid GPC" system as described in US Patents 6,491,816; 6,491,823; 6,475,391; 6,461,515; 6,436,292; 6,406,632; 6,175,409; 6,454,947; 6,260,407; and 6,294,388; each of which is incorporated herein by reference. Molecular weights (weight average molecular weight (Mw), number average molecular weight (Mn), z-average molecular weight (Mz)) and molecular weight distribution (PDI = MWD = Mw/Mn), which is also sometimes referred to as the polydispersity (PDI) of the polymer, were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with evaporative light scattering detector (ELSD) and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak Mw) between 5,000 and 3,390,000). Alternatively, samples were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with dual wavelength infrared detector and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak Mw) between 580 and 3,039,000). Samples (250 µL of a polymer solution in TCB were injected into the system) were run at an eluent flow rate of 2.0 ml/minute (135°C sample temperatures, 165°C oven/columns) using three Polymer Laboratories: PLgel 10µm Mixed-B 300 x 7.5mm columns in series. No column spreading corrections were employed. Numerical analyses were performed using Epoch® software available from Symyx Technologies or Automation Studio software available from Freeslate. The molecular weights obtained are relative to linear

polystyrene standards. Molecular weight data is reported in the Tables below under the headings Mn, Mw, Mz and PDI as defined above.

[0366] Differential Scanning Calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220°C for 15 minutes (first melt) and then allowed to cool to room temperature overnight. The samples were then heated to 220°C at a rate of 100°C/minute (2nd melt) and then cooled at a rate of 50°C/minute. Melting points were collected during the heating period. Values reported are the peak melting temperatures and for the purposes of this disclosure referred to as 2nd melts. The results are reported in the Tables under the heading, T_m.

10 [0367] **Table 1.** Propylene polymerization runs. Cat ID corresponds to the complex numbers indicated in the charts. Standard conditions include 1.1 equiv. activator when activator A, B or C used, or 500 equiv. activator when activator D is used. Activator IDs are [PhMe₂NH][B(C₆F₅)₄] is A where C₆F₅ is perfluorophenyl; [Ph₃C][B(C₆F₅)₄] is B; [PhMe₂NH][B(C₁₀F₇)₄] is C where C₁₀F₇ is perfluoronaphthalen-2-yl; and methylalumoxane
15 (MAO) is D. When activators A, B or C are used, 0.5 umol TnOAl (tri-n-octylaluminum) is used as a scavenger. 1 ml propylene and a total of 4.1 ml of solvents were used. The reaction was stirred at 800 rpm, and the reaction was quenched after 8 psi of pressure loss or a maximum of 30 minutes of reaction time is quench pressure not met.

[0368] **Table 9.** Propylene polymerization and co-polymerization runs. Cat ID corresponds to the complex numbers indicated in the charts. Standard conditions include 1.1 equiv. activator A, [PhMe₂NH][B(C₆F₅)₄], 1 ml propylene, 0, 100 or 200 ul of comonomer (1-octene, 1-decene or 1-tetradecene), 0.5 umol TnOAl (tri-n-octylaluminum) used as a scavenger, and 3.9-4.1 ml of solvent as indicated in the table. The reaction was carried out at 70°C and stirred at 800 rpm, and the reaction was quenched after 8 psi of pressure loss or a
25 maximum of 30 minutes of reaction time is quench pressure not met. If no T_m was reported in Table 9, the polymer was amorphous.

[0369] **Table 10.** Propylene co-polymerization runs using 4-methyl-1-pentene as the comonomer. Cat ID corresponds to the complex numbers indicated in the charts. Standard conditions include 1.1 equiv. activator A, [PhMe₂NH][B(C₆F₅)₄], 0.1 to 0.5 ml propylene (C₃)
30 as indicated in the table, 500 ul of 4-methyl-1-pentene, 0.5 umol TnOAl (tri-n-octylaluminum) used as a scavenger, and 4.1-4.5 ml of solvent as indicated in the table. The reaction was carried out at 100°C and stirred at 800 rpm, and the reaction was quenched after 8 psi of pressure loss or a maximum of 30 minutes of reaction time is quench pressure not met. The polymer produced were amorphous.

TABLE 1: Propylene homo-polymerizations

Ex#n	Cat-IDn	Act-IDn	Cat- (μmol) _n	iso- hexane- (μL) _n	Tol- ylene- (g) _n	T- (°C) _n	quench- time (s) _n	yield- (g) _n	Activity-(g- P/3000g- cat.hr) _n	$\bar{M}_w$ _n	$\bar{M}_{wH}$ _n	$\bar{M}_z$ _n	PD _n	T _m - (°C) _n
1a	1a	As	0.015a	3874a	226a	70a	73a	0.4563a	1,500,164a	114,466a	489,547a	1,650,145a	4.28a	159.3a
2a	1a	As	0.015a	3874a	226a	70a	85a	0.3556a	1,004,047a	140,999a	430,285a	1,428,541a	3.05a	159.0a
3a	1a	As	0.015a	3874a	226a	70a	107a	0.4111a	922,093a	24,847a	442,963a	1,925,442a	17.83a	156.6a
4a	1a	As	0.025a	3895a	205a	70a	45a	0.3795a	1,214,400a	78,229a	373,283a	1,617,577a	4.77a	157.6a
5a	1a	As	0.025a	3895a	205a	70a	59a	0.3355a	818,847a	96,301a	415,579a	1,697,802a	4.32a	157.4a
6a	1a	As	0.025a	3895a	205a	70a	52a	0.4031a	1,116,277a	84,820a	371,054a	1,348,438a	4.37a	156.9a
7a	1a	As	0.015a	3874a	226a	100a	55a	0.2204a	961,745a	75,757a	153,238a	419,644a	2.82a	150.4a
8a	1a	As	0.015a	3874a	226a	100a	44a	0.2229a	1,215,818a	75,647a	169,787a	606,761a	2.24a	158.4a
9a	1a	As	0.015a	3874a	226a	100a	46a	0.2208a	1,152,000a	80,499a	164,360a	471,760a	2.04a	157.6a
10a	1a	As	0.025a	3895a	205a	100a	24a	0.2518a	1,506,900a	51,229a	147,215a	576,352a	2.87a	157.1a
11a	1a	As	0.025a	3895a	205a	100a	30a	0.2502a	1,200,960a	50,400a	121,184a	346,391a	2.40a	157.1a
12a	1a	As	0.025a	3895a	205a	100a	26a	0.2602a	1,441,108a	38,370a	123,993a	441,392a	3.23a	156.9a
13a	2a	As	0.015a	3874a	226a	70a	75a	0.3729a	1,193,280a	125,777a	334,087a	1,073,650a	2.66a	160.7a
14a	2a	As	0.015a	3874a	226a	70a	80a	0.3253a	975,909a	165,597a	334,380a	903,938a	2.02a	160.6a
15a	2a	As	0.015a	3874a	226a	70a	75a	0.3297a	1,055,640a	114,722a	316,540a	1,030,692a	2.76a	160.4a
16a	2a	As	0.025a	3895a	205a	70a	62a	0.3619a	848,542a	60,069a	314,652a	1,329,302a	5.19a	159.3a
17a	2a	As	0.025a	3895a	205a	70a	57a	0.3694a	933,221a	111,718a	314,923a	1,136,460a	2.82a	159.1a
18a	2a	As	0.025a	3895a	205a	70a	58a	0.3826a	949,903a	103,234a	327,189a	1,166,677a	3.17a	158.5a
19a	2a	As	0.015a	3874a	226a	100a	59a	0.2647a	832,678a	61,125a	122,674a	253,423a	2.01a	160.7a
20a	2a	As	0.015a	3874a	226a	100a	54a	0.2662a	916,444a	62,140a	120,721a	248,648a	1.94a	160.6a
21a	2a	As	0.015a	3874a	226a	100a	62a	0.1908a	738,581a	60,611a	129,273a	256,101a	1.88a	160.2a
22a	2a	As	0.025a	3895a	205a	100a	64a	0.2433a	547,425a	53,787a	114,199a	333,094a	2.12a	158.9a
23a	2a	As	0.025a	3895a	205a	100a	40a	0.2190a	788,400a	59,497a	120,699a	312,369a	2.63a	158.4a
24a	2a	As	0.025a	3895a	205a	100a	35a	0.2276a	936,411a	56,450a	113,423a	298,556a	2.05a	158.3a
25a	3a	As	0.015a	3874a	226a	70a	14a	0.4037a	6,920,571a	67,290a	428,075a	1,753,319a	6.36a	148.1a
26a	3a	As	0.015a	3874a	226a	70a	15a	0.3543a	5,668,800a	57,753a	372,797a	1,464,190a	5.48a	147.5a
27a	3a	As	0.015a	3874a	226a	70a	13a	0.4127a	7,619,077a	64,376a	502,821a	2,141,863a	7.81a	147.3a
28a	3a	As	0.025a	3895a	205a	70a	9a	0.4117a	6,587,209a	47,260a	341,788a	1,130,024a	7.23a	146.4a
29a	3a	As	0.025a	3895a	205a	70a	12a	0.3839a	4,678,800a	30,862a	378,082a	1,226,563a	12.28a	145.3a
30a	3a	As	0.025a	3895a	205a	70a	18a	0.4025a	3,220,500a	49,716a	337,334a	1,045,032a	6.79a	144.9a
31a	3a	As	0.015a	3874a	226a	100a	20a	0.2250a	2,644,800a	48,586a	169,097a	624,268a	3.48a	147.0a
32a	3a	As	0.015a	3874a	226a	100a	18a	0.2821a	3,931,500a	28,782a	152,097a	646,846a	5.29a	145.8a
33a	3a	As	0.015a	3874a	226a	100a	17a	0.3151a	4,435,471a	34,553a	158,815a	595,846a	4.81a	145.8a
34a	3a	As	0.025a	3895a	205a	100a	19a	0.2373a	1,798,484a	52,628a	157,472a	494,188a	2.99a	146.6a
35a	3a	As	0.025a	3895a	205a	100a	12a	0.3252a	3,914,400a	18,362a	116,170a	578,848a	6.43a	143.9a
36a	4a	As	0.015a	3874a	226a	70a	29a	0.3914a	3,229,172a	18,581a	174,783a	1,115,891a	9.42a	150.9a
37a	4a	As	0.015a	3874a	226a	70a	24a	0.4204a	4,504,000a	27,130a	162,271a	999,810a	6.98a	150.6a
38a	4a	As	0.015a	3874a	226a	70a	23a	0.3712a	3,073,391a	17,744a	128,712a	777,532a	7.14a	150.3a
39a	4a	As	0.025a	3895a	205a	70a	17a	0.4162a	3,625,459a	11,852a	125,480a	517,409a	9.06a	149.0a
40a	4a	As	0.025a	3895a	205a	70a	15a	0.4075a	3,912,000a	22,516a	144,647a	758,294a	6.42a	148.8a
41a	4a	As	0.015a	3874a	226a	100a	25a	0.2923a	2,804,160a	15,017a	49,959a	158,779a	3.20a	140.9a
42a	4a	As	0.015a	3874a	226a	100a	23a	0.2986a	3,115,820a	14,340a	52,186a	182,311a	3.64a	148.9a
43a	4a	As	0.015a	3874a	226a	100a	19a	0.2991a	4,485,500a	12,896a	47,275a	197,729a	3.72a	147.4a
44a	4a	As	0.025a	3895a	205a	100a	9a	0.2473a	5,935,200a	19,080a	38,235a	113,476a	3.79a	146.9a
45a	4a	As	0.025a	3895a	205a	100a	10a	0.3095a	4,495,800a	12,330a	38,756a	113,564a	3.14a	146.0a
46a	4a	As	0.025a	3895a	205a	100a	10a	0.3071a	4,432,240a	8,151a	33,301a	109,122a	4.00a	145.8a
47a	5a	As	0.015a	3874a	226a	50a	65a	0.3110a	1,148,308a	362,503a	836,901a	2,313,280a	2.31a	161.1a
48a	5a	As	0.020a	3022a	256a	50a	41a	0.3343a	1,487,669a	323,213a	823,430a	2,436,278a	2.54a	160.5a
49a	5a	As	0.015a	3874a	226a	60a	77a	0.3518a	1,095,518a	221,689a	571,824a	1,714,974a	2.68a	152.8a
50a	5a	As	0.020a	3032a	260a	50a	62a	0.3572a	1,037,032a	187,965a	630,465a	2,287,541a	3.36a	156.4a
51a	5a	As	0.015a	3874a	226a	70a	58a	0.3295a	1,345,339a	165,932a	393,075a	1,312,570a	2.62a	159.1a
52a	5a	As	0.015a	3874a	226a	70a	68a	0.3641a	1,285,059a	148,071a	394,359a	1,105,989a	2.68a	158.8a
53a	5a	As	0.015a	3874a	226a	70a	64a	0.3418a	1,281,750a	97,346a	379,893a	1,591,938a	3.90a	158.1a
54a	5a	As	0.015a	3874a	226a	70a	57a	0.3852a	1,537,684a	73,834a	378,962a	1,587,366a	5.13a	157.9a
55a	5a	As	0.015a	3874a	226a	70a	70a	0.3701a	1,260,914a	115,043a	360,466a	1,191,071a	3.13a	157.8a
56a	5a	As	0.015a	3874a	226a	70a	53a	0.3412a	1,411,062a	145,118a	381,123a	1,231,459a	2.83a	157.7a
57a	5a	As	0.015a	3874a	226a	70a	72a	0.4134a	1,389,123a	78,863a	448,000a	2,319,812a	5.67a	157.1a

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#s	Cat-ID	Act-ID	Cat- (mg/g)	iso- hexane- (wt.%)	Isob. mg/g (wt.%)	T- (°C)	quench- time (s)	yield- (g)	Activity (g- Propylene/ cat.hr)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	PD	Tm- (°C)
58a	5a	Aa	0.020a	3632a	268a	70a	62a	0.3653a	1,360,548a	126,581a	411,551a	1,585,182a	3.25a	157.0a
59a	5a	Ac	0.025a	3895a	205a	70a	38a	0.1412a	535,074a	20,272a	310,784a	1,810,547a	15.33a	154.7a
60a	5a	Ac	0.025a	3895a	205a	70a	36a	0.4076a	1,620,000a	57,745a	274,363a	1,031,835a	4.05a	154.3a
61a	5a	Ac	0.025a	3895a	205a	70a	40a	0.2350a	846,000a	48,901a	244,435a	856,990a	5.68a	151.7a
62a	5a	Ac	0.015a	3674a	226a	100a	42a	0.2077a	1,186,857a	78,612a	162,336a	427,679a	2.97a	159.4a
63a	5a	Ac	0.015a	3674a	226a	100a	33a	0.2318a	1,585,818a	65,743a	137,626a	413,584a	2.99a	158.3a
64a	5a	Ac	0.015a	3674a	226a	100a	55a	0.2056a	901,527a	60,264a	144,653a	405,635a	2.40a	158.0a
65a	5a	Ac	0.015a	3674a	226a	100a	36a	0.2135a	1,423,333a	61,349a	119,262a	288,955a	1.94a	157.8a
66a	5a	Ac	0.015a	3674a	226a	100a	36a	0.2424a	1,616,000a	53,262a	113,175a	260,329a	2.12a	157.4a
67a	5a	Ac	0.015a	3674a	226a	100a	39a	0.2577a	1,585,846a	45,793a	110,904a	285,324a	2.42a	157.2a
68a	5a	Ac	0.015a	3674a	226a	100a	32a	0.2554a	1,915,506a	53,455a	132,919a	459,818a	2.49a	156.9a
69a	5a	Ac	0.020a	3632a	268a	100a	32a	0.2374a	1,335,375a	65,144a	129,333a	341,643a	1.99a	157.9a
70a	5a	Ac	0.025a	3895a	205a	100a	21a	0.2516a	1,725,257a	36,379a	112,218a	385,587a	3.09a	156.1a
71a	5a	Ac	0.025a	3895a	205a	100a	18a	0.2172a	1,737,608a	33,092a	121,551a	391,578a	3.67a	156.1a
72a	5a	Ac	0.025a	3895a	205a	100a	19a	0.2650a	2,008,421a	40,888a	123,561a	457,099a	3.02a	155.8a
73a	5a	Ac	0.015a	3674a	226a	110a	37a	0.1623a	1,052,757a	50,509a	97,179a	232,180a	1.92a	157.8a
74a	5a	Ac	0.020a	3632a	268a	110a	35a	0.2323a	1,194,686a	48,549a	94,167a	225,975a	1.94a	156.9a
75a	5a	Ac	0.015a	3674a	226a	115a	42a	0.1884a	1,076,571a	50,302a	95,952a	233,193a	1.72a	156.8a
76a	5a	Ac	0.020a	3632a	268a	115a	31a	0.1905a	1,106,129a	43,087a	79,855a	184,315a	1.85a	155.3a
77a	5a	Ba	0.015a	3674a	226a	70a	238a	0.2599a	262,084a	426,424a	756,222a	1,822,109a	1.77a	159.4a
78a	5a	Ba	0.015a	3674a	226a	70a	155a	0.2622a	405,987a	364,656a	616,635a	1,330,579a	1.69a	158.9a
79a	5a	Ba	0.015a	3674a	226a	70a	202a	0.2756a	327,446a	352,949a	670,255a	1,499,145a	1.58a	158.5a
80a	5a	Ba	0.015a	3674a	226a	100a	1809a	0.0064a	853a	~a	~a	~a	~a	~a
81a	5a	Ba	0.015a	3674a	226a	100a	1801a	0.0077a	1,025a	~a	~a	~a	~a	~a
82a	5a	Ba	0.015a	3674a	226a	100a	1881a	0.0056a	745a	~a	~a	~a	~a	~a
83a	5a	Ca	0.015a	3674a	226a	70a	61a	0.3718a	1,459,672a	102,011a	337,880a	1,133,722a	3.31a	157.6a
84a	5a	Ca	0.015a	3674a	226a	70a	58a	0.3853a	1,359,882a	119,203a	383,611a	1,513,227a	3.22a	157.6a
85a	5a	Ca	0.015a	3674a	226a	70a	59a	0.3922a	1,595,390a	93,290a	363,638a	1,313,735a	3.58a	156.8a
86a	5a	Ca	0.015a	3674a	226a	100a	43a	0.2326a	1,298,233a	62,879a	132,673a	364,902a	2.11a	157.9a
87a	5a	Ca	0.015a	3674a	226a	100a	37a	0.2425a	1,572,973a	56,814a	157,280a	655,515a	2.77a	157.6a
88a	5a	Ca	0.015a	3674a	226a	100a	33a	0.2392a	1,739,636a	69,889a	175,511a	750,768a	2.51a	157.3a
89a	6a	Ac	0.015a	3674a	226a	70a	7a	0.3795a	13,811,429a	118,914a	474,918a	1,790,054a	3.99a	148.8a
90a	6a	Ac	0.015a	3893a	201a	70a	17a	0.3559a	5,824,471a	76,437a	450,220a	1,929,618a	5.89a	148.5a
91a	6a	Ac	0.015a	3899a	201a	70a	29a	0.4118a	3,408,005a	105,184a	462,494a	1,888,421a	4.40a	148.1a
92a	6a	Ac	0.015a	3899a	201a	70a	21a	0.3950a	4,514,286a	103,834a	456,352a	1,650,650a	4.39a	147.8a
93a	6a	Ac	0.015a	3874a	226a	70a	15a	0.4021a	5,433,696a	56,318a	386,935a	1,832,132a	5.82a	147.7a
94a	6a	Ac	0.015a	3874a	226a	70a	11a	0.4079a	8,899,636a	158,183a	461,138a	1,272,034a	2.92a	147.7a
95a	6a	Ac	0.025a	3895a	205a	70a	10a	0.5049a	7,270,560a	54,923a	412,179a	1,583,284a	7.50a	150.9a
96a	6a	Ac	0.025a	3895a	205a	70a	14a	0.3719a	3,825,257a	55,439a	404,974a	1,360,776a	7.30a	148.9a
97a	6a	Ac	0.025a	3895a	205a	70a	8a	0.4157a	7,482,602a	53,264a	395,589a	1,792,391a	7.43a	146.2a
98a	6a	Ac	0.015a	3899a	201a	100a	13a	0.1592a	3,123,692a	70,532a	191,558a	622,897a	2.44a	148.5a
99a	6a	Ac	0.015a	3899a	201a	100a	21a	0.2995a	3,424,690a	59,868a	185,938a	608,943a	3.09a	147.9a
100a	6a	Ac	0.015a	3899a	201a	100a	19a	0.3025a	3,822,316a	47,864a	176,148a	658,186a	3.68a	145.7a
101a	6a	Ac	0.015a	3874a	226a	100a	17a	0.2957a	4,174,588a	41,605a	137,097a	437,336a	3.29a	145.7a
102a	6a	Ac	0.015a	3874a	226a	100a	16a	0.3116a	4,674,805a	36,075a	145,393a	558,114a	4.03a	146.7a
103a	6a	Ac	0.015a	3874a	226a	100a	34a	0.3299a	2,328,796a	40,450a	161,588a	782,341a	3.99a	146.2a
104a	6a	Ac	0.025a	3895a	205a	100a	12a	0.3261a	3,913,296a	15,045a	123,987a	812,911a	8.18a	144.6a
105a	6a	Ac	0.025a	3895a	205a	100a	10a	0.3294a	4,743,366a	21,293a	144,305a	621,716a	6.78a	144.1a
106a	6a	Ac	0.025a	3895a	205a	100a	15a	0.3198a	3,062,430a	23,333a	132,940a	1,035,127a	5.70a	143.5a
107a	6a	Ba	0.015a	3874a	226a	70a	105a	0.3591a	820,800a	245,294a	578,298a	1,523,246a	2.36a	151.1a
108a	6a	Ba	0.015a	3874a	226a	70a	48a	0.3526a	1,763,002a	134,888a	506,647a	1,589,263a	3.76a	149.7a
109a	6a	Ba	0.015a	3874a	226a	70a	82a	0.3363a	966,732a	205,620a	557,373a	1,694,146a	2.71a	149.7a
110a	6a	Ba	0.015a	3874a	226a	100a	1808a	0.0553a	7,373a	254,743a	411,777a	833,940a	1.59a	150.2a

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat-ID	Act-ID	Cat- (μmol)	Isa. hexane- (μL)	Toluene- (μL)	T- ($^{\circ}\text{C}$)	quench- time (s)	yield- (g)	Activity-(g- Phmmol- cat.hr)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	PD	T_m - ($^{\circ}\text{C}$)
111a	6a	Ba	0.015a	3874a	226a	100a	420a	0.0747a	42,686a	223,744a	353,740a	712,784a	1.59a	150.2a
112a	6a	Ba	0.015a	3874a	226a	100a	259a	0.0597a	55,320a	224,380a	324,573a	504,329a	1.45a	149.7a
113a	6a	Ca	0.015a	3874a	226a	70a	15a	0.4064a	6,406,400a	61,960a	359,365a	1,386,797a	5.80a	146.9a
114a	6a	Ca	0.015a	3874a	226a	70a	11a	0.4177a	9,113,455a	103,910a	420,388a	1,426,376a	4.04a	146.9a
115a	6a	Ca	0.015a	3874a	226a	70a	17a	0.4241a	5,987,294a	80,127a	382,187a	1,235,156a	4.77a	146.5a
116a	6a	Ca	0.015a	3874a	226a	100a	16a	0.3077a	4,615,500a	32,003a	167,446a	733,489a	5.23a	145.9a
117a	6a	Ca	0.015a	3874a	226a	100a	19a	0.3073a	3,881,664a	47,498a	155,800a	579,569a	3.28a	145.7a
118a	6a	Ca	0.015a	3874a	226a	100a	17a	0.3157a	4,456,941a	42,617a	156,382a	574,717a	3.67a	145.7a
119a	7a	As	0.015a	3874a	226a	70a	65a	0.3797a	1,368,738a	96,491a	420,880a	2,185,151a	4.36a	160.4a
120a	7a	As	0.015a	3874a	226a	70a	55a	0.3750a	1,636,364a	73,631a	416,915a	2,309,681a	5.66a	159.1a
121a	7a	As	0.015a	3874a	226a	70a	58a	0.3728a	1,542,621a	104,115a	408,527a	2,023,472a	3.92a	158.6a
122a	7a	As	0.025a	3895a	205a	70a	47a	0.3867a	1,184,763a	82,818a	418,093a	1,917,700a	5.05a	159.3a
123a	7a	As	0.025a	3895a	205a	70a	31a	0.3624a	1,683,406a	33,128a	341,316a	1,757,046a	10.38a	157.3a
124a	7a	As	0.025a	3895a	205a	70a	34a	0.4134a	1,759,871a	36,855a	327,546a	1,507,616a	8.89a	156.8a
125a	7a	As	0.015a	3874a	226a	100a	29a	0.2755a	2,286,600a	33,147a	109,233a	357,333a	3.30a	158.0a
126a	7a	As	0.015a	3874a	226a	100a	34a	0.2756a	1,945,412a	30,104a	91,877a	246,715a	3.05a	157.5a
127a	7a	As	0.015a	3874a	226a	100a	31a	0.2734a	2,116,645a	41,093a	102,267a	254,470a	2.49a	157.4a
128a	7a	As	0.025a	3895a	205a	100a	20a	0.2582a	1,859,040a	31,837a	108,214a	428,914a	3.48a	157.1a
129a	7a	As	0.025a	3895a	205a	100a	21a	0.2567a	1,769,229a	45,982a	117,786a	362,307a	2.56a	156.8a
130a	7a	As	0.025a	3895a	205a	100a	19a	0.2640a	2,000,842a	38,903a	118,110a	469,640a	3.04a	156.6a
131a	8a	As	0.015a	3874a	226a	70a	69a	0.1396a	485,565a	221,954a	414,051a	948,937a	1.87a	153.0a
132a	8a	As	0.015a	3874a	226a	70a	132a	0.2025a	368,182a	217,410a	410,493a	959,131a	1.89a	152.8a
133a	8a	As	0.015a	3874a	226a	70a	117a	0.1833a	376,000a	219,456a	388,248a	912,947a	1.77a	152.7a
134a	8a	As	0.025a	3895a	205a	70a	71a	0.2931a	594,456a	94,693a	305,434a	808,807a	3.23a	151.5a
135a	8a	As	0.025a	3895a	205a	70a	73a	0.2732a	538,915a	118,590a	310,029a	773,287a	2.61a	151.3a
136a	8a	As	0.025a	3895a	205a	70a	65a	0.2663a	576,665a	153,571a	299,372a	665,532a	1.96a	151.2a
137a	8a	As	0.015a	3874a	226a	100a	155a	0.1025a	158,710a	92,421a	157,438a	357,993a	1.70a	153.2a
138a	8a	As	0.015a	3874a	226a	100a	80a	0.1523a	456,900a	76,265a	141,310a	337,323a	1.85a	153.1a
139a	8a	As	0.015a	3874a	226a	100a	102a	0.1334a	313,882a	89,643a	150,761a	334,179a	1.68a	152.6a
140a	8a	As	0.025a	3895a	205a	100a	46a	0.2106a	659,270a	46,511a	122,427a	364,279a	2.63a	151.7a
141a	8a	As	0.025a	3895a	205a	100a	54a	0.2152a	573,867a	58,371a	122,681a	345,441a	2.10a	151.1a
142a	8a	As	0.025a	3895a	205a	100a	53a	0.2220a	603,170a	50,235a	118,356a	321,957a	2.36a	150.8a
143a	9a	As	0.015a	3899a	201a	70a	51a	0.3773a	1,775,529a	117,874a	310,304a	915,337a	2.63a	160.4a
144a	9a	As	0.015a	3899a	201a	70a	50a	0.3469a	1,665,120a	124,917a	330,194a	1,050,495a	2.64a	159.7a
145a	9a	As	0.015a	3899a	201a	70a	50a	0.4035a	1,614,600a	96,278a	345,774a	1,434,603a	3.59a	159.4a
146a	9a	As	0.025a	3895a	205a	70a	51a	0.4035a	1,139,294a	52,073a	323,282a	1,536,029a	6.21a	158.9a
147a	9a	As	0.025a	3895a	205a	70a	38a	0.4195a	1,589,684a	30,074a	296,559a	1,362,544a	9.86a	156.8a
148a	9a	As	0.025a	3895a	205a	70a	35a	0.3982a	1,638,309a	13,956a	230,370a	1,045,408a	16.51a	156.6a
149a	9a	As	0.015a	3899a	201a	100a	40a	0.2391a	1,434,600a	58,972a	139,520a	443,404a	2.37a	159.7a
150a	9a	As	0.015a	3899a	201a	100a	31a	0.1557a	1,205,419a	74,814a	150,248a	399,543a	2.01a	159.5a
151a	9a	As	0.015a	3899a	201a	100a	55a	0.2251a	962,255a	64,509a	147,679a	437,771a	2.29a	159.2a
152a	9a	As	0.025a	3895a	205a	100a	25a	0.2493a	1,435,968a	38,869a	110,626a	382,210a	2.85a	157.9a
153a	9a	As	0.025a	3895a	205a	100a	30a	0.2616a	1,255,560a	35,121a	93,168a	297,224a	2.65a	157.6a
154a	9a	As	0.025a	3895a	205a	100a	22a	0.2682a	1,755,491a	37,020a	112,848a	434,741a	3.05a	156.9a
155a	10a	As	0.015a	3874a	226a	70a	59a	0.2298a	934,780a	84,383a	132,546a	247,855a	1.57a	160.2a
156a	10a	As	0.015a	3874a	226a	70a	56a	0.2461a	1,054,714a	71,943a	126,703a	289,153a	1.76a	159.7a
157a	10a	As	0.025a	3895a	205a	70a	29a	0.3488a	1,731,972a	55,761a	103,795a	241,351a	1.86a	158.7a
158a	10a	As	0.025a	3895a	205a	70a	29a	0.3259a	1,618,262a	58,998a	105,251a	242,181a	1.78a	157.9a
159a	10a	As	0.025a	3895a	205a	70a	39a	0.4229a	1,561,477a	55,906a	102,374a	238,789a	1.83a	157.2a
160a	10a	As	0.015a	3874a	226a	100a	80a	0.1018a	305,400a	51,447a	85,250a	150,973a	1.66a	157.2a

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat- ID	Act- ID	Cat- (mmol)	Isop- hexane- (wt.%)	Isop- hexane- (wt.%)	T- (°C)	quench- time (s)	yield- (g)	Activity-(g- P/mmol- cat.hr)	M _{np}	M _w	M _z	PDI	T _m - (°C)
161a	10a	Aa	0.015a	3874a	226a	100a	60a	0.1099a	439,680a	49,474a	81,942a	144,672a	1.66a	157.2a
162a	19a	Ac	0.015a	3874a	226a	100a	56a	0.1086a	465,429a	50,590a	82,800a	146,533a	1.64a	157.1a
163a	10a	Ac	0.025a	3895a	205a	100a	32a	0.2023a	910,350a	33,780a	66,144a	139,537a	1.96a	156.4a
164a	10a	Ac	0.025a	3895a	205a	100a	28a	0.2162a	1,111,886a	31,032a	66,306a	163,729a	2.14a	155.9a
165a	19a	Ac	0.025a	3895a	205a	100a	27a	0.2096a	1,117,867a	41,870a	71,790a	148,567a	1.71a	155.5a
166a	11a	Ac	0.025a	3895a	205a	70a	190a	0.1405a	106,484a	185,619a	328,172a	708,555a	1.77a	162.0a
167a	11a	Ac	0.025a	3895a	205a	70a	180a	0.1435a	114,800a	183,168a	294,337a	667,126a	2.85a	161.4a
168a	11a	Ac	0.025a	3895a	205a	70a	182a	0.1560a	123,429a	159,195a	279,173a	562,263a	1.75a	161.0a
169a	11a	Ac	0.025a	3895a	205a	100a	155a	0.1046a	97,177a	80,933a	139,494a	284,659a	1.72a	161.9a
170a	11a	Ac	0.025a	3895a	205a	100a	125a	0.0672a	7,692a	33,884a	113,848a	267,437a	3.37a	160.6a
171a	11a	Ac	0.025a	3895a	205a	100a	141a	0.1137a	116,119a	63,852a	125,563a	255,692a	1.97a	159.8a
172a	12a	Ac	0.015a	3874a	226a	70a	44a	0.2709a	1,521,273a	146,270a	290,344a	703,139a	1.98a	158.9a
173a	12a	Ac	0.015a	3874a	226a	70a	38a	0.2896a	1,829,053a	139,309a	282,465a	778,339a	2.03a	158.5a
174a	12a	Ac	0.015a	3874a	226a	70a	41a	0.3211a	1,879,610a	115,357a	249,864a	664,624a	2.17a	157.6a
175a	12a	Ac	0.025a	3895a	205a	70a	27a	0.3953a	2,108,267a	42,082a	194,664a	647,170a	4.63a	156.9a
176a	12a	Ac	0.025a	3895a	205a	70a	28a	0.3939a	2,025,771a	45,776a	211,847a	756,521a	4.63a	156.2a
177a	12a	Ac	0.025a	3895a	205a	70a	27a	0.3731a	1,989,867a	45,677a	224,458a	934,294a	4.91a	155.5a
178a	12a	Ac	0.015a	3874a	226a	100a	44a	0.1443a	787,991a	89,441a	166,845a	523,735a	1.87a	157.6a
179a	12a	Ac	0.015a	3874a	226a	100a	37a	0.1451a	941,189a	90,435a	152,608a	349,816a	1.69a	157.3a
180a	12a	Ac	0.015a	3874a	226a	100a	38a	0.1515a	956,842a	58,429a	144,936a	423,058a	2.48a	157.1a
181a	12a	Ac	0.025a	3895a	205a	100a	20a	0.2352a	1,693,440a	37,414a	105,899a	296,643a	2.83a	156.0a
182a	12a	Ac	0.025a	3895a	205a	100a	22a	0.2175a	1,423,636a	33,047a	108,680a	322,118a	3.29a	156.0a
183a	12a	Ac	0.025a	3895a	205a	100a	16a	0.2159a	1,943,100a	35,788a	110,117a	341,042a	3.08a	155.9a
184a	13a	Ac	0.015a	3874a	226a	70a	16a	0.3873a	5,817,880a	49,236a	161,383a	648,392a	3.28a	145.5a
185a	13a	Ac	0.015a	3874a	226a	70a	26a	0.4131a	4,957,206a	45,927a	159,308a	617,869a	3.47a	145.5a
186a	13a	Ac	0.015a	3874a	226a	70a	17a	0.4334a	6,118,588a	40,362a	150,799a	619,430a	3.74a	145.3a
187a	13a	Ac	0.025a	3895a	205a	70a	17a	0.3988a	3,378,871a	38,456a	153,387a	539,355a	3.99a	145.0a
188a	13a	Ac	0.025a	3895a	205a	70a	14a	0.4163a	4,281,943a	23,991a	134,186a	502,686a	5.59a	144.5a
189a	13a	Ac	0.025a	3895a	205a	70a	13a	0.4107a	4,549,292a	22,317a	127,256a	444,171a	5.79a	144.1a
190a	13a	Ac	0.015a	3874a	226a	100a	26a	0.2807a	3,368,406a	35,649a	82,850a	252,359a	2.32a	144.0a
191a	13a	Ac	0.015a	3874a	226a	100a	19a	0.2893a	3,654,316a	34,679a	77,908a	205,082a	2.25a	143.5a
192a	13a	Ac	0.015a	3874a	226a	100a	17a	0.2765a	3,903,529a	31,341a	70,550a	160,080a	2.25a	143.5a
193a	13a	Ac	0.025a	3895a	205a	100a	27a	0.2479a	1,322,133a	36,394a	97,399a	256,208a	2.68a	144.7a
194a	13a	Ac	0.025a	3895a	205a	100a	12a	0.3057a	3,668,430a	16,468a	65,201a	220,490a	3.96a	142.8a
195a	13a	Ac	0.025a	3895a	205a	100a	12a	0.3158a	3,789,600a	14,516a	61,810a	236,516a	4.26a	142.2a
196a	14a	Ac	0.015a	3874a	226a	70a	129a	0.1976a	367,628a	135,871a	278,711a	597,323a	2.05a	161.6a
197a	14a	Ac	0.015a	3874a	226a	70a	129a	0.1889a	351,442a	167,562a	276,114a	554,940a	1.65a	161.4a
198a	14a	Ac	0.015a	3874a	226a	70a	127a	0.2059a	389,102a	160,217a	294,473a	612,269a	1.63a	160.6a
199a	14a	Ac	0.025a	3895a	205a	70a	93a	0.2268a	351,174a	145,962a	275,670a	647,259a	1.89a	162.5a
200a	14a	Ac	0.025a	3895a	205a	70a	111a	0.2282a	296,043a	162,443a	317,515a	721,467a	1.74a	161.5a
201a	14a	Ac	0.025a	3895a	205a	70a	92a	0.2242a	350,922a	171,325a	296,987a	616,445a	1.73a	161.1a
202a	14a	Ac	0.015a	3874a	226a	100a	114a	0.1465a	308,421a	76,607a	129,124a	232,401a	1.68a	160.5a
203a	14a	Ac	0.015a	3874a	226a	100a	113a	0.1296a	275,257a	94,439a	144,461a	254,721a	1.53a	160.3a
204a	14a	Ac	0.015a	3874a	226a	100a	118a	0.1415a	292,759a	76,166a	132,181a	241,002a	1.74a	160.2a
205a	14a	Ac	0.025a	3895a	205a	100a	94a	0.1598a	244,800a	70,536a	122,926a	268,329a	1.74a	160.1a
206a	14a	Ac	0.025a	3895a	205a	100a	85a	0.1691a	286,475a	71,117a	121,627a	247,730a	1.71a	160.0a
207a	14a	Ac	0.025a	3895a	205a	100a	77a	0.1699a	317,735a	70,244a	121,280a	273,876a	1.73a	159.0a
208a	15a	Ac	0.015a	3874a	226a	70a	74a	0.3575a	1,159,459a	119,886a	290,039a	942,218a	2.42a	161.6a
209a	15a	Ac	0.015a	3874a	226a	70a	77a	0.3860a	1,203,117a	107,158a	320,828a	1,122,488a	2.99a	161.6a
210a	15a	Ac	0.015a	3874a	226a	70a	77a	0.3735a	1,164,156a	110,748a	310,245a	984,005a	2.80a	160.8a

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (μmol)	Isoc-hexane (μL)	Isoc-hexane (wt%)	T (°C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
211	15	A	0.025	3895	205	70	47	0.3817	1,169,464	51,310	267,244	989,989	5.21	159.9
212	15	A	0.025	3895	205	70	48	0.4079	1,223,700	50,171	292,892	1,186,319	5.84	159.6
213	15	A	0.025	3895	205	70	54	0.3908	1,042,133	56,452	331,496	1,598,621	5.87	159.4
214	15	A	0.015	3874	226	100	56	0.2208	946,266	62,463	118,588	253,690	1.90	161.3
215	15	A	0.015	3874	226	100	43	0.2332	1,301,581	59,080	111,122	235,729	1.88	160.9
216	15	A	0.015	3874	226	100	45	0.2523	1,345,600	48,008	115,829	402,984	2.41	160.6
217	15	A	0.025	3895	205	100	129	0.1431	159,740	76,634	178,963	421,736	2.34	160.8
218	15	A	0.025	3895	205	100	27	0.2643	1,409,600	26,000	94,589	343,952	3.64	159.4
219	15	A	0.025	3895	205	100	36	0.2671	1,068,400	40,468	100,265	331,014	2.48	159.2
220	16	A	0.015	3874	226	70	168	0.1514	216,286	211,948	353,711	695,938	1.67	162.4
221	16	A	0.015	3874	226	70	166	0.1629	234,217	220,371	363,530	706,255	1.65	162.1
222	16	A	0.015	3874	226	70	174	0.1427	196,828	232,443	383,689	752,363	1.65	161.4
223	16	A	0.025	3895	205	70	131	0.1787	196,434	179,724	303,763	613,969	1.69	162.5
224	16	A	0.025	3895	205	70	120	0.2056	246,720	173,961	316,662	720,440	1.82	162.2
225	16	A	0.025	3895	205	70	128	0.2306	259,425	181,492	312,026	669,414	1.72	161.6
226	16	A	0.015	3874	226	100	1801	0.0379	4,931	112,191	186,280	378,163	1.66	162.5
227	16	A	0.015	3874	226	100	1801	0.0147	1,959	113,776	188,756	372,742	1.66	161.1
228	16	A	0.015	3874	226	100	226	0.0744	79,609	100,327	170,565	343,646	1.70	160.9
229	16	A	0.025	3895	205	100	183	0.0859	67,593	88,984	143,365	270,561	1.61	161.0
230	16	A	0.025	3895	205	100	103	0.1348	188,458	77,457	127,688	245,796	1.65	160.5
231	16	A	0.025	3895	205	100	122	0.1210	142,820	81,642	135,052	267,052	1.65	160.2
232	17	A	0.015	3874	226	70	1800	0.0975	1,000					
233	17	A	0.015	3874	226	70	1802	0.0078	1,039					
234	17	A	0.015	3874	226	70	1801	0.0956	746					
235	17	A	0.025	3895	205	70	1800	0.0154	1,232	109,727	172,348	344,763	1.57	161.7
236	17	A	0.025	3895	205	70	1801	0.0147	1,175	96,648	154,141	288,452	1.59	161.4
237	17	A	0.025	3895	205	70	1801	0.0142	1,135	62,583	100,850	198,483	1.61	160.5
238	17	A	0.015	3874	226	100	1800	0.0002	27					
239	17	A	0.015	3874	226	100	1801	-0.0906	-80					
240	17	A	0.015	3874	226	100	1801	0.0010	133					
241	17	A	0.025	3895	205	100	1801	0.0272	2,175	42,811	71,127	139,719	1.66	156.9
242	17	A	0.025	3895	205	100	1802	0.0221	1,766	39,718	68,569	146,013	1.73	156.7
243	17	A	0.025	3895	205	100	1800	0.0238	1,904	36,219	65,197	134,551	1.80	156.0
244	18	A	0.015	3874	226	70	1801	0.0289	3,851	94,741	157,074	318,366	1.66	161.7
245	18	A	0.015	3874	226	70	1800	0.0277	3,693	89,484	141,777	275,634	1.58	160.7
246	18	A	0.015	3874	226	70	1800	0.0194	2,587	104,985	168,698	355,199	1.61	160.4
247	18	A	0.025	3895	205	70	1801	0.0458	3,662	181,664	161,824	308,669	1.59	160.5
248	18	A	0.025	3895	205	70	1801	0.0389	3,110	72,866	122,210	239,343	1.68	160.4
249	18	A	0.025	3895	205	70	1802	0.0505	4,036	85,819	145,585	284,728	1.70	159.9
250	18	A	0.015	3874	226	100	1801	0.0902	27					
251	18	A	0.015	3874	226	100	1800	-0.0906	-80					
252	18	A	0.015	3874	226	100	1801	-0.0906	-80					
253	18	A	0.025	3895	205	100	1466	0.0555	5,452	50,863	79,492	159,373	1.56	157.0
254	18	A	0.025	3895	205	100	1801	0.0467	3,734	47,598	76,559	147,217	1.61	156.9
255	18	A	0.025	3895	205	100	1802	0.0298	2,381	45,554	74,549	146,381	1.64	155.5
256	19	A	0.015	3874	226	50	277	0.1462	126,671	606,451	962,850	1,807,015	1.59	165.4
257	19	A	0.020	3832	268	50	228	0.1372	108,316	480,870	859,208	1,824,424	1.79	166.1
258	19	A	0.015	3874	226	60	358	0.0915	61,341	504,203	738,710	1,326,316	1.47	164.6
259	19	A	0.020	3832	268	60	209	0.1576	135,732	394,004	653,605	1,246,132	1.66	165.7
260	19	A	0.015	3874	226	70	197	0.1291	157,279	389,178	534,771	895,536	1.37	164.9

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (μmol)	Iso-hexane (wt.%)	Isobutylene (wt.%)	T (°C)	quench time (s)	yield (g)	Activity (g P _{prop} /mol cat.hr)	M _n	M _w	M _z	PDI	T _m (°C)
261	19	A	0.015	3874	226	70	222	0.1112	129,216	412,937	682,452	1,379,885	1.65	164.1
262	19	A	0.015	3874	226	70	213	0.1351	152,225	366,407	556,215	1,064,994	1.52	163.5
263	19	A	0.015	3874	226	70	219	0.1268	138,959	313,864	504,232	930,019	1.61	163.5
264	19	A	0.020	3832	268	70	157	0.1599	183,325	343,357	545,008	1,066,069	1.59	164.9
265	19	A	0.015	3874	226	180	1801	0.0628	8,369					162.9
266	19	A	0.015	3874	226	100	1800	0.0579	7,720	173,584	279,481	550,649	1.61	161.9
267	19	A	0.015	3874	226	180	1800	0.0596	7,973	134,605	220,586	404,685	1.64	160.9
268	19	A	0.015	3874	226	180	1354	0.0603	19,688	154,983	254,230	538,930	1.64	160.1
269	19	A	0.020	3832	268	100	219	0.0809	66,493	165,493	287,548	707,080	1.74	163.1
270	19	A	0.015	3874	226	110	224	0.0750	88,357	133,188	228,284	475,556	1.71	160.2
271	19	A	0.020	3832	268	110	218	0.0806	66,550	97,080	165,474	332,197	1.70	159.9
272	19	A	0.015	3874	226	115	184	0.0670	87,391	108,550	170,979	338,263	1.58	159.9
273	19	A	0.020	3832	268	115	225	0.0894	71,520	105,431	158,882	291,198	1.51	160.5
274	20	A	0.015	3874	226	70	51	0.2961	1,393,412	91,504	180,050	482,488	1.97	156.8
275	20	A	0.015	3874	226	70	59	0.2944	1,197,559	111,683	224,774	579,509	2.81	155.9
276	20	A	0.015	3874	226	70	57	0.3251	1,368,842	186,054	191,739	441,346	1.81	155.7
277	20	A	0.015	3874	226	180	76	0.1811	571,895	46,262	85,694	200,460	1.85	153.9
278	20	A	0.015	3874	226	100	49	0.2147	1,051,592	38,212	64,587	151,954	1.69	153.6
279	20	A	0.015	3874	226	180	45	0.2941	1,088,533	36,396	69,386	173,368	1.91	153.4
280	21	A	0.015	3874	226	70	89	0.2498	673,618	290,087	522,788	1,256,300	1.80	160.5
281	21	A	0.015	3874	226	70	103	0.2777	647,068	265,095	467,578	1,005,189	1.76	160.1
282	21	A	0.015	3874	226	70	123	0.2502	488,195	254,920	520,019	1,153,915	2.04	160.1
283	21	A	0.015	3874	226	100	77	0.1493	465,351	116,895	213,507	455,527	1.83	159.6
284	21	A	0.015	3874	226	180	75	0.1306	417,920	129,205	229,975	512,124	1.78	159.1
285	21	A	0.015	3874	226	100	63	0.1537	585,524	143,333	252,722	564,805	1.76	158.9
286	23	A	0.015	3874	226	50	168	0.2134	384,857	337,494	518,394	912,721	1.54	164.8
287	23	A	0.020	3832	268	50	145	0.3337	414,248	324,526	494,489	883,505	1.52	164.1
288	23	A	0.015	3874	226	60	121	0.2309	457,963	275,114	428,037	800,354	1.56	163.9
289	23	A	0.020	3832	268	60	106	0.3851	518,094	227,610	377,058	731,405	1.66	163.2
290	23	A	0.015	3874	226	70	131	0.1550	283,969	236,065	379,539	787,141	1.61	163.3
291	23	A	0.015	3874	226	70	104	0.1861	429,462	241,281	369,976	707,824	1.53	162.6
292	23	A	0.015	3874	226	70	102	0.2184	513,882	193,764	349,127	715,200	1.80	162.4
293	23	A	0.015	3874	226	70	112	0.1871	406,929	213,875	345,238	656,339	1.61	162.2
294	23	A	0.020	3832	268	70	74	0.2126	517,135	211,641	324,925	594,111	1.54	163.2
295	23	A	0.025	3895	205	70	79	0.2886	525,056	188,096	314,208	645,088	1.67	162.0
296	23	A	0.025	3895	205	70	80	0.2997	539,460	69,284	302,072	699,279	4.36	160.6
297	23	A	0.025	3895	205	70	82	0.3203	562,478	180,646	327,583	740,348	1.81	160.3
298	23	A	0.015	3874	226	100	1801	0.0566	7,542	90,558	160,712	432,645	1.77	161.2
299	23	A	0.015	3874	226	100	148	0.0833	135,081	74,952	145,111	280,595	1.94	161.1
300	23	A	0.015	3874	226	100	1105	0.0769	16,702	101,096	165,958	324,701	1.64	160.9
301	23	A	0.015	3874	226	100	764	0.0805	27,443	118,048	180,668	336,268	1.53	160.7
302	23	A	0.020	3832	268	100	84	0.1119	239,786	96,678	151,524	281,712	1.57	161.6
303	23	A	0.025	3895	205	100	75	0.1500	387,200	64,220	141,167	355,711	2.20	160.1
304	23	A	0.025	3895	205	100	68	0.1736	387,624	78,118	147,424	325,451	1.89	160.1
305	23	A	0.025	3895	205	100	60	0.1802	432,480	45,329	132,969	292,492	2.93	158.8
306	23	A	0.015	3874	226	110	1860	0.0700	9,333	70,979	114,730	209,637	1.62	159.9
307	23	A	0.020	3832	268	110	139	0.0774	106,230	53,974	89,649	175,927	1.66	158.6
308	23	A	0.015	3874	226	115	1801	0.0406	5,410	54,791	89,068	176,609	1.63	157.8
309	23	A	0.020	3832	268	115	392	0.0746	34,255	53,096	76,753	139,547	1.45	156.9
310	24	A	0.015	3874	226	70	54	0.2594	1,152,889	122,299	265,834	638,521	2.17	155.6
311	24	A	0.015	3874	226	70	68	0.2214	781,412	225,712	382,689	790,954	1.70	155.3
312	24	A	0.015	3874	226	70	40	0.3031	1,818,600	143,976	283,789	696,323	1.97	154.3
313	24	A	0.025	3790	310	70	37	0.3414	1,328,692	76,664	205,265	685,408	2.73	154.1
314	24	A	0.025	3790	310	70	22	0.3565	2,333,455	37,846	189,474	704,394	5.01	153.8
315	24	A	0.025	3790	310	70	25	0.3207	1,847,232	92,568	237,070	742,756	2.56	153.5

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (μmol)	Iso-hexane (wt.%)	Isobutene (wt.%)	T (°C)	quench time (s)	yield (g)	Activity (g P _{prop} /mol cat.hr)	M ₀	M _w	M _z	PDI	T _m (°C)
316	24	A	0.015	3874	226	190	1801	0.0693	9,235	189,183	183,055	379,218	1.68	154.3
317	24	A	0.015	3874	226	190	37	0.1880	1,219,459	42,141	93,868	242,159	2.23	152.8
318	24	A	0.015	3874	226	190	1801	0.0267	3,825	57,058	162,395	391,985	2.85	152.3
319	24	A	0.025	3790	310	190	49	0.1762	517,812	58,434	127,635	301,381	1.87	153.3
320	24	A	0.025	3790	310	180	38	0.1887	715,074	46,028	102,123	258,196	2.22	153.0
321	24	A	0.025	3790	310	190	27	0.2579	1,375,467	31,372	85,995	259,584	2.76	150.6
322	25	A	0.015	3874	226	50	1801	0.0519	6,916	546,225	876,921	1,664,221	1.61	165.9
323	25	A	0.020	3832	268	50	426	0.0838	35,408	525,088	896,484	1,810,902	1.71	166.4
324	25	A	0.015	3874	226	60	1801	0.0679	9,048	461,036	773,309	1,525,688	1.68	165.1
325	25	A	0.020	3832	268	60	228	0.1153	91,026	523,967	814,072	1,526,165	1.55	164.6
326	25	A	0.015	3874	226	70	1801	0.0495	6,596	473,707	664,232	1,140,439	1.40	167.2
327	25	A	0.015	3874	226	70	235	0.0785	86,170	385,641	734,499	1,975,384	1.90	165.7
328	25	A	0.015	3874	226	70	1803	0.0582	7,747	481,757	696,025	1,266,140	1.44	165.4
329	25	A	0.015	3874	226	70	1800	0.0526	7,013	359,476	628,998	1,229,198	1.75	164.5
330	25	A	0.020	3832	268	70	172	0.1027	107,477	433,344	703,524	1,351,140	1.62	166.3
331	25	A	0.015	3874	226	190	1801	0.0171	2,279	190,283	316,542	631,651	1.66	163.7
332	25	A	0.015	3874	226	180	1801	0.0246	3,278	208,678	335,750	633,282	1.61	163.3
333	25	A	0.015	3874	226	190	1801	0.0181	2,412	220,076	331,240	609,515	1.51	162.6
334	25	A	0.015	3874	226	180	1801	0.0165	2,199	181,681	303,158	627,729	1.67	161.6
335	25	A	0.020	3832	268	190	1800	0.0375	3,750	181,724	296,099	546,615	1.63	162.8
336	25	A	0.015	3874	226	110	1801	0.0193	2,572	147,667	232,744	475,337	1.58	162.2
337	25	A	0.020	3832	268	110	1801	0.0335	3,348	125,497	203,596	406,458	1.62	162.6
338	25	A	0.015	3874	226	115	1800	0.0050	667					
339	25	A	0.020	3832	268	115	1801	0.0227	2,269	87,615	131,220	240,872	1.50	160.1
340	26	A	0.025	3895	295	70	24	0.3654	2,192,400	47,488	90,386	201,296	1.91	151.3
341	26	A	0.025	3895	295	70	23	0.3858	2,415,443	45,291	92,784	221,513	2.05	151.1
342	26	A	0.025	3895	295	70	22	0.3841	2,514,109	50,123	92,438	210,009	1.84	150.5
343	26	A	0.025	3895	295	100	24	0.2807	1,204,200	35,206	64,314	127,614	1.83	149.0
344	26	A	0.025	3895	295	180	26	0.1983	1,098,277	36,868	67,959	152,188	1.84	148.6
345	26	A	0.025	3895	295	190	20	0.2150	1,548,000	41,257	72,399	159,327	1.75	148.6
346	26	D	0.040	0	4099	70	445	0.0887	17,939	32,098	71,005	161,619	2.21	143.9
347	26	D	0.040	0	4099	70	416	0.0800	17,308	40,480	76,360	171,690	1.89	143.7
348	26	D	0.040	0	4099	70	476	0.0929	17,565	41,955	76,450	161,992	1.82	143.6
349	26	D	0.040	0	4099	100	341	0.0674	17,789	29,210	58,239	125,850	1.99	139.6
350	26	D	0.040	0	4099	190	316	0.0724	20,620	27,371	56,549	122,506	2.07	139.4
351	26	D	0.040	0	4099	190	314	0.0763	21,869	26,615	56,239	126,559	2.10	139.2
352	27	A	0.015	3874	226	70	23	0.6217	6,487,304	57,344	91,990	166,659	1.60	143.7
353	27	A	0.015	3874	226	70	22	0.6582	7,180,364	41,329	86,747	176,312	2.10	142.7
354	27	A	0.015	3874	226	70	17	0.4999	7,057,412	49,320	80,825	156,835	1.64	141.2
355	27	A	0.025	3895	295	70	14	0.3770	3,877,714	40,843	72,333	149,855	1.77	140.4
356	27	A	0.025	3895	295	70	14	0.3656	3,760,457	38,735	72,031	159,041	1.86	140.1
357	27	A	0.025	3895	295	70	12	0.3625	4,350,008	42,200	72,576	157,569	1.72	139.7
358	27	A	0.015	3874	226	180	31	0.3777	2,924,129	34,608	69,789	144,535	2.01	138.6
359	27	A	0.015	3874	226	180	30	0.4522	3,217,608	22,700	66,289	146,317	2.92	137.6
360	27	A	0.015	3874	226	180	23	0.3991	4,164,522	35,351	70,752	154,141	2.00	137.5
361	27	A	0.025	3895	295	180	17	0.2922	2,475,106	32,158	57,565	136,661	1.79	135.4
362	27	A	0.025	3895	295	180	13	0.2607	2,887,754	28,319	50,983	107,353	1.80	135.0
363	27	A	0.025	3895	295	180	17	0.2910	2,464,941	22,635	50,793	125,347	2.24	134.9
364	27	D	0.040	0	4099	70	33	0.3596	980,727	42,431	70,966	141,394	1.67	135.6
365	27	D	0.040	0	4099	70	32	0.3700	1,046,625	39,300	68,483	146,415	1.74	135.5

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (mmol)	iso-hexane (ul.)	Tot. (ul.)	T (°C)	quench time (s)	yield (g)	Activity (g P _{prop} /cat.hr)	M _n	M _w	M _z	PDI	T _m (°C)
366	27	D	0.040	0	4099	70	32	0.3869	1,088,156	39,075	70,139	153,931	1.80	135.3
367	27	D	0.040	0	4099	100	27	0.2434	811,333	31,692	56,547	118,175	1.78	132.5
368	27	D	0.040	0	4099	100	25	0.2677	963,720	48,435	58,765	75,969	1.21	132.5
369	27	D	0.040	0	4099	100	25	0.2561	921,960	33,662	56,854	118,546	1.69	132.5
370	33	A	0.025	3895	205	70	63	0.2557	584,457	67,934	123,267	259,601	1.81	149.6
371	33	A	0.025	3895	205	70	68	0.2751	582,565	74,940	126,229	274,709	1.68	149.3
372	33	A	0.025	3895	205	70	73	0.2674	527,474	77,220	127,126	270,238	1.65	149.3
373	33	A	0.025	3895	205	100	54	0.1932	515,200	41,965	67,051	126,992	1.60	145.3
374	33	A	0.025	3895	205	100	61	0.2200	519,344	39,354	65,785	126,722	1.67	144.3
375	33	A	0.025	3895	205	100	60	0.2121	509,040	43,070	67,982	126,466	1.58	144.2
376	34	A	0.025	3895	205	70	1801	0.0714	5,709	47,079	75,250	147,993	1.60	146.8
377	34	A	0.025	3895	205	70	1881	0.0675	5,397	46,549	79,275	150,246	1.70	145.8
378	34	A	0.025	3895	205	70	1861	0.0718	5,741	44,957	73,959	136,915	1.65	145.6
379	34	A	0.025	3895	205	100	1862	0.0612	4,891	16,240	34,782	79,209	2.14	139.2
380	34	A	0.025	3895	205	100	1752	0.0627	5,153	14,667	33,959	76,432	2.32	138.7
381	34	A	0.025	3895	205	100	1860	0.0543	4,344	16,491	33,641	74,759	2.04	138.4
382	35	A	0.025	3895	205	70	54	0.2788	743,467	40,499	67,743	136,916	1.67	153.7
383	35	A	0.025	3895	205	70	51	0.2896	817,594	39,524	65,375	126,248	1.65	153.1
384	35	A	0.025	3895	205	70	50	0.3056	888,128	31,837	59,611	123,424	1.87	152.9
385	35	A	0.025	3895	205	100	57	0.1846	466,358	25,286	43,542	87,780	1.72	148.4
386	35	A	0.025	3895	205	100	48	0.1891	567,309	29,557	46,375	88,719	1.57	147.8
387	35	A	0.025	3895	205	100	52	0.1903	526,985	26,669	45,114	87,614	1.57	147.5
388	36	A	0.025	3895	205	70	32	0.2245	1,010,250	28,369	45,782	87,286	1.61	140.3
389	36	A	0.025	3895	205	70	29	0.2373	1,178,317	24,604	43,776	89,513	1.78	140.2
390	36	A	0.025	3895	205	70	33	0.2434	1,062,109	25,531	42,807	81,299	1.68	139.4
391	36	A	0.025	3895	205	100	53	0.1864	506,445	16,396	32,695	67,559	1.78	134.1
392	36	A	0.025	3895	205	100	44	0.1852	606,109	18,305	33,055	70,147	1.81	133.6
393	36	A	0.025	3895	205	100	55	0.1868	489,076	17,369	31,629	67,885	1.82	133.4
394	37	A	0.025	3895	205	70	100	0.1162	167,328	25,014	42,171	90,563	1.69	146.3
395	37	A	0.025	3895	205	70	84	0.1218	208,808	22,998	39,417	75,534	1.71	146.3
396	37	A	0.025	3895	205	70	92	0.1114	174,365	22,482	39,338	81,835	1.75	146.1
397	37	A	0.025	3895	205	100	739	0.0787	15,335	11,943	20,931	40,946	1.75	140.9
398	37	A	0.025	3895	205	100	591	0.0855	20,832	12,742	20,963	41,680	1.65	139.9
399	37	A	0.025	3895	205	100	543	0.0839	22,250	15,018	22,527	42,826	1.58	139.6
400	37	D	0.040	0	4099	70	33	0.2386	650,727	23,297	38,421	73,038	1.65	143.2
401	37	D	0.040	0	4099	70	35	0.2341	601,971	24,083	37,902	71,825	1.57	142.7
402	37	D	0.040	0	4099	70	34	0.2311	611,735	23,127	38,855	82,769	1.68	142.5
403	37	D	0.040	0	4099	100	56	0.1265	203,304	12,590	24,762	77,875	1.97	137.1
404	37	D	0.040	0	4099	100	53	0.1308	222,113	10,635	24,086	57,317	2.26	137.1
405	37	D	0.040	0	4099	100	56	0.1313	211,018	14,048	24,798	50,588	1.77	136.9
406	38	A	0.025	3895	205	70	295	0.1084	52,914	42,254	71,283	138,082	1.69	155.6
407	38	A	0.025	3895	205	70	294	0.1045	51,184	41,432	67,881	131,873	1.64	155.4
408	38	A	0.025	3895	205	70	288	0.1036	51,880	40,015	70,977	153,465	1.77	155.3
409	38	A	0.025	3895	205	100	386	0.0865	40,786	15,374	25,817	52,593	1.68	147.8
410	38	A	0.025	3895	205	100	256	0.0794	44,663	16,969	25,985	50,903	1.53	147.6
411	38	A	0.025	3895	205	100	274	0.0904	47,589	15,672	27,249	60,600	1.74	147.3
412	38	D	0.040	0	4099	70	221	0.1173	47,769	38,294	62,763	128,161	1.64	151.6
413	38	D	0.040	0	4099	70	196	0.1036	47,571	29,688	65,976	398,825	2.22	151.3
414	38	D	0.040	0	4099	70	197	0.1011	46,188	25,999	63,972	280,261	2.46	151.1
415	38	D	0.040	0	4099	100	235	0.0849	32,515	20,259	30,189	52,767	1.49	148.3

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (mmol)	IsQ-hexane (uL)	Toluene (uL)	T (°C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
416	38	D	0.040	0	4099	190	207	0.0943	41.080	16,007	29,825	57,614	1.86	147.0
417	38	D	0.040	0	4099	190	223	0.0952	38.422	15,370	29,744	59,150	1.94	146.9
418	39	A	0.025	3895	205	70	253	0.1002	57.031	1,254	2,091	3,913	1.67	128.1
419	39	A	0.025	3895	205	70	270	0.0924	49.280	1,154	1,944	4,059	1.68	125.6
420	39	A	0.025	3895	205	70	257	0.0953	53.398	1,116	1,864	3,880	1.67	124.3
421	39	A	0.025	3895	205	190	166	0.0982	85.186	1,244	2,066	3,900	1.66	125.3
422	39	A	0.025	3895	205	190	140	0.1050	108.080	1,336	2,331	5,141	1.75	124.9
423	39	A	0.025	3895	205	190	124	0.1077	125.071	1,459	2,366	4,228	1.62	124.9
424	39	D	0.040	0	4099	70	1801	0.0054	270					
425	39	D	0.040	0	4099	70	1801	0.0056	280					
426	39	D	0.040	0	4099	70	1800	0.0036	180					
427	39	D	0.040	0	4099	190	1800	0.0101	585	1,079	1,676	3,224	1.55	71.1
428	39	D	0.040	0	4099	190	1801	0.0091	455					
429	39	D	0.040	0	4099	190	1801	0.0088	440					
430	40	A	0.015	3874	226	70	1800	0.0102	1,360	99,168	150,788	291,025	1.52	162.5
431	40	A	0.015	3874	226	70	1801	0.0142	1,892	99,510	154,136	288,795	1.55	162.5
432	40	A	0.015	3874	226	70	1801	0.0160	2,132	102,729	158,781	288,132	1.55	162.3
433	40	A	0.025	3790	310	70	1801	0.0267	2,135	85,451	152,166	312,837	1.78	161.0
434	40	A	0.025	3790	310	70	1801	0.0263	2,183	98,629	159,634	315,675	1.62	163.0
435	40	A	0.025	3790	310	70	1802	0.0277	2,214	107,103	163,521	295,436	1.53	161.8
436	40	A	0.015	3874	226	100	1801	0.0129	1,719	59,333	90,756	160,693	1.53	159.0
437	40	A	0.015	3874	226	190	1801	0.0179	2,385	65,028	99,147	187,466	1.52	159.2
438	40	A	0.015	3874	226	190	1801	0.0189	2,519	77,254	111,036	199,658	1.44	158.5
439	40	A	0.025	3790	310	190	1801	0.0156	1,247	50,100	85,489	173,219	1.71	159.0
440	40	A	0.025	3790	310	190	1800	0.0301	2,468	57,306	92,223	173,759	1.61	158.3
441	40	A	0.025	3790	310	190	1800	0.0308	2,464	57,296	95,290	204,404	1.65	158.8
442	41	A	0.015	3874	226	70	975	0.0768	18,905	50,828	74,302	131,559	1.46	150.8
443	41	A	0.015	3874	226	70	838	0.0820	23,484	52,917	80,753	150,610	1.53	152.0
444	41	A	0.015	3874	226	70	602	0.0829	33,050	56,890	81,229	144,750	1.43	152.1
445	41	A	0.015	3874	226	190	562	0.0530	22,633	18,831	29,581	52,551	1.57	145.8
446	41	A	0.015	3874	226	100	619	0.0571	22,139	21,808	32,885	57,704	1.51	147.2
447	41	A	0.015	3874	226	190	628	0.0943	36,038	19,445	30,510	52,571	1.57	146.1
448	42	A	0.015	3874	226	70	1801	0.0250	3,331	49,901	74,728	134,686	1.50	161.8
449	42	A	0.015	3874	226	70	1800	0.0299	3,987	52,315	77,845	137,617	1.49	161.8
450	42	A	0.015	3874	226	70	1801	0.0167	2,225	51,778	77,230	137,579	1.49	161.3
451	42	A	0.015	3874	226	190	1800	0.0119	1,587	34,828	50,688	85,115	1.46	157.3
452	42	A	0.015	3874	226	190	1801	0.0260	3,465	38,912	55,840	98,875	1.44	158.0
453	42	A	0.015	3874	226	190	1800	0.0218	2,907	32,167	52,962	112,315	1.65	157.8
454	43	A	0.015	3874	226	70	199	0.0995	120.060	20,071	29,635	49,748	1.48	149.8
455	43	A	0.015	3874	226	70	235	0.1123	114.689	17,250	28,184	53,480	1.63	149.3
456	43	A	0.015	3874	226	70	283	0.1004	85,145	18,380	29,681	56,466	1.61	150.0
457	43	A	0.015	3874	226	100	238	0.0809	81,580	11,053	18,488	34,454	1.67	144.2
458	43	A	0.015	3874	226	190	229	0.1384	145.048	13,532	21,132	41,650	1.56	145.7
459	43	A	0.015	3874	226	190	386	0.0953	59,254	16,640	24,594	41,668	1.48	147.5
460	44	A	0.040	3664	436	70	1800	0.0203	1,015	76,863	124,841	244,688	1.62	162.2

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (μmol)	iso-hexane (μL)	Tol. hept. (μL)	T (°C)	quench time (s)	yield (g)	Activity (g P/μmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
461	44	A	0.040	3664	436	70	1880	0.0196	950	69,348	114,181	213,087	1.65	159.7
462	44	A	0.040	3664	436	70	1882	0.0191	954	83,066	130,140	229,862	1.57	160.7
463	44	A	0.040	3664	436	100	1880	0.0268	1,340	50,125	81,205	155,542	1.62	159.3
464	44	A	0.040	3664	436	100	1800	0.0267	1,335	51,920	84,310	165,231	1.62	159.0
465	44	A	0.040	3664	436	100	1800	0.0262	1,310	60,190	96,324	195,639	1.60	158.7
466	45	A	0.015	3874	226	70	1800	0.0307	4,093	67,453	97,174	166,626	1.44	153.7
467	45	A	0.015	3874	226	70	1881	0.0314	4,184	71,118	102,327	170,332	1.44	153.7
468	45	A	0.015	3874	226	70	776	0.0296	8,969	68,379	103,825	191,130	1.52	153.2
469	45	A	0.040	3664	436	70	516	0.0803	14,006	52,194	82,034	160,680	1.57	152.6
470	45	A	0.040	3664	436	70	598	0.0814	12,251	50,766	83,596	153,652	1.65	153.6
471	45	A	0.040	3664	436	70	542	0.0868	14,413	57,550	88,753	162,881	1.54	152.7
472	45	A	0.015	3874	226	100	1881	0.0316	4,211	23,068	35,964	64,587	1.56	147.7
473	45	A	0.015	3874	226	100	1881	0.0661	8,808	23,229	35,537	63,583	1.53	146.7
474	45	A	0.015	3874	226	100	1665	0.0557	8,029	23,561	36,325	66,140	1.54	146.7
475	45	A	0.040	3664	436	100	372	0.0745	18,024	16,641	28,662	62,468	1.72	147.8
476	45	A	0.040	3664	436	100	435	0.1001	20,710	17,961	29,427	56,683	1.64	147.7
477	45	A	0.040	3664	436	100	329	0.0658	18,000	16,133	26,647	51,129	1.65	147.2
478	46	A	0.015	3874	226	70	40	0.1280	768,000	241,971	396,626	819,061	1.64	159.0
479	46	A	0.015	3874	226	70	52	0.1506	695,077	237,440	374,600	710,984	1.58	159.2
480	46	A	0.015	3874	226	70	62	0.2337	904,645	228,726	380,009	759,735	1.66	159.5
481	46	A	0.015	3874	226	100	92	0.1254	327,130	123,955	198,082	367,438	1.60	159.1
482	46	A	0.015	3874	226	100	87	0.1799	496,276	99,752	175,606	390,135	1.76	158.3
483	46	A	0.015	3874	226	100	56	0.1257	538,714	115,590	189,795	392,714	1.64	158.1
484	47	A	0.015	3874	226	70	35	0.3055	2,094,857	106,333	175,439	360,361	1.65	141.1
485	47	A	0.015	3874	226	70	67	0.1843	660,179	150,684	232,403	446,157	1.54	142.1
486	47	A	0.015	3874	226	70	24	0.3419	3,419,000	85,061	153,033	335,033	1.80	141.1
487	47	A	0.015	3874	226	100	30	0.2499	1,999,200	64,627	106,989	227,559	1.66	140.1
488	47	A	0.015	3874	226	100	24	0.2313	2,313,000	62,747	97,547	186,298	1.55	139.6
489	47	A	0.015	3874	226	100	44	0.3398	1,849,091	47,753	84,988	172,618	1.78	138.8
490	48	A	0.015	3874	226	70	68	0.2367	835,412	333,293	563,196	1,224,397	1.69	162.0
491	48	A	0.015	3874	226	70	71	0.2606	880,981	320,505	547,286	1,178,612	1.71	161.5
492	48	A	0.015	3874	226	70	50	0.2385	1,144,800	229,731	471,227	1,289,171	2.05	159.6
493	48	A	0.015	3874	226	100	69	0.1629	566,609	122,354	209,331	435,953	1.64	160.3
494	48	A	0.015	3874	226	100	60	0.1632	652,800	113,442	187,016	381,183	1.65	161.1
495	48	A	0.015	3874	226	100	45	0.1455	776,000	107,526	189,344	453,902	1.76	160.1
496	49	A	0.015	3874	226	70	31	0.3585	2,775,484	101,529	256,690	747,407	2.53	146.6
497	49	A	0.015	3874	226	70	45	0.3815	2,034,667	130,996	299,548	848,069	2.29	146.6
498	49	A	0.015	3874	226	70	31	0.3866	2,993,032	106,997	271,984	775,467	2.54	145.8
499	49	A	0.015	3874	226	100	29	0.2717	2,248,552	67,593	139,831	411,235	2.07	145.6
500	49	A	0.015	3874	226	100	21	0.2208	2,523,429	67,519	130,825	332,725	1.94	145.4
501	49	A	0.015	3874	226	100	18	0.2118	2,824,000	59,229	127,550	324,707	2.15	145.2
502	50	A	0.015	3874	226	70	134	0.2848	510,090	359,005	597,487	1,294,056	1.66	162.6
503	50	A	0.015	3874	226	70	119	0.3662	617,546	305,675	563,609	1,374,894	1.84	162.7
504	50	A	0.015	3874	226	100	71	0.1375	464,789	103,444	173,971	344,309	1.68	160.1
505	50	A	0.015	3874	226	100	73	0.1431	470,466	116,244	189,183	382,891	1.63	161.0
506	50	A	0.015	3874	226	100	61	0.1594	627,148	102,487	161,116	380,669	1.57	160.7
507	51	A	0.015	3874	226	70	29	0.2495	2,064,828	117,996	269,868	771,498	2.29	149.1
508	51	A	0.015	3874	226	70	54	0.3885	1,726,667	115,395	290,100	867,225	2.51	149.2
509	51	A	0.015	3874	226	70	30	0.3339	2,671,200	107,686	306,761	945,424	2.85	149.9
510	51	A	0.015	3874	226	100	34	0.1268	895,059	78,329	136,705	317,192	1.75	148.4

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (μmol)	iso-hexane (ul.)	toluene (ul.)	T (°C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
511	51	A	0.015	3874	226	100	55	0.3243	1,415,127	42,029	87,174	254,258	2.07	146.4
512	51	A	0.015	3874	226	100	26	0.1991	1,837,846	52,395	103,266	267,446	1.97	147.2
513	52	A	0.015	3874	226	70	149	0.0952	153,342	180,181	278,591	546,034	1.55	163.3
514	52	A	0.015	3874	226	70	214	0.1227	137,607					
515	52	A	0.015	3874	226	70	201	0.1377	164,418	179,130	280,609	498,516	1.57	163.4
516	52	A	0.015	3874	226	100	227	0.0896	94,731	89,293	143,132	280,030	1.66	160.8
517	52	A	0.015	3874	226	100	226	0.1306	138,690	84,416	130,603	230,560	1.55	160.4
518	52	A	0.015	3874	226	100	238	0.1363	137,445	83,825	134,263	246,956	1.60	160.1
519	53	A	0.015	3874	226	70	63	0.1998	761,143	83,212	136,736	268,787	1.64	155.9
520	53	A	0.015	3874	226	70	81	0.2294	679,704	82,945	131,446	269,119	1.58	155.7
521	53	A	0.015	3874	226	70	62	0.2590	1,002,581	74,767	125,585	259,762	1.68	156.2
522	53	A	0.015	3874	226	100	79	0.1358	412,557	27,714	42,425	74,824	1.53	151.3
523	53	A	0.015	3874	226	100	47	0.1649	842,043	22,913	39,191	90,433	1.71	150.6
524	53	A	0.015	3874	226	100	47	0.1675	855,319	19,644	37,992	103,817	1.93	150.1
525	54	A	0.015	3874	226	70	562	0.0790	33,737	293,905	438,425	776,699	1.49	165.4
526	54	A	0.015	3874	226	70	695	0.0864	29,793	286,705	451,266	834,675	1.57	164.8
527	54	A	0.015	3874	226	70	499	0.0899	43,238	304,125	471,930	872,689	1.55	164.9
528	54	A	0.025	3790	310	70	295	0.0885	43,200	260,417	429,381	798,539	1.65	164.5
529	54	A	0.025	3790	310	70	337	0.1050	44,866	261,397	472,474	953,743	1.81	163.2
530	54	A	0.025	3790	310	70	313	0.0975	44,856	305,136	523,776	1,172,178	1.72	163.2
531	54	A	0.015	3874	226	100	1800	0.0417	5,560	126,649	200,896	366,335	1.59	162.8
532	54	A	0.015	3874	226	100	419	0.0624	35,742	134,212	220,113	448,580	1.64	161.6
533	54	A	0.015	3874	226	100	556	0.0634	27,367	152,791	246,989	501,730	1.62	162.8
534	54	A	0.025	3790	310	100	848	0.1125	19,104	133,966	248,425	592,006	1.85	161.3
535	54	A	0.025	3790	310	100	441	0.1144	37,355	124,519	212,634	437,774	1.71	160.6
536	54	A	0.025	3790	310	100	270	0.0834	44,480	125,810	210,026	392,625	1.67	161.2
537	56	A	0.015	3874	226	70	1801	-0.0013	-173					
538	56	A	0.015	3874	226	70	1801	0.0111	1,479	162,275	264,072	508,019	1.63	165.3
539	56	A	0.015	3874	226	70	1800	0.0511	6,813	217,120	322,092	590,243	1.48	163.3
540	56	A	0.040	3664	436	70	787	0.0759	8,680	157,345	250,730	471,613	1.59	163.5
541	56	A	0.040	3664	436	70	816	0.0789	8,702	159,242	273,689	581,167	1.72	163.8
542	56	A	0.040	3664	436	70	868	0.0831	8,616	192,622	302,144	626,955	1.57	163.8
543	56	A	0.015	3874	226	100	1800	-0.0008	-107					
544	56	A	0.015	3874	226	100	1801	0.0262	3,491	43,485	69,330	125,621	1.59	160.3
545	56	A	0.015	3874	226	100	1801	0.0274	3,651	47,833	73,153	129,934	1.53	160.3
546	56	A	0.040	3664	436	100	816	0.0790	8,713	34,092	58,192	106,648	1.71	159.8
547	56	A	0.040	3664	436	100	631	0.0570	8,130	36,040	59,018	116,281	1.64	160.8
548	56	A	0.040	3664	436	100	665	0.0507	7,944	38,616	61,071	120,482	1.58	160.6
549	57	A	0.015	3874	226	70	1800	0.0160	2,133	292,884	456,077	807,319	1.56	164.6
550	57	A	0.015	3874	226	70	1801	0.0635	8,462	365,586	608,076	1,222,436	1.66	163.6
551	57	A	0.015	3874	226	70	177	0.1209	163,932	451,100	726,152	1,476,551	1.61	164.3
552	57	A	0.025	3790	310	70	147	0.2087	204,441	322,213	529,416	1,044,495	1.64	165.7
553	57	A	0.025	3790	310	70	161	0.2241	200,437	325,996	539,562	1,032,593	1.66	165.5
554	57	A	0.025	3790	310	70	159	0.2321	210,204	316,103	547,215	1,051,284	1.73	165.3
555	57	A	0.015	3874	226	100	1801	0.0004	53					
556	57	A	0.015	3874	226	100	1801	0.0545	7,263	213,623	327,142	602,574	1.53	161.7
557	57	A	0.015	3874	226	100	1801	0.0541	7,209	203,110	306,293	557,386	1.51	161.6
558	57	A	0.025	3790	310	100	127	0.0871	98,759	141,271	225,127	415,707	1.59	161.9
559	57	A	0.025	3790	310	100	104	0.1044	144,554	125,463	221,448	429,231	1.77	162.0
560	57	A	0.025	3790	310	100	98	0.1065	156,490	126,786	237,728	492,520	1.88	162.7

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (μmol)	iso-hexane (wt.)	Tot. wgt. (wt.)	T (°C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
561	58	A	0.015	3874	226	70	57	0.2814	1,184,842	259,386	400,944	784,025	1.55	155.5
562	58	A	0.015	3874	226	70	39	0.3145	1,935,385	114,134	300,790	910,448	2.64	155.6
563	58	A	0.015	3874	226	70	69	0.3185	1,107,826	158,598	315,682	839,405	1.99	155.2
564	58	A	0.015	3874	226	70	50	0.3625	1,746,008	189,237	296,781	922,025	2.72	155.8
565	58	A	0.015	3874	226	70	44	0.3377	1,842,000	120,451	262,216	694,798	2.18	154.2
566	58	A	0.015	3874	226	70	39	0.3413	2,106,308	132,331	315,667	937,592	2.39	157.3
567	58	A	0.015	3874	226	100	201	0.0886	105,791	138,079	209,039	384,833	1.51	155.5
568	58	A	0.015	3874	226	100	50	0.1997	958,560	68,724	121,886	246,513	1.77	155.7
569	58	A	0.015	3874	226	100	44	0.1925	1,956,900	71,784	120,605	261,208	1.68	154.7
570	58	A	0.015	3874	226	100	39	0.1686	1,937,538	59,900	136,970	404,891	2.29	156.4
571	58	A	0.015	3874	226	100	46	0.1924	1,803,826	69,613	117,801	251,117	1.69	154.3
572	58	A	0.015	3874	226	100	42	0.2222	1,269,714	61,740	128,750	316,534	2.09	154.8
573	59	A	0.015	3874	226	70	1881	0.0236	3,145	47,513	69,623	119,075	1.47	153.0
574	59	A	0.015	3874	226	70	1880	0.0307	4,693	49,752	79,636	117,376	1.42	153.0
575	59	A	0.015	3874	226	70	1881	0.0430	5,738	51,072	72,949	123,669	1.43	152.7
576	59	A	0.025	3790	310	70	1881	0.0157	1,255	39,687	60,881	108,867	1.53	150.7
577	59	A	0.025	3790	310	70	1880	0.0250	2,909	42,109	68,472	140,117	1.63	151.9
578	59	A	0.025	3790	310	70	1650	0.0729	6,362	46,053	69,149	120,788	1.50	153.2
579	59	A	0.015	3874	226	100	1881	0.0169	2,252	6,937	10,603	19,482	1.53	142.0
580	59	A	0.015	3874	226	100	1881	0.0239	3,185	21,308	32,244	56,447	1.51	148.1
581	59	A	0.025	3790	310	100	1880	0.0288	2,304	8,131	12,449	22,976	1.53	142.2
582	59	A	0.025	3790	310	100	1881	0.0400	3,198	8,051	12,075	21,446	1.50	142.1
583	59	A	0.025	3790	310	100	1881	0.0443	3,542	7,961	13,192	26,781	1.66	142.0
584	66	A	0.015	3874	226	70	14	0.3851	6,601,714	159,342	411,847	1,959,227	2.58	147.9
585	66	A	0.015	3874	226	70	12	0.4152	8,304,008	135,485	459,460	1,348,474	3.39	148.0
586	66	A	0.015	3874	226	70	9	0.4090	10,906,667	182,946	454,632	1,253,701	2.79	148.2
587	66	A	0.015	4895	105	70	2	0.3177	38,124,908	151,115	447,103	1,271,334	2.96	148.6
588	66	A	0.015	4895	105	70	6	0.4778	19,112,908	210,339	501,665	1,299,984	2.39	147.8
589	66	A	0.015	4895	105	70	5	0.4552	21,849,608	140,310	417,751	1,181,311	2.98	147.4
590	66	A	0.015	4895	105	70	10	0.3463	8,311,208	140,870	391,436	1,075,826	2.78	147.6
591	66	A	0.020	4945	55	70	3	0.4389	26,334,900	187,389	513,970	1,491,780	2.74	147.2
592	66	A	0.020	4945	55	70	24	0.3309	2,481,756	375,945	682,203	1,548,200	1.81	150.9
593	66	A	0.020	4945	55	70	11	0.4498	7,366,364	167,844	476,684	1,345,683	2.84	147.4
594	66	A	0.020	4945	55	70	22	0.4167	3,409,364	237,220	527,252	1,325,162	2.22	148.7
595	66	A	0.020	4945	55	70	2	0.4382	39,438,608	155,332	450,488	1,250,302	2.98	147.1
596	66	A	0.020	4945	55	70	2	0.4397	39,573,608	165,647	441,561	1,161,349	2.67	147.2
597	66	A	0.015	3874	226	100	29	0.3560	2,946,207	50,670	178,199	564,757	3.52	145.0
598	66	A	0.015	3874	226	100	17	0.1448	2,044,235	46,548	145,190	580,428	3.12	144.0
599	66	A	0.015	3874	226	100	13	0.2665	4,926,900	72,969	183,907	489,338	2.52	145.9
600	66	A	0.015	4895	105	100	11	0.2471	5,391,273	88,168	189,600	463,270	2.15	146.6
601	66	A	0.015	4895	105	100	16	0.2438	3,657,900	88,455	192,599	483,761	2.18	148.1
602	66	A	0.015	4895	105	100	16	0.2633	3,949,500	93,225	209,126	587,516	2.24	147.3
603	66	A	0.015	4895	105	100	14	0.2368	4,859,429	88,566	208,187	561,582	2.35	147.8
604	66	A	0.020	4945	55	100	34	0.2287	1,218,765	144,257	261,362	568,066	1.81	148.2
605	66	A	0.020	4945	55	100	50	0.1954	703,440	195,778	314,110	640,818	1.60	149.1
606	66	A	0.020	4945	55	100	23	0.3215	2,516,887	104,631	211,831	520,313	2.02	146.4
607	66	A	0.020	4945	55	100	19	0.2972	2,815,579	79,986	191,379	531,146	2.39	146.4
608	66	A	0.020	4945	55	100	22	0.3160	2,585,455	65,369	195,189	585,188	2.99	145.7
609	66	A	0.020	4945	55	100	19	0.2479	2,348,526	80,058	196,994	554,076	2.46	145.7
610	62	A	0.015	3874	226	70	159	0.3470	523,774	425,988	731,854	1,551,140	1.72	153.0

TABLE 1: Propylene homo-polymerizations (Cont.)

Ex#	Cat ID	Act ID	Cat (μmol)	iso-hexane (wt.)	Tot. wgt. (wt.)	T (°C)	quench time (s)	yield (g)	Activity (g P/mmol cat.hr)	Mn	Mw	Mz	PDI	Tm (°C)
611	62	A	0.015	3874	226	70	155	0.3307	512.952	445,527	810,960	1,904,855	1.82	152.0
612	62	A	0.015	3874	226	70	109	0.2145	472.294	496,297	843,255	1,774,860	1.7	152.6
613	62	A	0.015	3874	226	100	98	0.1558	381.551	189,582	326,415	650,653	1.72	149.9
614	62	A	0.015	3874	226	100	78	0.1309	402.769	166,731	319,094	800,071	1.91	151.4
615	62	A	0.015	3874	226	100	117	0.1462	299.897	209,797	336,548	698,532	1.6	149.7
616	63	A	0.015	3874	226	70	13	0.4206	7,764.923	75,331	421,253	1,578,065	5.59	148.9
617	63	A	0.015	3874	226	70	12	0.3705	7,410.000	98,122	448,941	1,696,313	4.58	149.4
618	63	A	0.015	3874	226	70	11	0.3438	7,501.091	149,128	486,789	1,465,216	3.26	150.7
619	63	A	0.015	3874	226	100	18	0.2914	3,885.333	38,824	139,868	486,111	3.6	146.6
620	63	A	0.015	3874	226	100	12	0.2497	4,994.900	37,610	149,403	551,958	3.97	147.0
621	63	A	0.015	3874	226	100	17	0.1459	2,859.765	27,625	120,442	474,367	4.36	143.7

TABLE 9: Propylene homo- and co-polymerizations

Ex#	Cat ID	Cat (umol)	Comon-omer	Comon-omer (uL)	Iso-hexane (uL)	Tol-uene (uL)	Quench time (s)	Yield (g)	Activity (g P/ mmol cathr)	Mn	Mw	Mz	PDI	Tm (°C)
622	5	0.020	-	0	3832	268	49	0.3676	1,350,367	84,070	262,040	852,508	3.12	158.5
623	5	0.020	-	0	3832	268	53	0.3345	1,136,038	127,569	370,689	1,349,145	2.91	159.1
624	5	0.020	-	0	3832	268	53	0.3558	1,208,377	87,224	308,309	1,164,102	3.53	159.5
625	5	0.020	-	0	3832	268	36	0.3371	1,685,500	91,839	318,737	1,196,357	3.47	159.6
626	5	0.020	C8	100	3732	268	52	0.2781	962,654	143,213	314,629	858,328	2.20	98.3
627	5	0.020	C8	100	3732	268	62	0.2757	800,419	170,387	334,559	847,908	1.96	99.8
628	5	0.020	C8	200	3632	268	54	0.2322	774,000	146,237	276,727	609,153	1.89	
629	5	0.020	C8	200	3632	268	64	0.2528	711,000	136,252	304,303	810,841	2.23	
630	5	0.020	C10	100	3732	268	52	0.2464	852,923	134,150	314,690	853,662	2.35	101.8
631	5	0.020	C10	100	3732	268	59	0.3469	1,058,339	130,404	298,937	856,309	2.29	113.7
632	5	0.020	C10	200	3632	268	80	0.1865	419,625	189,620	360,832	798,111	1.90	
633	5	0.020	C10	200	3632	268	66	0.3103	846,273	130,794	290,852	767,592	2.22	
634	5	0.020	C14	100	3732	268	51	0.2451	865,059	128,282	355,778	1,024,468	2.77	115.8
635	5	0.020	C14	100	3732	268	57	0.3616	1,141,895	124,970	301,217	811,646	2.41	122.8
636	5	0.020	C14	200	3632	268	57	0.2862	903,789	115,484	336,936	894,349	2.92	87.0
637	5	0.020	C14	200	3632	268	47	0.2223	851,362	159,821	326,789	829,025	2.04	
638	6	0.020	-	0	3832	268	9	0.3969	7,938,000	70,869	358,986	1,488,658	5.07	147.9
639	6	0.020	-	0	3832	268	15	0.3976	4,771,200	63,781	356,482	1,334,195	5.59	148.4
640	6	0.020	C8	100	3732	268	60	0.4938	1,481,400	48,096	225,988	912,754	4.70	97.0
641	6	0.020	C8	200	3632	268	81	0.5364	1,192,000	63,024	198,902	721,079	3.16	
642	6	0.020	C10	200	3632	268	67	0.5446	1,463,104	47,304	228,972	1,225,088	4.84	
643	6	0.020	C14	100	3732	268	49	0.4800	1,763,265	55,787	289,382	1,118,389	5.19	118.3
644	6	0.020	C14	200	3632	268	66	0.5052	1,377,818	71,963	275,586	1,091,173	3.83	
645	57	0.025	-	0	3790	310	142	0.2098	212,755	312,208	559,318	1,159,003	1.79	164.6
646	57	0.025	-	0	3790	310	173	0.1318	109,706	264,086	501,589	1,040,883	1.90	165.1
647	57	0.025	C8	100	3690	310	134	0.2061	221,481	172,851	401,395	964,719	2.32	91.5
648	57	0.025	C8	100	3690	310	137	0.2291	240,806	168,688	354,843	778,576	2.10	93.3
649	57	0.025	C8	200	3590	310	145	0.2117	210,240	161,543	315,000	690,976	1.95	
650	57	0.025	C8	200	3590	310	150	0.2264	217,344	152,856	323,327	746,490	2.12	
651	57	0.025	C10	100	3690	310	131	0.2204	242,272	199,340	372,534	743,550	1.87	94.4
652	57	0.025	C10	200	3590	310	143	0.2535	255,273	184,951	351,512	735,846	1.90	
653	57	0.025	C10	200	3590	310	140	0.2729	280,697	153,628	343,332	843,815	2.23	
654	57	0.025	C14	100	3690	310	127	0.1785	202,394	216,764	450,995	1,028,077	2.08	100.1
655	57	0.025	C14	100	3690	310	128	0.2346	263,925	239,524	470,156	1,067,185	1.96	116.8
656	57	0.025	C14	200	3590	310	165	0.2923	255,098	201,143	408,989	939,956	2.03	
657	57	0.025	C14	200	3590	310	124	0.2655	308,323	198,445	388,950	862,735	1.96	

TABLE 10: Propylene co-polymerizations with 4-methyl-1-pentene

Ex#	Cat ID	Cat (umol)	C3 (dL)	iso-texane (dL)	Tol-pentene (dL)	quench time (s)	yield (g)	Activity Is (mmol/mol cat hr)	Mn	Mw	Mz	PDI	[MFI] (mod %)	C3 (mod %)	[PFI] (mod %)	[4MP-1-P] (mod %)	[4MP-1-40P-1] (mod %)
658	1	0.080	100	4064	436	21	0.3644	780.957	18,872	43,079	114,324	2.28					
659	1	0.080	100	4064	436	21	0.3772	808,288	16,481	40,164	103,543	2.44	39.8	60.2	0.346	0.512	0.142
660	1	0.080	300	3864	436	16	0.4556	1,281,375	17,016	47,231	148,876	2.78					
661	1	0.080	300	3864	436	16	0.4106	1,154,813	17,666	43,562	118,076	2.47					
662	1	0.080	500	3664	436	14	0.4145	1,332,321	12,405	45,203	143,116	3.64					
663	1	0.080	500	3664	436	12	0.4616	1,693,500	14,749	42,580	116,095	2.89	33.0	67.0	0.429	0.484	0.088
664	3	0.080	100	4064	436	91	0.1757	86,085	11,658	20,829	39,798	1.79	39.8	60.2	0.346	0.512	0.142
665	3	0.080	100	4064	436	88	0.1684	86,114	9,582	20,519	44,565	2.14					
666	3	0.080	300	3864	436	43	0.2726	285,279	16,173	29,243	59,275	1.81					
667	3	0.080	300	3864	436	42	0.2388	255,857	14,044	26,642	52,989	1.90					
668	3	0.080	500	3664	436	29	0.2691	417,569	16,565	32,267	71,868	1.95					
669	3	0.080	500	3664	436	32	0.2984	419,625	15,509	28,554	60,370	1.84	29.9	70.1	0.472	0.457	0.070
670	5	0.080	100	4064	436	25	0.4680	842,400	18,284	44,149	122,245	2.41	46.0	54.0	0.297	0.485	0.218
671	5	0.080	100	4064	436	29	0.4102	636,517	15,864	40,905	104,106	2.58					
672	5	0.080	300	3864	436	15	0.4852	1,455,609	12,835	42,602	126,013	3.32					
673	5	0.080	300	3864	436	13	0.4939	1,709,654	16,785	48,494	136,966	2.89	38.0	62.0	0.370	0.500	0.130
674	5	0.080	500	3664	436	13	0.4983	1,724,885	15,205	47,598	143,633	3.13	35.8	64.2	0.480	0.484	0.116
675	5	0.080	500	3664	436	12	0.4649	1,743,375	9,564	41,148	143,959	4.30					
676	6	0.080	100	4064	436	80	0.2222	124,988	15,453	28,256	53,831	1.70	39.6	60.4	0.351	0.508	0.143
677	6	0.080	100	4064	436	94	0.2149	102,878	12,091	22,974	45,220	1.83					
678	6	0.080	300	3864	436	38	0.2567	383,987	17,901	31,862	74,385	1.79					
679	6	0.080	300	3864	436	37	0.2531	397,824	16,964	30,900	69,477	1.92	33.4	66.6	0.430	0.471	0.099
680	6	0.080	500	3664	436	30	0.3823	453,450	17,273	29,821	57,073	1.73	32.1	67.9	0.448	0.482	0.090
681	6	0.080	500	3664	436	29	0.2887	447,983	18,144	31,419	65,484	1.73					
682	48	0.080	100	4064	436	26	0.3634	628,962	21,802	48,148	128,964	2.21	42.7	57.3	0.316	0.516	0.169
683	48	0.080	100	4064	436	28	0.3443	595,904	23,432	47,359	121,821	2.02					
684	48	0.080	300	3864	436	23	0.3881	759,325	24,847	46,091	100,546	1.85					
685	48	0.080	300	3864	436	22	0.3795	776,250	20,851	47,125	118,463	2.25					
686	48	0.080	500	3664	436	18	0.3876	969,006	19,444	49,287	136,556	2.48					
687	48	0.080	500	3664	436	18	0.4078	1,019,506	16,106	43,545	137,060	2.70	34.0	66.0	0.418	0.485	0.097
688	49	0.080	100	4064	436	183	0.1443	35,484	10,292	19,633	38,392	1.91					
689	49	0.080	100	4064	436	198	0.1543	35,068	10,013	18,598	38,198	1.88	40.2	59.8	0.336	0.523	0.140
690	49	0.080	300	3864	436	71	0.1783	113,807	15,571	25,741	50,738	1.65					
691	49	0.080	300	3864	436	86	0.1585	82,936	9,980	21,063	43,176	2.11					
692	49	0.080	500	3664	436	51	0.1905	168,088	15,215	28,991	51,365	1.71					
693	49	0.080	500	3664	436	54	0.1912	159,333	14,853	28,247	51,870	1.77	31.9	68.1	0.440	0.482	0.078
694	64	0.080	100	4064	436	32	0.2927	411,609	7,306	13,139	28,137	1.89					
695	64	0.080	100	4064	436	33	0.2968	407,455	6,492	11,473	23,442	1.77	38.4	60.5	0.358	0.500	0.144
696	64	0.080	300	3864	436	22	0.3138	641,864	7,574	13,713	29,828	1.81					
697	64	0.080	300	3864	436	26	0.3397	587,942	7,344	12,951	28,305	1.84	33.4	66.6	0.430	0.471	0.099
698	64	0.080	500	3664	436	22	0.3379	691,159	7,737	14,264	29,998	1.94					
699	64	0.080	500	3664	436	24	0.4130	774,375	6,158	14,865	38,639	2.28	30.4	69.6	0.474	0.444	0.082
700	65	0.080	100	4064	436	137	0.1399	45,953	2,439	4,234	9,401	1.74					
701	65	0.080	100	4064	436	123	0.1476	54,000	2,735	4,558	9,083	1.67	34.6	65.4	0.427	0.454	0.119
702	65	0.080	300	3864	436	93	0.1571	76,016	2,911	5,121	11,539	1.79					
703	65	0.080	300	3864	436	89	0.1556	78,674	2,933	5,359	12,632	1.83					
704	65	0.080	500	3664	436	78	0.1690	97,509	2,928	5,256	11,083	1.79					
705	65	0.080	500	3664	436	80	0.1836	103,275	3,576	5,693	11,000	1.59	28.4	71.6	0.519	0.395	0.086

Table 2. Comparative propylene polymerization data using highly isotactic catalysts.

Standard conditions include 1.1 equiv. activator when activator A, or C used, or 500 equiv. activator when activator D is used. Activator IDs are [PhMe₂NH][B(C₆F₅)₄] is A where C₆F₅ is perfluorophenyl; [PhMe₂NH][B(C₁₀F₇)₄] is C where C₁₀F₇ is perfluoronaphthalen-2-yl; and methylalumoxane (MAO) is D. When activators A, B or C are used, 0.5 umol TnOAl (tri-n-octylaluminum) is used as a scavenger. 1 ml propylene and a total of 4.1 mL of solvents were used. The reaction was stirred at 800 rpm, and the reaction was quenched after 8 psi of pressure loss or a maximum of 30 minutes of reaction time is quench pressure was not met, or unless specified otherwise. Catalyst C₁ was preactivated with 20 equiv. of MAO prior to injection into the reactor with a total of 500 equiv. of MAO was used for the reaction. **a quench pressure of 20 psi pressure loss was used. *a quench pressure of 15 psi pressure loss or a maximum of 15 minutes reaction time was used. Equivalents (equiv.) are given as molar ratios.

Ex#	Cat ID	Act ID	Cat (umol)	iso-hexane (uL)	Tol-uene (uL)	T (°C)	quench time (s)	yield (g)	Activity (g P/ mmol cat hr)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	PDI (Mw/Mn)	Tm (°C)
C-1**	C1	D	0.080	3839	259	40	961	0.0194	969	473,913	682,112		1.44	158.7
C-2**	C1	D	0.080	3839	259	40	900	0.0234	1,170	626,564	902,587		1.44	158.3
C-3**	C1	D	0.080	3839	259	40	900	0.0214	1,070	531,283	810,946		1.53	158.2
C-4**	C1	D	0.080	3839	259	40	990	0.0155	775	461,513	616,297		1.34	158.1
C-5**	C1	D	0.080	3839	259	40	961	0.0302	1,568	483,465	828,673		1.70	157.3
C-6**	C1	D	0.080	3839	259	40	981	0.0425	2,124	542,135	936,373		1.73	152.2
C-7**	C1	D	0.080	3839	259	70	652	0.1789	12,349	751,244	1,072,754		1.43	159.9
C-8**	C1	D	0.080	3839	259	70	680	0.1325	8,765	772,366	1,173,134		1.52	157.9
C-9**	C1	D	0.080	3839	259	70	588	0.2026	15,516	525,234	991,247		1.89	157.8
C-10**	C1	D	0.080	3839	259	70	796	0.1980	12,513	728,609	1,124,262		1.54	157.3
C-11**	C1	D	0.080	3839	259	70	656	0.1355	9,289	765,034	1,101,564		1.44	157.2
C-12**	C1	D	0.080	3839	259	70	691	0.1708	11,125	819,208	1,150,050		1.40	157.1
C-13**	C1	D	0.080	3839	259	100	363	0.1501	22,306	214,360	316,777		1.48	158.2
C-14**	C1	D	0.080	3839	259	100	286	0.1363	21,453	197,114	310,112		1.57	157.8
C-15**	C1	D	0.080	3839	259	100	322	0.1384	19,318	207,479	318,331		1.53	156.8
C-16**	C1	D	0.080	3839	259	100	304	0.1369	20,285	190,725	316,437		1.56	156.6
C-17**	C1	D	0.080	3839	259	100	360	0.1259	19,504	179,814	288,837		1.61	156.5
C-18**	C1	D	0.080	3839	259	100	320	0.1191	16,733	171,710	271,795		1.58	155.9
C-19*	C2	A	0.020	3890	210	70	1089	0.2852	47,149	772,875	1,187,870		1.54	160.6
C-20*	C2	A	0.020	3890	210	70	1179	0.2381	36,367	523,109	765,580		1.46	160.5
C-21*	C2	A	0.020	3890	210	70	1079	0.1993	33,241	853,584	1,212,983		1.42	160.0
C-22	C2	A	0.025	3895	205	70	417	0.1074	37,988	723,734	1,269,304	2,907,247	1.75	163.6
C-23	C2	A	0.025	3895	205	70	323	0.2909	129,609	516,715	963,614	2,385,727	1.86	162.4
C-24	C2	A	0.025	3895	205	70	268	0.3633	195,206	251,696	665,814	2,086,521	2.65	161.7
C-25*	C2	A	0.020	3890	210	100	654	0.1398	38,507	182,851	318,301		1.74	156.7

Table 2. Comparative propylene polymerization data using highly isotactic catalysts. (Cont.)

Standard conditions include 1.1 equiv. activator when activator A, or C used, or 500 equiv. activator when activator D is used. Activator IDs are [PhMe₂NH][B(C₆F₅)₄] is A where C₆F₅ is perfluorophenyl; [PhMe₂NH][B(C₁₀F₇)₄] is C where C₁₀F₇ is perfluoronaphthalen-2-yl; and methylalumoxane (MAO) is D. When activators A, B or C are used, 0.5 umol TnOAl (tri-n-octylaluminum) is used as a scavenger. 1 ml propylene and a total of 4.1 mL of solvents were used. The reaction was stirred at 800 rpm, and the reaction was quenched after 8 psi of pressure loss or a maximum of 30 minutes of reaction time is quench pressure was not met, or unless specified otherwise. Catalyst C₁ was preactivated with 20 equiv. of MAO prior to injection into the reactor with a total of 500 equiv. of MAO was used for the reaction. **a quench pressure of 20 psi pressure loss was used. *a quench pressure of 15 psi pressure loss or a maximum of 15 minutes reaction time was used. Equivalents (equiv.) are given as molar ratios.

Ex#	Cat ID	Act ID	Cat (umol)	Iso-hexane (ul)	Toluene (ul)	T (C)	quench time (s)	yield (g)	Activity (g P/mmol cat hr)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	PDI (Mw/Mn)	Tm (°C)
C-26*	C2	A	0.020	3890	210	100	533	0.1509	50.961	214,187	313,219		1.46	156.6
C-27*	C2	A	0.020	3890	210	100	535	0.1451	48.436	191,837	273,363		1.42	156.3
C-28	C2	A	0.025	3895	205	100	97	0.1605	223,423	125,819	215,082	445,762	1.72	155.8
C-29	C2	A	0.025	3895	205	100	120	0.1669	208,280	105,326	208,174	489,364	1.98	155.5
C-30	C2	A	0.025	3895	205	100	254	0.0678	38,438	140,442	243,853	502,914	1.74	154.8
C-31*	C2	C	0.020	3890	210	70	459	0.3234	126,879	505,090	869,397		1.70	161.4
C-32*	C2	C	0.020	3890	210	70	482	0.3581	133,675	438,764	786,227		1.79	160.0
C-33*	C2	C	0.020	3890	210	70	546	0.3704	122,043	400,607	880,474		2.20	158.9
C-36*	C2	C	0.020	3890	210	100	282	0.1732	110,671	191,899	283,522		1.48	157.3
C-37*	C2	C	0.020	3890	210	100	305	0.1669	98,466	162,543	258,939		1.58	156.4
C-38*	C2	C	0.020	3890	210	100	276	0.1636	108,851	183,044	266,686		1.46	155.9
C-39	C2	D	0.040	0	4099	70	188	0.3404	162,957	298,482	630,605	1,671,736	2.11	159.6
C-40	C2	D	0.040	0	4099	70	256	0.4490	157,852	224,554	560,175	1,621,450	2.49	159.5
C-41	C2	D	0.040	0	4099	70	234	0.4033	155,115	203,125	534,216	1,609,964	2.63	158.1
C-42	C2	D	0.040	0	4099	100	123	0.1486	108,732	166,877	308,565	674,227	1.85	157.7
C-43	C2	D	0.040	0	4099	100	114	0.1373	108,395	166,844	307,246	685,825	1.84	156.3
C-44	C2	D	0.040	0	4099	100	115	0.1392	108,939	163,385	298,673	629,187	1.83	156.3
C-45	55	A	0.025	3790	310	70	1801	-0.0012	-96					
C-46	55	A	0.025	3790	310	70	1800	-0.0013	-104					
C-47	55	A	0.025	3790	310	70	1801	-0.0012	-96					
C-48	55	A	0.025	3790	310	100	1801	-0.0010	-60					
C-49	55	A	0.025	3790	310	100	1801	-0.0011	-88					
C-50	55	A	0.025	3790	310	100	1800	-0.0004	-32					

Table 3. ^{13}C NMR data for select examples and comparative examples from Tables 1 and 2.

5 ^Indicates samples that were combined for NMR analysis. More specifically, the following examples were combined for ^{13}C NMR analysis: 160-161; 169 & 171; 179-179; 230-231; 260 & 262; 266-268; 298-300; 326, 328 & 329; 349-351; 376-378; 379-381; 394 & 396; 397-399; 404-405; 406-408; 409-411; 412-413; 415-417; 418-420; 421-423; 454-456; 457-459; 469-471; 475-477; 514-515; 517-518; 523-524; 528-530; 534-536; 552-553; 558-560.

Ex#	Cat ID	Act ID	mmmm	mmmr	mmrf	mmrr	mmrm + mrrr	mmrm	rrrr	mrrr	rrrm	stereo defects /10000 monomer	2,1-regio (ee) defects /10000 monomer	2,1-regio (et) defects /10000 monomer	2,1-regio (se) defects /10000 monomer	1,3-regio defects /10000 monomer	ave. meso run length
1	1	A	0.972	0.005	0.006	0.007	0.003	0.001	0.001	0.002	0.004	52.1	24.3	5.6	0.0	0.0	122.0
4	1	A	0.974	0.005	0.004	0.008	0.003	0.001	0.000	0.001	0.003	59.8	17.3	4.6	0.0	0.0	122.4
7	1	A	0.965	0.006	0.007	0.008	0.003	0.002	0.002	0.003	0.005	64.7	23.0	6.2	0.0	0.0	106.5
11	1	A	0.961	0.006	0.009	0.011	0.005	0.002	0.001	0.001	0.004	88.2	15.0	3.3	0.0	0.0	93.9
14	2	A	0.977	0.003	0.007	0.004	0.003	0.001	0.001	0.002	0.002	41.3	14.9	3.1	0.0	0.0	168.6
17	2	A	0.981	0.004	0.003	0.004	0.003	0.001	0.000	0.001	0.002	39.3	15.3	2.1	0.0	0.0	176.4
20	2	A	0.966	0.005	0.009	0.007	0.005	0.001	0.001	0.002	0.004	62.5	18.3	4.0	0.0	0.0	117.9
24	2	A	0.962	0.006	0.009	0.008	0.007	0.002	0.001	0.001	0.003	86.8	16.0	0.0	0.0	0.0	97.3
26	3	A	0.964	0.008	0.006	0.010	0.004	0.002	0.000	0.001	0.004	78.0	64.9	9.1	0.0	3.8	64.2
28	3	A	0.968	0.010	0.004	0.008	0.004	0.001	0.001	0.001	0.004	62.4	68.4	10.2	0.0	2.9	69.5
32	3	A	0.953	0.008	0.007	0.011	0.006	0.003	0.002	0.002	0.007	100.5	66.5	11.0	0.0	0.0	56.2
35	3	A	0.941	0.013	0.011	0.013	0.007	0.005	0.002	0.002	0.007	120.6	68.2	10.7	0.0	11.5	47.4
38	4	A	0.964	0.005	0.009	0.007	0.008	0.001	0.001	0.003	0.003	74.1	48.8	6.1	0.0	0.0	77.5
39	4	A	0.947	0.005	0.007	0.007	0.007	0.004	0.002	0.010	0.011	84.9	48.3	0.0	0.0	21.3	64.7
41	4	A	0.945	0.008	0.009	0.010	0.016	0.001	0.002	0.004	0.004	132.8	50.9	0.0	0.0	0.0	54.4
45	4	A	0.944	0.010	0.008	0.010	0.016	0.003	0.002	0.003	0.004	137.2	47.3	0.0	0.0	7.8	52.0
47	5	A	0.977	0.004	0.005	0.004	0.003	0.001	0.001	0.002	0.003	42.1	14.7	3.6	0.0	0.0	165.6
49	5	A	0.976	0.004	0.006	0.004	0.003	0.001	0.000	0.002	0.002	43.6	15.0	3.6	0.0	0.0	160.8
51	5	A	0.975	0.005	0.005	0.006	0.003	0.000	0.001	0.002	0.003	45.0	17.9	3.9	0.0	0.0	149.7
52	5	A	0.979	0.005	0.005	0.004	0.003	0.000	0.000	0.001	0.002	35.9	16.9	3.9	0.0	0.0	176.4
53	5	A	0.968	0.005	0.007	0.007	0.004	0.002	0.001	0.002	0.004	63.7	16.0	4.7	0.0	0.0	118.5
61	5	A	0.972	0.008	0.004	0.007	0.003	0.001	0.000	0.000	0.004	58.9	56.0	9.9	0.0	2.6	78.5
62	5	A	0.958	0.005	0.010	0.007	0.007	0.003	0.001	0.005	0.006	81.2	15.7	0.0	0.0	0.0	103.2
63	5	A	0.961	0.007	0.007	0.008	0.005	0.002	0.002	0.003	0.005	71.6	17.3	4.5	0.0	0.0	107.1
66	5	A	0.935	0.007	0.016	0.012	0.012	0.004	0.002	0.004	0.008	139.4	16.6	0.0	0.0	0.0	64.1
71	5	A	0.954	0.009	0.009	0.009	0.007	0.003	0.002	0.001	0.005	97.9	19.6	0.0	0.0	0.0	85.1
73	5	A	0.962	0.006	0.011	0.007	0.006	0.001	0.001	0.003	0.003	69.0	15.1	4.5	0.0	0.0	112.9
75	5	A	0.956	0.006	0.011	0.008	0.007	0.002	0.001	0.004	0.005	84.4	14.9	4.4	0.0	0.0	96.4
78	5	B	0.964	0.007	0.010	0.007	0.004	0.001	0.001	0.003	0.004	63.7	22.3	4.3	0.0	0.0	110.7
83	5	C	0.971	0.005	0.007	0.006	0.004	0.001	0.000	0.002	0.003	51.5	17.2	4.9	0.0	0.0	135.9
88	5	C	0.961	0.006	0.008	0.008	0.005	0.002	0.001	0.003	0.005	75.4	24.5	4.2	0.0	0.0	96.1
91	6	A	0.958	0.008	0.008	0.010	0.005	0.003	0.001	0.001	0.005	89.9	60.6	9.9	0.0	3.9	60.9
93	6	A	0.950	0.008	0.007	0.008	0.006	0.002	0.001	0.002	0.005	80.4	71.9	8.5	0.0	0.0	62.2
96	6	A	0.954	0.009	0.009	0.010	0.006	0.003	0.002	0.001	0.005	95.9	56.9	9.5	0.0	4.3	60.0
99	6	A	0.960	0.013	0.005	0.010	0.004	0.002	0.001	0.001	0.005	76.2	68.9	11.2	0.0	3.8	62.5
102	6	A	0.960	0.009	0.009	0.001	0.007	0.003	0.001	0.004	0.007	47.1	168.3	10.4	0.0	0.0	44.3
106	6	A	0.959	0.012	0.005	0.011	0.005	0.002	0.000	0.000	0.005	87.1	61.5	10.2	0.0	11.9	58.6
107	6	B	0.969	0.007	0.010	0.000	0.005	0.001	0.001	0.003	0.005	28.0	161.2	8.8	0.0	0.0	50.5
113	6	C	0.958	0.008	0.008	0.009	0.005	0.002	0.001	0.003	0.005	80.2	75.9	10.1	0.0	0.0	60.2

Table 3. ¹³C NMR data for select examples and comparative examples from Tables 1 and 2. (Cont)

^aIndicates samples that were combined for NMR analysis. More specifically, the following examples were combined for ¹³C NMR analysis: 160-161; 169 & 171; 179-179; 230-231; 260 & 262; 266-268; 298-300; 326, 328 & 329; 349-351; 376-378; 379-381; 394 & 396; 397-399; 404-405; 406-408; 409-411; 412-413; 415-417; 418-420; 421-423; 454-456; 457-459; 469-471; 475-477; 514-515; 517-518; 523-524; 528-530; 534-536; 552-553; 558-560.

Ex#	Cat ID	Act ID	mmmm	mmmr	mmrf	mmrr	mmrm + mmrr	mmrm	mmrr	mmrr	mmrm	stereo defects /10000 monomer	2,1-regio (ee) defects /10000 monomer	2,1-regio (et) defects /10000 monomer	2,1-regio (se) defects /10000 monomer	1,3-regio defects /10000 monomer	ave. meso run length
116	6	C	0.953	0.009	0.009	0.010	0.006	0.002	0.001	0.003	0.006	91.9	80.7	9.9	0.0	0.0	54.8
119	7	A	0.975	0.004	0.007	0.005	0.003	0.001	0.001	0.002	0.003	43.8	12.8	4.1	0.0	0.0	164.7
123	7	A	0.979	0.005	0.004	0.005	0.003	0.001	0.001	0.001	0.002	43.8	11.4	2.6	0.0	1.0	170.1
126	7	A	0.960	0.006	0.010	0.009	0.006	0.002	0.001	0.002	0.005	83.8	10.4	0.0	0.0	0.0	106.2
130	7	A	0.968	0.008	0.006	0.007	0.004	0.002	0.001	0.001	0.003	61.2	13.3	3.7	0.0	3.1	123.0
133	8	A	0.953	0.011	0.007	0.014	0.004	0.001	0.001	0.003	0.007	93.7	32.2	11.0	0.0	0.0	73.0
136	8	A	0.960	0.010	0.004	0.013	0.003	0.002	0.001	0.001	0.007	85.3	30.1	11.5	0.0	1.7	77.8
138	8	A	0.945	0.011	0.010	0.015	0.005	0.003	0.001	0.003	0.008	109.4	25.7	12.9	0.0	0.0	67.6
141	8	A	0.947	0.011	0.008	0.015	0.005	0.003	0.002	0.002	0.008	113.2	27.3	9.6	0.0	4.9	64.5
144	9	A	0.980	0.004	0.004	0.005	0.003	0.001	0.001	0.001	0.003	44.0	13.6	2.0	0.0	0.0	165.6
148	9	A	0.976	0.005	0.004	0.006	0.003	0.001	0.001	0.001	0.003	52.9	13.0	2.2	0.0	2.3	142.0
151	9	A	0.962	0.006	0.009	0.008	0.006	0.003	0.002	0.002	0.004	82.0	14.6	0.0	0.0	0.0	103.5
154	9	A	0.962	0.009	0.007	0.007	0.006	0.003	0.001	0.001	0.004	80.5	13.7	0.0	0.0	0.0	106.2
155	10	A	0.961	0.005	0.011	0.008	0.006	0.001	0.001	0.003	0.004	72.4	17.5	0.0	0.0	0.0	111.2
158	10	A	0.971	0.005	0.005	0.007	0.004	0.002	0.001	0.001	0.004	65.8	22.6	3.6	0.0	0.0	108.7
160 ^a	10	A	0.958	0.005	0.012	0.009	0.007	0.002	0.001	0.003	0.003	86.7	22.2	0.0	0.0	0.0	91.8
161 ^a	10	A	0.958	0.005	0.012	0.009	0.007	0.002	0.001	0.003	0.003	86.7	22.2	0.0	0.0	0.0	91.8
163	10	A	0.953	0.007	0.011	0.010	0.009	0.003	0.001	0.001	0.004	111.2	23.4	0.0	0.0	0.0	74.3
168	11	A	0.979	0.003	0.006	0.004	0.004	0.002	0.001	0.000	0.002	48.1	16.7	0.0	0.0	0.0	154.3
169 ^a	11	A	0.968	0.004	0.009	0.006	0.006	0.002	0.001	0.001	0.003	70.9	18.7	0.0	0.0	0.0	111.6
171 ^a	11	A	0.968	0.004	0.009	0.006	0.006	0.002	0.001	0.001	0.003	70.9	18.7	0.0	0.0	0.0	111.6
172	12	A	0.973	0.006	0.005	0.008	0.002	0.001	0.001	0.002	0.004	52.8	19.3	4.9	0.0	0.0	129.9
177	12	A	0.962	0.007	0.005	0.010	0.005	0.003	0.001	0.001	0.006	88.4	18.2	3.0	0.0	0.0	90.6
178 ^a	12	A	0.964	0.007	0.007	0.009	0.003	0.001	0.001	0.002	0.005	66.1	23.9	7.2	0.0	0.0	102.9
179 ^a	12	A	0.964	0.007	0.007	0.009	0.003	0.001	0.001	0.002	0.005	66.1	23.9	7.2	0.0	0.0	102.9
182	12	A	0.948	0.008	0.010	0.011	0.009	0.004	0.002	0.002	0.006	121.0	17.7	0.0	0.0	0.0	72.1
184	13	A	0.960	0.008	0.007	0.012	0.005	0.002	0.001	0.002	0.005	89.3	89.7	12.6	0.0	0.0	52.2
189	13	A	0.956	0.009	0.007	0.012	0.008	0.003	0.001	0.001	0.004	105.9	81.8	11.9	0.0	5.2	48.6
192	13	A	0.951	0.009	0.008	0.013	0.007	0.002	0.002	0.003	0.006	105.9	96.2	13.8	0.0	0.0	46.3
195	13	A	0.939	0.010	0.009	0.014	0.011	0.005	0.002	0.002	0.008	141.2	88.1	12.5	0.0	9.4	39.8
198	14	A	0.974	0.003	0.007	0.005	0.004	0.001	0.001	0.002	0.003	51.2	14.2	0.0	0.0	0.0	152.9
199	14	A	0.967	0.006	0.007	0.007	0.005	0.002	0.001	0.001	0.003	68.0	15.3	0.0	0.0	0.0	120.0
202	14	A	0.967	0.005	0.007	0.007	0.004	0.002	0.001	0.003	0.004	63.3	19.6	3.7	0.0	0.0	115.5
205	14	A	0.955	0.005	0.009	0.010	0.006	0.003	0.001	0.001	0.010	92.0	18.4	0.0	0.0	0.0	90.6
208	15	A	0.977	0.004	0.007	0.005	0.003	0.001	0.000	0.002	0.002	45.4	13.0	3.1	0.0	0.0	162.6
211	15	A	0.982	0.004	0.003	0.005	0.002	0.001	0.000	0.000	0.002	40.6	12.4	2.1	0.0	0.0	181.5
215	15	A	0.954	0.005	0.009	0.007	0.006	0.002	0.001	0.002	0.004	74.9	13.7	0.0	0.0	0.0	112.9

Table 3. ¹³C NMR data for select examples and comparative examples from Tables 1 and 2. (Cont)

5 ^Indicates samples that were combined for NMR analysis. More specifically, the following examples were combined for ¹³C NMR analysis: 160-161; 169 & 171; 179-179; 230-231; 260 & 262; 266-268; 298-300; 326, 328 & 329; 349-351; 376-378; 379-381; 394 & 396; 397-399; 404-405; 406-408; 409-411; 412-413; 415-417; 418-420; 421-423; 454-456; 457-459; 469-471; 475-477; 514-515; 517-518; 523-524; 528-530; 534-536; 552-553; 558-560.

Ex#	Cat ID	Act ID	mmmm	mmmr	mmrr	mmrr	mmrr + mrrr	rrmm	rrrr	rrrr	rrrr	stereo defects /10000 monomer	2,1-regio (ee) defects /10000 monomer	2,1-regio (et) defects /10000 monomer	2,1-regio (te) defects /10000 monomer	1,3-regio defects /10000 monomer	ave. meso run length
219	15	A	0.964	0.006	0.008	0.010	0.005	0.002	0.001	0.001	0.002	87.7	13.2	0.0	0.0	0.0	99.1
224	16	A	0.980	0.004	0.004	0.003	0.004	0.001	0.000	0.000	0.002	44.9	11.4	0.0	0.0	0.0	177.6
230^	16	A	0.962	0.005	0.008	0.005	0.008	0.003	0.002	0.002	0.005	84.0	17.1	0.0	0.0	0.0	98.9
231^	16	A	0.962	0.005	0.008	0.005	0.008	0.003	0.002	0.002	0.005	84.0	17.1	0.0	0.0	0.0	98.9
257	19	A	0.987	0.001	0.005	0.002	0.002	0.000	0.000	0.001	0.001	23.6	5.4	0.0	0.0	0.0	344.8
260^	19	A	0.990	0.002	0.002	0.002	0.002	0.001	0.000	0.000	0.001	22.8	8.9	0.0	0.0	0.0	315.5
262^	19	A	0.990	0.002	0.002	0.002	0.002	0.001	0.000	0.000	0.001	22.8	8.9	0.0	0.0	0.0	315.5
264	19	A	0.984	0.001	0.006	0.002	0.002	0.001	0.001	0.001	0.001	26.5	8.9	0.0	0.0	0.0	282.5
266^	19	A	0.981	0.004	0.003	0.004	0.003	0.001	0.001	0.001	0.002	42.7	15.8	0.0	0.0	0.0	170.9
267^	19	A	0.981	0.004	0.003	0.004	0.003	0.001	0.001	0.001	0.002	42.7	15.8	0.0	0.0	0.0	170.9
268^	19	A	0.981	0.004	0.003	0.004	0.003	0.001	0.001	0.001	0.002	42.7	15.8	0.0	0.0	0.0	170.9
274	20	A	0.986	0.003	0.001	0.003	0.003	0.001	0.000	0.000	0.001	34.7	49.7	0.0	0.0	0.0	118.5
278	20	A	0.975	0.005	0.007	0.006	0.005	0.002	0.000	0.000	0.000	64.3	57.6	0.0	0.0	0.0	82.0
281	21	A	0.986	0.002	0.003	0.003	0.002	0.001	0.000	0.000	0.001	32.2	21.3	0.0	0.0	0.0	186.9
283	21	A	0.980	0.003	0.004	0.005	0.003	0.002	0.000	0.000	0.002	46.6	25.5	0.0	0.0	0.0	138.7
287	23	A	0.980	0.002	0.006	0.003	0.003	0.001	0.001	0.002	0.002	36.3	10.6	0.0	0.0	0.0	213.2
291	23	A	0.982	0.003	0.006	0.004	0.002	0.000	0.000	0.001	0.001	31.4	11.4	0.0	0.0	0.0	233.6
294	23	A	0.980	0.003	0.006	0.003	0.003	0.001	0.000	0.001	0.002	36.5	11.9	0.0	0.0	0.0	206.6
295	23	A	0.973	0.005	0.007	0.005	0.004	0.002	0.001	0.001	0.003	52.5	15.3	0.0	0.0	0.0	147.5
298^	23	A	0.974	0.004	0.009	0.006	0.004	0.000	0.000	0.002	0.000	48.8	18.5	0.0	0.0	0.0	148.6
299^	23	A	0.974	0.004	0.009	0.006	0.004	0.000	0.000	0.002	0.000	48.8	18.5	0.0	0.0	0.0	148.6
300^	23	A	0.974	0.004	0.009	0.006	0.004	0.000	0.000	0.002	0.000	48.8	18.5	0.0	0.0	0.0	148.6
305	23	A	0.963	0.005	0.008	0.008	0.006	0.002	0.002	0.002	0.004	80.6	16.1	0.0	0.0	0.0	103.4
310	24	A	0.980	0.005	0.003	0.005	0.003	0.001	0.001	0.001	0.003	42.8	50.5	3.2	0.0	0.0	103.6
313	24	A	0.974	0.006	0.004	0.006	0.004	0.001	0.001	0.001	0.003	54.9	52.2	3.4	0.0	0.0	90.5
317	24	A	0.974	0.006	0.004	0.007	0.004	0.001	0.001	0.001	0.003	59.7	61.4	3.6	0.0	0.0	80.2
321	24	A	0.971	0.007	0.004	0.007	0.004	0.001	0.001	0.001	0.004	62.0	60.5	3.8	0.0	1.8	78.1
326^	25	A	0.984	0.004	0.003	0.003	0.002	0.001	0.000	0.000	0.001	33.7	8.8	0.0	0.0	0.0	235.3
328^	25	A	0.984	0.004	0.003	0.003	0.002	0.001	0.000	0.000	0.001	33.7	8.8	0.0	0.0	0.0	235.3
329^	25	A	0.984	0.004	0.003	0.003	0.002	0.001	0.000	0.000	0.001	33.7	8.8	0.0	0.0	0.0	235.3
340	26	A	0.936	0.014	0.009	0.019	0.008	0.002	0.001	0.001	0.009	145.0	14.5	0.0	11.0	0.0	58.7
344	26	A	0.913	0.018	0.011	0.024	0.012	0.004	0.003	0.002	0.012	198.4	18.3	0.0	17.2	0.0	42.8
349^	26	D	0.894	0.025	0.006	0.035	0.014	0.004	0.003	0.003	0.015	262.6	58.7	0.0	46.4	0.0	27.2
350^	26	D	0.894	0.025	0.006	0.035	0.014	0.004	0.003	0.003	0.015	262.6	58.7	0.0	46.4	0.0	27.2
351^	26	D	0.894	0.025	0.006	0.035	0.014	0.004	0.003	0.003	0.015	262.6	58.7	0.0	46.4	0.0	27.2
353	27	A	0.916	0.017	0.013	0.024	0.010	0.003	0.002	0.004	0.012	182.8	51.9	29.0	0.0	0.0	37.9
355	27	A	0.918	0.020	0.010	0.027	0.011	0.003	0.000	0.000	0.012	196.1	53.8	41.2	0.0	0.0	34.4
360	27	A	0.899	0.020	0.012	0.030	0.013	0.005	0.002	0.004	0.015	229.6	57.0	35.2	0.0	0.0	31.1
361	27	A	0.890	0.027	0.016	0.034	0.015	0.006	0.001	0.002	0.008	268.1	71.1	51.2	0.0	0.0	25.6
365	27	D	0.919	0.025	0.005	0.029	0.005	0.001	0.001	0.000	0.015	174.1	63.8	42.6	47.9	0.0	30.5
368	27	D	0.898	0.027	0.008	0.036	0.009	0.002	0.001	0.002	0.018	228.8	72.9	47.1	56.9	0.0	24.6

Table 3. ¹³C NMR data for select examples and comparative examples from Tables 1 and 2. (Cont)

5 ^Indicates samples that were combined for NMR analysis. More specifically, the following examples were combined for ¹³C NMR analysis: 160-161; 169 & 171; 179-179; 230-231; 260 & 262; 266-268; 298-300; 326, 328 & 329; 349-351; 376-378; 379-381; 394 & 396; 397-399; 404-405; 406-408; 409-411; 412-413; 415-417; 418-420; 421-423; 454-456; 457-459; 469-471; 475-477; 514-515; 517-518; 523-524; 528-530; 534-536; 552-553; 558-560.

Ex#	Cat ID	Act ID	mmmm	mmmr	mmrr	mmrr	mmrr + mrrr	rrmm	rrrr	rrrr	rrrr	stereo defects /10000 monomer	2,1-regio (ee) defects /10000 monomer	2,1-regio (ef) defects /10000 monomer	2,1-regio (fe) defects /10000 monomer	1,3-regio defects /10000 monomer	ave. meso run length
372	33	A	0.955	0.009	0.009	0.014	0.005	0.002	0.000	0.001	0.005	103.1	57.4	15.5	0.0	0.0	56.8
374	33	A	0.933	0.011	0.010	0.022	0.007	0.003	0.002	0.002	0.008	162.5	75.9	21.8	0.0	0.0	38.4
375^	34	A	0.933	0.010	0.011	0.020	0.009	0.004	0.002	0.003	0.008	163.1	72.0	27.3	0.0	0.0	38.1
377^	34	A	0.933	0.010	0.011	0.020	0.009	0.004	0.002	0.003	0.008	163.1	72.0	27.3	0.0	0.0	38.1
378^	34	A	0.933	0.010	0.011	0.020	0.009	0.004	0.002	0.003	0.008	163.1	72.0	27.3	0.0	0.0	38.1
379^	34	A	0.907	0.014	0.009	0.032	0.011	0.007	0.003	0.004	0.014	238.8	88.9	27.7	0.0	0.0	28.1
380^	34	A	0.907	0.014	0.009	0.032	0.011	0.007	0.003	0.004	0.014	238.8	88.9	27.7	0.0	0.0	28.1
381^	34	A	0.907	0.014	0.009	0.032	0.011	0.007	0.003	0.004	0.014	238.8	88.9	27.7	0.0	0.0	28.1
383	35	A	0.949	0.011	0.011	0.016	0.005	0.002	0.001	0.001	0.006	113.9	19.3	9.0	0.0	0.0	70.3
385	35	A	0.931	0.014	0.009	0.022	0.008	0.002	0.001	0.001	0.010	160.5	27.7	12.6	4.7	0.0	48.7
390	36	A	0.930	0.014	0.009	0.026	0.007	0.002	0.002	0.001	0.009	172.2	77.9	29.5	11.9	0.0	34.3
391	36	A	0.914	0.017	0.009	0.032	0.009	0.003	0.002	0.002	0.013	211.8	95.9	37.8	17.7	0.0	27.5
394^	37	A	0.936	0.015	0.005	0.018	0.008	0.005	0.002	0.000	0.011	152.8	44.0	0.0	0.0	0.0	50.8
396^	37	A	0.936	0.015	0.005	0.018	0.008	0.005	0.002	0.000	0.011	152.8	44.0	0.0	0.0	0.0	50.8
397^	37	A	0.904	0.021	0.005	0.025	0.019	0.006	0.004	0.002	0.016	236.3	62.3	14.7	0.0	0.0	31.9
398^	37	A	0.904	0.021	0.005	0.025	0.019	0.006	0.004	0.002	0.016	236.3	62.3	14.7	0.0	0.0	31.9
399^	37	A	0.904	0.021	0.005	0.025	0.019	0.006	0.004	0.002	0.016	236.3	62.3	14.7	0.0	0.0	31.9
402	37	D	0.918	0.005	0.015	0.023	0.017	0.004	0.003	0.003	0.012	216.0	61.3	12.9	0.0	0.0	34.5
404^	37	D	0.910	0.019	0.010	0.026	0.017	0.003	0.002	0.001	0.013	218.0	87.8	23.6	0.0	0.0	30.4
405^	37	D	0.910	0.019	0.010	0.026	0.017	0.003	0.002	0.001	0.013	218.0	87.8	23.6	0.0	0.0	30.4
406^	38	A	0.951	0.011	0.009	0.013	0.004	0.004	0.001	0.000	0.009	100.3	8.7	0.0	0.0	0.0	91.7
407^	38	A	0.951	0.011	0.009	0.013	0.004	0.004	0.001	0.000	0.009	100.3	8.7	0.0	0.0	0.0	91.7
408^	38	A	0.951	0.011	0.009	0.013	0.004	0.004	0.001	0.000	0.009	100.3	8.7	0.0	0.0	0.0	91.7
409^	38	A	0.910	0.004	0.009	0.021	0.022	0.008	0.004	0.007	0.015	250.4	15.1	0.0	0.0	0.0	37.7
410^	38	A	0.910	0.004	0.009	0.021	0.022	0.008	0.004	0.007	0.015	250.4	15.1	0.0	0.0	0.0	37.7
411^	38	A	0.910	0.004	0.009	0.021	0.022	0.008	0.004	0.007	0.015	250.4	15.1	0.0	0.0	0.0	37.7
412^	38	D	0.961	0.009	0.005	0.013	0.005	0.001	0.000	0.000	0.006	90.1	21.4	4.9	0.0	0.0	85.9
413^	38	D	0.961	0.009	0.005	0.013	0.005	0.001	0.000	0.000	0.006	90.1	21.4	4.9	0.0	0.0	85.9
415^	38	D	0.937	0.015	0.005	0.021	0.009	0.002	0.001	0.001	0.010	156.0	28.4	7.9	0.0	0.0	52.0
416^	38	D	0.937	0.015	0.005	0.021	0.009	0.002	0.001	0.001	0.010	156.0	28.4	7.9	0.0	0.0	52.0
417^	38	D	0.937	0.015	0.005	0.021	0.009	0.002	0.001	0.001	0.010	156.0	28.4	7.9	0.0	0.0	52.0
418^	39	A	0.771	0.104	0.014	0.009	0.073	0.006	0.011	-0.003	0.014	366.8	42.8	23.6	0.0	16.7	22.2
419^	39	A	0.771	0.104	0.014	0.009	0.073	0.006	0.011	-0.003	0.014	366.8	42.8	23.6	0.0	16.7	22.2
420^	39	A	0.771	0.104	0.014	0.009	0.073	0.006	0.011	-0.003	0.014	366.8	42.8	23.6	0.0	16.7	22.2
421^	39	A	0.738	0.103	0.016	0.020	0.078	0.008	0.012	0.007	0.018	443.7	61.6	33.9	0.0	25.0	17.7
422^	39	A	0.738	0.103	0.016	0.020	0.078	0.008	0.012	0.007	0.018	443.7	61.6	33.9	0.0	25.0	17.7
423^	39	A	0.738	0.103	0.016	0.020	0.078	0.008	0.012	0.007	0.018	443.7	61.6	33.9	0.0	25.0	17.7
454^	43	A	0.949	0.010	0.014	0.006	0.010	0.002	0.002	0.004	0.003	84.8	76.3	0.0	0.0	0.0	62.1
457^	43	A	0.939	0.015	0.015	0.007	0.013	0.003	0.001	0.003	0.003	114.1	99.6	0.0	0.0	0.0	46.8
469^	45	A	0.969	0.004	0.011	0.004	0.007	0.001	0.001	0.002	0.001	59.5	85.8	0.0	0.0	0.0	68.8
475^	45	A	0.927	0.018	0.008	0.009	0.021	0.003	0.003	0.005	0.006	159.3	119.3	0.0	0.0	0.0	35.9
480	46	A	0.979	0.003	0.006	0.004	0.003	0.000	0.001	0.002	0.002	33.5	34.0	0.0	0.0	0.0	148.1

Table 3. ^{13}C NMR data for select examples and comparative examples from Tables 1 and 2. (Cont)

5 ^Indicates samples that were combined for NMR analysis. More specifically, the following examples were combined for ^{13}C NMR analysis: 160-161; 169 & 171; 179-179; 230-231; 260 & 262; 266-268; 298-300; 326, 328 & 329; 349-351; 376-378; 379-381; 394 & 396; 397-399; 404-405; 406-408; 409-411; 412-413; 415-417; 418-420; 421-423; 454-456; 457-459; 469-471; 475-477; 514-515; 517-518; 523-524; 528-530; 534-536; 552-553; 558-560.

Ex#	Cat ID	Act ID	mmmm	mmmr	rrmm	rrmr	rrmm + rrrr	rrmm	rrrr	rrrr	rrrr	stereo defects /10000 monomer	2,1-regio (ee) defects /10000 monomer	2,1-regio (et) defects /10000 monomer	2,1-regio (te) defects /10000 monomer	1,3-regio defects /10000 monomer	ave. meso run length
480	46	A	0.979	0.003	0.006	0.004	0.003	0.000	0.001	0.002	0.002	33.5	34.0	0.0	0.0	0.0	140.1
482	46	A	0.968	0.004	0.008	0.005	0.004	0.001	0.001	0.002	0.005	53.0	40.8	0.0	0.0	0.0	106.6
484	47	A	0.966	0.005	0.009	0.005	0.006	0.002	0.001	0.003	0.003	59.1	179.7	6.2	0.0	0.0	40.8
489	47	A	0.965	0.005	0.010	0.006	0.006	0.002	0.001	0.002	0.003	64.5	183.9	5.8	0.0	0.0	39.3
490	48	A	0.984	0.002	0.005	0.003	0.002	0.000	0.001	0.001	0.001	25.5	25.0	0.0	0.0	0.0	198.0
494	48	A	0.978	0.003	0.007	0.004	0.003	0.001	0.000	0.002	0.002	39.7	30.7	0.0	0.0	0.0	142.0
497	49	A	0.978	0.003	0.007	0.003	0.004	0.001	0.001	0.002	0.002	38.3	120.6	0.0	0.0	0.0	62.9
500	49	A	0.976	0.004	0.008	0.004	0.004	0.001	0.001	0.002	0.001	41.5	132.9	0.0	0.0	0.0	57.3
503	50	A	0.979	0.003	0.008	0.003	0.003	0.000	0.000	0.002	0.001	33.5	23.4	0.0	0.0	0.0	175.7
506	50	A	0.982	0.003	0.005	0.003	0.002	0.000	0.001	0.002	0.002	30.0	29.3	0.0	0.0	0.0	168.6
509	51	A	0.975	0.003	0.009	0.003	0.004	0.001	0.001	0.002	0.002	39.7	99.7	0.0	0.0	0.0	71.7
512	51	A	0.968	0.004	0.007	0.005	0.006	0.002	0.002	0.003	0.003	64.5	111.8	0.0	0.0	0.0	56.7
514^	52	A	0.977	0.004	0.007	0.004	0.003	0.000	0.000	0.002	0.002	35.8	14.8	0.0	0.0	0.0	197.6
517^	52	A	0.967	0.006	0.008	0.006	0.004	0.002	0.002	0.003	0.003	57.8	23.7	0.0	0.0	0.0	122.7
520	53	A	0.954	0.005	0.009	0.007	0.008	0.003	0.004	0.005	0.006	86.4	52.8	0.0	0.0	0.0	71.8
523^	53	A	0.960	0.008	0.009	0.007	0.009	0.001	0.001	0.003	0.003	79.6	61.6	0.0	0.0	0.0	70.8
528^	54	A	0.976	0.003	0.008	0.003	0.004	0.001	0.001	0.003	0.002	41.0	12.0	0.0	0.0	0.0	188.7
534^	54	A	0.969	0.004	0.009	0.004	0.005	0.002	0.001	0.003	0.003	51.5	20.3	0.0	0.0	0.0	139.3
552^	57	A	0.978	0.002	0.008	0.003	0.003	0.001	0.001	0.003	0.002	31.9	12.0	0.0	0.0	0.0	227.8
558^	57	A	0.976	0.004	0.008	0.003	0.003	0.000	0.001	0.003	0.002	34.3	22.8	0.0	0.0	0.0	175.1
562	58	A	0.983	0.002	0.005	0.003	0.003	0.001	0.001	0.002	0.002	31.1	60.5	1.9	0.0	0.0	187.0
572	58	A	0.973	0.002	0.008	0.004	0.005	0.002	0.001	0.002	0.002	52.9	68.9	0.0	0.0	0.0	82.1
C-7	C1	D	0.989	0.003	0.001	0.003	0.001	0.001	0.000	0.000	0.001	23.1	21.7	0.0	0.0	2.3	212.3
C-15	C1	D	0.975	0.006	0.001	0.007	0.003	0.002	0.001	0.001	0.003	60.4	18.4	0.0	0.0	11.5	110.7
C-19	C2	A	0.976	0.013	0.005	0.003	0.002	0.001	0.000	0.000	0.001	27.0	18.0	0.0	0.0	3.0	208.3
C-23	C2	A	0.988	0.003	0.000	0.003	0.003	0.001	0.000	0.001	0.001	35.6	16.0	0.0	0.0	4.8	177.3
C-26	C2	A	0.964	0.019	0.007	0.004	0.002	0.001	0.001	0.001	0.003	34.0	36.0	0.0	0.0	13.0	120.5
C-29	C2	A	0.973	0.010	0.005	0.007	0.002	0.001	0.000	0.000	0.003	47.8	13.9	0.0	0.0	13.3	133.3
C-33	C2	C	0.975	0.013	0.004	0.003	0.002	0.001	0.000	0.000	0.001	33.0	17.0	0.0	0.0	6.0	178.6
C-36	C2	C	0.964	0.016	0.005	0.006	0.003	0.002	0.000	0.001	0.003	52.5	15.0	0.0	0.0	11.0	127.4
C-39	C2	D	0.985	0.003	0.003	0.004	0.002	0.001	0.000	0.000	0.002	32.7	21.6	0.0	0.0	7.1	162.9
C-42	C2	D	0.977	0.005	0.005	0.005	0.003	0.001	0.000	0.000	0.002	47.7	17.7	0.0	0.0	12.4	128.5

Table 4. ¹H NMR data illustrating chain end unsaturation for select examples.

Ex#	Cat ID	Act ID	vinyl- enes/ 1000C	trisubs/ 1000C	vinyls/ 1000C	vinyl- idenes/ 1000C	total unsat/ 1000C	% vinyl- ene	% trisub	% vinyl	% vinyl- idene
14	2	A	0.07	0.07	0.04	0.12	0.3	23.3	23.3	13.3	40.0
19	2	A	0.15	0.11	0.11	0.28	0.7	23.1	16.9	16.9	43.1
38	4	A	0.74	0.17	0.14	0.44	1.5	49.7	11.4	9.4	29.5
41	4	A	1.02	0.15	0.18	0.53	1.9	54.3	8.0	9.6	28.2
51	5	A	0.04	0.07	0.09	0.15	0.4	11.4	20.0	25.7	42.9
53	5	A	0.06	0.15	0.12	0.14	0.5	12.8	31.9	25.5	29.8
65	5	A	0.18	0.14	0.22	0.29	0.8	21.7	16.9	26.5	34.9
67	5	A	0.20	0.17	0.23	0.27	0.9	23.0	19.5	26.4	31.0
93	6	A	0.13	0.05	0.19	0.18	0.6	23.6	9.1	34.5	32.7
101	6	A	0.22	0.07	0.27	0.23	0.8	27.8	8.9	34.2	29.1
119	7	A	0.10	0.07	0.10	0.19	0.5	21.7	15.2	21.7	41.3
125	7	A	0.23	0.14	0.24	0.35	1.0	24.0	14.6	25.0	36.5
144	9	A	0.10	0.11	0.09	0.20	0.5	20.0	22.0	18.0	40.0
149	9	A	0.10	0.06	0.07	0.22	0.5	22.2	13.3	15.6	48.9
211	15	A	0.12	0.06	0.08	0.24	0.5	24.0	12.0	16.0	48.0
218	15	A	0.31	0.09	0.18	0.47	1.1	29.5	8.6	17.1	44.8
224	16	A	0.01	0.09	0.08	0.28	0.5	2.2	19.6	17.4	60.9
313	24	A	0.13	0.09	0.07	0.24	0.5	24.5	17.0	13.2	45.3
319	24	A	0.18	0.10	0.08	0.30	0.7	27.3	15.2	12.1	45.5

[0370] Continuous stirred tank reactor runs: Polymerizations were carried out in a continuous stirred tank reactor. Autoclave reactor (1L) was equipped with a stirrer, a water cooling/steam heating element with a temperature controller and a pressure controller. The reactor was maintained at a pressure in excess of the bubbling point pressure of the reactant mixture to keep the reactants in the liquid phase. The reactors were operated liquid full. Isohexane (used as the solvent), and propylene were purified over beds of alumina and molecular sieves. Toluene for preparing catalyst solutions was also purified by the same technique. All feeds were pumped into the reactors by a Pulsar feed pump. All liquid flow rates were controlled using Brooks mass flow controller. Propylene feed was mixed with a pre-chilled isohexane stream that had been cooled to at least 0°C. The mixture was fed into the reactor through a single port.

[0371] An isohexane solution of tri-n-octyl aluminum (TNOAL) (25 wt% in hexane, Sigma Aldrich) scavenger was added to the combined solvent and monomer stream just before it entered the reactor to further reduce any catalyst poisons. The feed rate of the scavenger solution was adjusted to optimize catalyst activity.

[0372] The catalyst used was complex 6 described above. The catalyst (ca. 20 mg) was activated with N,N-dimethylanilinium tetrakis(perfluorophenyl)borate (Activator A) at a molar

ratio of about 1:1 in 900 ml of toluene. The catalyst solution was then fed into the reactor through a separate port using an ISCO syringe pump.

- [0373] The polymer produced in the reactor exited through a back pressure control valve that reduced the pressure to atmospheric. This caused the unconverted monomers in the solution to flash into a vapor phase which was vented from the top of a vapor liquid separator. The liquid phase, comprising mainly polymer and solvent, was collected for polymer recovery. The collected samples were first air-dried in a hood to evaporate most of the solvent, and then dried in a vacuum oven at a temperature of about 90°C for about 12 hours. The vacuum oven dried samples were weighed to obtain yields. The detailed polymerization process conditions are listed in Tables 5-8 below. The scavenger feed rate and catalyst feed rate were adjusted to reach the targeted conversion listed. All the reactions were carried out at a pressure of about 2.4 MPa/g unless otherwise mentioned.

Table 5: Continuous stirred tank reactor runs making polypropylene.

Example	PP-1	PP-2	PP-3
Rxr T (C)	100	120	93
Catalyst/Activator	6/A	6/A	6/A
Cat (mol/min)	3.23E-08	3.64E-08	2.43E-08
Scavenger (mol/min)	7.39E-06	7.39E-06	7.39E-06
Propylene (g/min)	14	14	14
Isohexane (g/min)	47.7	47.7	47.7
polymer made (g/min)	12.8	12.6	4.7
polymer made (g)	255.6	252.2	66.0
Catalyst Productivity (g cat/g polymer)	433,038	378,037	211,463
Conversion (%)	91.4	90.0	33.6
MFR (g/ 10 min)	17.3	882.7	11.1
Mn_FTIR (g/mol)	103,850	32,663	117,473
Mw_FTIR (g/mol)	296,814	89,494	410,583
Mz_FTIR (g/mol)	598,942	173,187	946,259
MWD FTIR (Mw/Mn)	2.86	2.74	3.50
Mn_LS (g/mol)	103,709	35,214	125,866
Mw_LS (g/mol)	342,866	101,586	412,246
Mz_LS (g/mol)	818,795	204,293	885,121
g'vis	0.842	0.834	0.973
Tc (°C)	108.8	109.3	108.4
Tm (°C)	147.8	145.0	148.3
delta H (J/g)	92.5	97.0	95.2
¹ H NMR data			
vinyl %	27.3	26.5	36.4
Vinyls /1000C	0.03	0.13	0.04

Table 5: Continuous stirred tank reactor runs making polypropylene. (Cont.)

Example	PP-1	PP-2	PP-3
Vinylenes /1000C	0.00	0.03	0.01
Vinylidenes /1000C	0.08	0.15	0.01
trisubstituted olefin/1000C	0.00	0.08	0.00
¹³ C NMR Data			
[mmmm]	0.966	0.955	0.973
[mmmr]	0.009	0.011	0.008
[rmmr]	0.005	0.007	0.003
[mmrr]	0.009	0.010	0.008
[mmrm+ rmrr]	0.004	0.006	0.003
[rmrm]	0.002	0.003	0.001
[rrrr]	0.001	0.001	0.000
[mrrr]	0.001	0.002	0.000
[mrrm]	0.005	0.006	0.004
stereo defects/ 10000 monomer	71.6	95.9	57.6
2,1-regio (ee) defects/ 10000 monomer	65.0	66.7	65.9
2,1-regio (et) defects/ 10000 monomer	9.1	10.8	10.1
2,1-regio (te) defects/ 10000 monomer	0.0	0.0	0.0
1,3 regio defects/ 10000 monomer	0.0	0.0	0.0
total regio defects/ 10000 monomer	74.1	77.5	76.0
total regio and stereo defects/ 10000 monomer	145.7	173.4	133.6
Avg. meso Run Length	68.6	57.7	74.9

*Conversion % = [(polymer yield)/(propylene feed)]x100

Table 6: Continuous stirred tank reactor runs making polypropylene.

Example	PP-4	PP-5	PP-6
Rxr T (C)	120	110	100
Catalyst/Activator	5/A	5/A	5/A
Cat (mol/min)	4.43E-08	4.43E-08	4.43E-08
Scavenger (mol/min)	7.39E-06	7.39E-06	7.39E-06
Propylene (g/min)	14.0	14.0	14.0
Isohexane (g/min)	47.7	47.7	47.7
polymer made (g/min)	3.6	4.6	4.7
polymer made (g)	72.0	91.1	47.1
Catalyst Productivity (g cat/g polymer)	81,011	102,502	105,990
Conversion (%)	25.7%	32.5%	33.6%
MFR (g/10 min)	407.0	72.4	17.6
Mn_FTIR (g/mol)	44,398	72,855	116,176
Mw_FTIR (g/mol)	94,588	160,766	245,067
Mz_FTIR (g/mol)	158,486	290,189	413,606
MWD FTIR (Mw/Mn)	2.13	2.21	2.11

Table 6: Continuous stirred tank reactor runs making polypropylene. (Cont.)

Example	PP-4	PP-5	PP-6
Mn_LS (g/mol)	47,297	79,783	124,115
Mw_LS (g/mol)	97,536	165,215	249,622
Mz_LS (g/mol)	155,206	271,176	390,773
g'vis	0.991	0.990	1.001
Tc (°C)	115.5	112.9	114.8
Tm (°C)	154.6	156.2	158.6
delta H (J/g)	106.1	105.1	103.2
¹³ C NMR Data			
[mmmm]	0.966	0.969	0.978
[mmmr]	0.007	0.006	0.005
[rmmr]	0.006	0.005	0.003
[mmrr]	0.008	0.007	0.007
[mmrm+rmrr]	0.005	0.004	0.002
[rmrm]	0.002	0.002	0.001
[rrrr]	0.001	0.001	0.001
[mrrr]	0.001	0.001	0.001
[mrrm]	0.004	0.004	0.003
stereo defects/ 10000 monomer	77.1	67.3	48.8
2,1-regio (ee) defects/ 10000 monomer	16.9	16.4	15.1
2,1-regio (et) defects/ 10000 monomer	4.5	4.5	4.3
2,1-regio (te) defects/ 10000 monomer	0	0	0
1,3 regio defects/ 10000 monomer	0	0	0
total regio defects/ 10000 monomer	21.4	20.9	19.4
total regio and stereo defects/ 10000 monomer	98.5	88.2	68.2
Avg. meso Run Length	102	113	147

*Conversion % = [(polymer yield)/(propylene feed)]x100

Table 7: Continuous stirred tank reactor runs making polypropylene.

Example	PP-7	PP-8	PP-9
Rxr T (C)	130	120	110
Catalyst/Activator	25/A	25/A	25/A
Cat (mol/min)	1.27E-07	1.27E-07	1.27E-07
Scavenger (mol/min)	7.39E-06	7.39E-06	7.39E-06
Propylene (g/min)	14.0	14.0	14.0
Isohexane (g/min)	47.7	47.7	47.7
polymer made (g/min)	4.2	3.4	4.5
polymer made (g)	83.6	68.7	89.3
Catalyst Productivity (g cat/g polymer)	30,089	24,726	32,141
Conversion (%)	29.9	24.5	31.9
MFR (g/10 min)	509.0	108.0	21.7
MFR HL			1727.2

Table 7: Continuous stirred tank reactor runs making polypropylene. (Cont.)

Example	PP-7	PP-8	PP-9
Mn_FTIR (g/mol)	45,371	67,086	101,759
Mw_FTIR (g/mol)	93,593	138,233	213,356
Mz_FTIR (g/mol)	153,407	223,683	348,288
MWD FTIR (Mw/Mn)	2.06	2.06	2.10
Tc (°C)	120.7	119.7	118.6
Tm (°C)	157.1	159.0	161.4
delta H (J/g)	111.9	111.0	110.7
¹³ C NMR Data			
[mmmm]	0.960	0.956	0.951
[mmmr]	0.007	0.006	0.006
[rmmr]	0.011	0.010	0.013
[mmrr]	0.008	0.008	0.008
[mmrm+rmrr]	0.005	0.007	0.007
[rmrm]	0.001	0.002	0.004
[rrrr]	0.001	0.002	0.003
[mrrr]	0.004	0.004	0.004
[mrrm]	0.004	0.005	0.005
stereo defects/ 10000 monomer	67.8	83.7	88.9
2,1-regio (ee) defects/ 10000 monomer	21.3	20.4	17.4
2,1-regio (et) defects/ 10000 monomer	0	0	0
2,1-regio (te) defects/ 10000 monomer	0	0	0
1,3 regio defects/ 10000 monomer	0	0	0
total regio defects/ 10000 monomer	21.3	20.4	17.4
total regio and stereo defects/ 10000 monomer	89.1	104.1	106.3
Avg. meso Run Length	112	96	94

*Conversion % = [(polymer yield)/(propylene feed)]x100

Table 8: Comparative continuous stirred tank reactor runs making polypropylene.

Example	CPP-1	CPP-2	CPP-3
Rxr T (C)	130	120	110
Catalyst/Activator	C2/A	C2/A	C2/A
Cat (mol/min)	1.44E-06	1.44E-06	1.44E-06
Scavenger (mol/min)			
Propylene (g/min)	14.0	14.0	14.0
hexane (g/min)	80.0	80.0	80.0
polymer made (g/min)	10.28	10.74	11.45
polymer made (g)			
Catalyst Productivity (g cat/g polymer)	9,317	9,734	10,378
Conversion (%)	73.4	76.7	81.8
Mn_DRI (g/mol)	19,370	28,690	48,450
Mw_DRI (g/mol)	44,460	66,420	106,260
Mz_DRI (g/mol)	75,600	112,660	185,190
MWD DRI (Mw/Mn)	2.3	2.32	2.19
Tc (°C)	101.3	100.2	105.3
Tm (°C)	144.7	147.8	150.2
delta H (J/g)	88.9	93	92.8

*Conversion % = [(polymer yield)/(propylene feed)]x100

- 5 **[0374]** Figure 1 illustrates the high polypropylene Tm (°C) at a given reactor polymerization temperature (°C) for the polymers produced from hafnium based inventive catalysts 6 and 25, as compared to the zirconium based analog, 5, and the comparative catalyst C₂.

Test Methods

10 ¹³C-NMR Spectroscopy on Polyolefins – large scale and small scale experiments

- [0375]** ¹³C NMR spectroscopy was used to characterize some polypropylene polymer samples produced in experiments. Unless otherwise indicated the polymer samples for ¹³C NMR spectroscopy were dissolved in d₂-1,1,2,2-tetrachloroethane and the samples were recorded at 120°C using a NMR spectrometer with a ¹³C NMR frequency of 125 MHz or greater. Polymer resonance peaks are referenced to mmmm=21.83 ppm. Calculations involved in the characterization of polymers by NMR follow the work of Bovey, F. A. (1969) in *Polymer Conformation and Configuration*, Academic Press, New York and Randall, J. (1977) in *Polymer Sequence Determination, Carbon-¹³NMR Method*, Academic Press, New York.

- [0376]** 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. Methods for measuring 2,1 regio defects/10,000 monomers and 1,3 regio defects/10,000 monomers follow standard methods. Additional references include Grassi, A. et.al. (1988) *Macromolecules*, v.21, pp. 617-622 and Busico et.al. (1994) *Macromolecules*, v.27, pp. 7538-7543. Total regio defects/10,000 monomer units is the sum of the 2,1-regio (ee) defects/10,000 monomer units, 2,1-regio (et) defects/10,000 monomer units, 2,1-regio (te) defects/10,000 monomer units and 1,3-regio defects/10,000 monomer units. The average meso run length = $10,000 / [(\text{stereo defects} / 10,000 \text{ monomer units}) + (2,1\text{-regio defects} / 10,000 \text{ monomer units}) + (1,3\text{-regio-defects} / 10,000 \text{ monomer units})]$.

[0377] For some samples, polymer end-group analysis was determined by ^1H NMR using a Bruker 600 MHz instrument run with a single 30° flip angle, RF pulse. 512 pulses with a delay of 5 seconds between pulses were signal averaged. The polymer sample was dissolved in heated $\text{d}_2\text{-1,1,2,2-tetrachloroethane}$ and signal collection took place at 120°C . Vinylenes were measured as the number of vinylenes per 1,000 carbon atoms using the resonances between 5.55-5.31 ppm. Trisubstituted end-groups ("trisubs") were measured as the number of trisubstituted groups per 1,000 carbon atoms using the resonances between 5.30-5.11 ppm. Vinyl end-groups were measured as the number of vinyls per 1,000 carbon atoms using the resonances between 5.13-4.98 ppm. Vinylidene end-groups were measured as the number of vinylidenes per 1,000 carbon atoms using the resonances between 4.88-4.69 ppm. The values reported are % vinylene, % trisubstituted (% trisub), % vinyl and % vinylidene where the percentage is relative to the total olefinic unsaturation per 1,000 carbon atoms.

[0378] Propylene-4-methyl-1-pentene copolymers were dissolved in deuterated 1,1,2,2-tetrachloroethane (tce-d_2) at a concentration of 67 mg/mL at 140°C . Spectra were recorded at 120°C using a Bruker NMR spectrometer of at least 600MHz with a 10mm cryoprobe. A 90° pulse, 60 second delay, 512 transients, and inverse gated decoupling were used for measuring the ^{13}C NMR. Polymer resonance peaks are referenced to the CH_3 at 21.83 ppm for propylene based materials. Assignments were determined from S. Losio et.al. *Macromolecules*, 2011, v.44, pp. 3276-3286. The diads were determined from the $\alpha\alpha$ CH_2 region of the spectra ($\alpha\alpha$ defined in the paper). The peak integration regions were as follows:

Integration Region	Assignment	Chemical shift range (ppm)	Diads
A	$\alpha\alpha$ (P) + CH_2 (sc)	47-45	$2\text{PP} + 0.5 \times \text{PY}$
B	$\alpha\alpha$ (PY)	45-43	PY
C	$\alpha\alpha$ (YY)	43-41	YY

sc= side chain of the 4-methyl-1-pentene, Y=4-methyl-1-pentene, P=propylene

To determine PP diad, region $A=2PP+0.5*PY$, so $PP=((A-0.5*B)/2)/total$, $PY=B/total$, and region $YY=C/total$.
 $Total=PP+PY+YY$. For mole fraction, $P=PP+0.5*PY$, and $Y=YY+0.5*PY$ times 100 to give mole%.

DSC – large scale polymerizations.

[0379] Peak melting point, T_m , (also referred to as melting point), peak crystallization
 5 temperature, T_c , (also referred to as crystallization temperature), glass transition temperature
 (T_g), heat of fusion (ΔH_f), and percent crystallinity were determined using the following DSC
 procedure according to ASTM D3418-03. Differential scanning calorimetric (DSC) data were
 obtained using a TA Instruments model Q200 machine or similar machine. Samples weighing
 approximately 5-10 mg were sealed in an aluminum hermetic sample pan. The DSC data were
 10 recorded by first gradually heating the sample to 200°C at a rate of 10°C/minute. The sample
 was kept at 200°C for 2 minutes, then cooled to -90°C at a rate of 10°C/minute, followed by
 an isothermal for 2 minutes and heating to 200°C at 10°C/minute. Both the first and second
 cycle thermal events were recorded. Areas under the endothermic peaks were measured and
 used to determine the heat of fusion and the percent of crystallinity. The percent crystallinity
 15 is calculated using the formula, $[area\ under\ the\ melting\ peak\ (Joules/gram) / B\ (Joules/gram)]$
 $* 100$, where B is the heat of fusion for the 100% crystalline homopolymer of the major
 monomer component. These values for B are to be obtained from the *Polymer Handbook*,
 Fourth Edition, published by John Wiley and Sons, New York 1999, provided however that a
 value of 189 J/g (B) is used as the heat of fusion for 100% crystalline polypropylene, a value
 20 of 290 J/g is used for the heat of fusion for 100% crystalline polyethylene. The melting and
 crystallization temperatures reported here were obtained during the second heating/cooling
 cycle unless otherwise noted. This DSC technique described was used for polymers produced
 from continuous stirred tank reactor runs.

[0380] Melt flow rate (MFR) was determined according to ASTM D1238 using a load of
 25 2.16 kg at a temperature of 230°C. The melt flow rate at the high load condition (HL MFR)
 was determined according to ASTM D1238 using a load of 21.6 kg at a temperature of 230°C.

GPC 4D Procedure for Molecular Weight and Comonomer Composition Determination by GPC-IR Hyphenated with Multiple Detectors (GPC-4D).

[0381] Unless otherwise indicated, the distribution and the moments of molecular weight
 30 (M_w , M_n , M_w/M_n , etc.) and the comonomer content (C_2 , C_3 , C_6 , etc.) are determined by using
 a high temperature Gel Permeation Chromatography (Polymer Char GPC-IR) equipped with a
 multiple-channel band-filter based Infrared detector IR5, an 18-angle light scattering detector
 and a viscometer. Three Agilent PLgel 10- μ m Mixed-B LS columns are used to provide
 polymer separation. Aldrich reagent grade 1,2,4-trichlorobenzene (TCB) with 300 ppm

antioxidant butylated hydroxytoluene (BHT) is used as the mobile phase. The TCB mixture is filtered through a 0.1- μ m Teflon filter and degassed with an online degasser before entering the GPC instrument. The nominal flow rate is 1.0 mL/min and the nominal injection volume is 200 μ L. The whole system including transfer lines, columns, and detectors are contained in an oven maintained at 145°C. The polymer sample is weighed and sealed in a standard vial with 80- μ L flow marker (Heptane) added to it. After loading the vial in the auto-sampler, polymer is automatically dissolved in the instrument with 8 mL added TCB solvent. The polymer is dissolved at 160°C with continuous shaking for about 1 hour for most PE samples or 2 hours for PP samples. The TCB densities used in concentration calculation are 1.463 g/mL at room temperature and 1.284 g/mL at 145°C. The sample solution concentration is from 0.2 to 2.0 mg/mL, with lower concentrations being used for higher molecular weight samples. The concentration (c), at each point in the chromatogram is calculated from the baseline-subtracted IR5 broadband signal intensity (I), using the following equation: $c = \beta I$, where β is the mass constant. The mass recovery is calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume. 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 g/mol to 10,000,000 g/mol. The MW at each elution volume is calculated with (1):

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

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 $K_{PS} = 0.000175$ while α and K are for other materials as calculated and published in literature (Sun, T. et al. (2001) *Macromolecules*, v. 34, 6812 pgs.), except that for purposes of this invention and claims thereto, $\alpha = 0.695$ and $K = 0.000579$ for linear ethylene polymers, $\alpha = 0.705$ and $K = 0.0002288$ for linear propylene polymers, $\alpha = 0.695$ and $K = 0.000181$ for linear butene polymers. Concentrations are expressed in g/cm³, molecular weight is expressed in g/mol, and intrinsic viscosity (hence K in the Mark-Houwink equation) is expressed in dL/g unless otherwise noted.

[0382] The comonomer composition is determined by the ratio of the IR5 detector intensity corresponding to CH₂ and CH₃ channel calibrated with a series of PE and PP homo/copolymer standards whose nominal value are predetermined by NMR or FTIR. In particular, this

provides the methyls per 1,000 total carbons (CH₃/1000TC) as a function of molecular weight. The short-chain branch (SCB) content per 1000TC (SCB/1000TC) is then computed as a function of molecular weight by applying a chain-end correction to the CH₃/1000TC function, assuming each chain to be linear and terminated by a methyl group at each end. The weight % comonomer is then obtained from the following expression in which f is 0.3, 0.4, 0.6, 0.8, and so on for C₃, C₄, C₆, C₈, and so on co-monomers, respectively:

$$w_2 = f * \text{SCB}/1000\text{TC} \quad (2)$$

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

$$\text{Bulk IR ratio} = \frac{\text{Area of CH}_3 \text{ signal within integration limits}}{\text{Area of CH}_2 \text{ signal within integration limits}} \quad (3)$$

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

$$w_2b = f * \text{bulk CH}_3/1000\text{TC} \quad (4)$$

$$\text{bulk SCB}/1000\text{TC} = \text{bulk CH}_3/1000\text{TC} - \text{bulk CH}_3\text{end}/1000\text{TC} \quad (5)$$

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

[0383] The LS detector is the 18-angle Wyatt Technology High Temperature DAWN HELEOSII. The LS molecular weight (M) at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (*Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press, 1972.):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c \quad (6)$$

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

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A} \quad (7)$$

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 $\lambda = 665$ nm.

[0384] A high temperature Agilent (or Viscotek Corporation) viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the equation $[\eta] = \eta_s/c$, where c is concentration and is determined from the IR5 broadband channel output. The viscosity MW at each point is calculated as $M = K_{PS} M_{PS}^{\alpha_{PS}+1} / [\eta]$, where α_{PS} is 0.67 and K_{PS} is 0.000175.

10 [0385] 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 invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby. Likewise, the term "comprising" is considered
15 synonymous with the term "including." Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of", "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

Gel Permeation Chromatography (GPC-DRI).

[0386] The analysis was performed using a Waters 2000 (Gel Permeation Chromatograph) with DRI detector. The detailed GPC conditions are listed in Table 11 below. Standards and samples were prepared in inhibited TCB (1,2,4-trichlorobenzene) solvent. Nineteen
25 polystyrene standards (PS) were used for calibrating the GPC. PS standards used are from EasiCal Pre-prepared Polymer calibrants (PL Laboratories). Calculation for converting narrow polystyrene standard peak molecular weight (for example 7,500,000 polystyrene) to polypropylene peak molecular weight (4630505) is:
 $M_{pp} = 10^{(\log_{10}(0.000175/0.0002288)/(1+0.705) + \log_{10}(M_{ps}) * (1+0.67)/(1+0.705))}$, where M_{pp}
30 is molecular weight for polypropylene and M_{ps} is the molecular weight for polystyrene. From this, an elution retention time to polypropylene molecular weight relationship is obtained.

[0387] The samples were accurately weighed and diluted to a ~0.75 mg/mL concentration and recorded. The standards and samples were placed on a PL Labs 260 Heater/Shaker at 160°C for two hours. These were filtered through a 0.45 micron steel filter cup then analyzed.

Table 11: Gel Permeation Chromatography (GPC) measurement conditions

Instrument		Waters 2000
Column	Type:	3 x Mixed Bed Type "LS" "B" 10 Micron PD (high porosity col.'s)
	Length:	300mm
	ID:	7.8mm
	Supplier:	Polymer Labs
Solvent Program		
		0.5 ml/min TCB inhibited
		(inhibited with BHT at 1,500ppm w/v%)
		BHT is 2,6-di-tert-butyl-4-methyl phenol
Detector		Differential Refractive Index (DRI)
Temperature	Injector:	135°C
	Detector:	135°C
	Column:	135°C
Injection Volume		301.5 µL
Sample Concentration		(0.75 mg./ml.)
		(6 mg polymer to 8ml TCB)(135°C)
Solvent Diluent		TCB inhibited
Alpha & K Values in TCB @ 135°C		
Polymer	Alpha (α)	K
Polystyrene	0.670	1.750X10 ⁻⁴
Polypropylene	0.705	2.288x10 ⁻⁴