

SUBSTITUTED METALLOCENE CATALYSTS

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PRIORITY

[0001] This application claims the benefit of and priority to USSN 61/847,442, filed July 17, 2013.

FIELD OF THE INVENTION

10 [0002] This invention relates to novel bridged hafnium metallocene compounds comprising indenyl ligands substituted at the 4 position.

BACKGROUND OF THE INVENTION

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

[0004] Catalysts for olefin polymerization are often based on metallocenes as catalyst precursors, which are activated either with the help of an alumoxane, or with an activator containing a non-coordinating anion.

[0005] Useful metallocene catalysts have been based upon bis-indenyl transition metal compounds. In particular, bridged bis-2-substituted indenyl transition metal compounds and bridged bis-2,4-disubstituted indenyl transition metal compounds have found use in polymerizing propylene, see for example US 5,276,208 and EP 576 970.

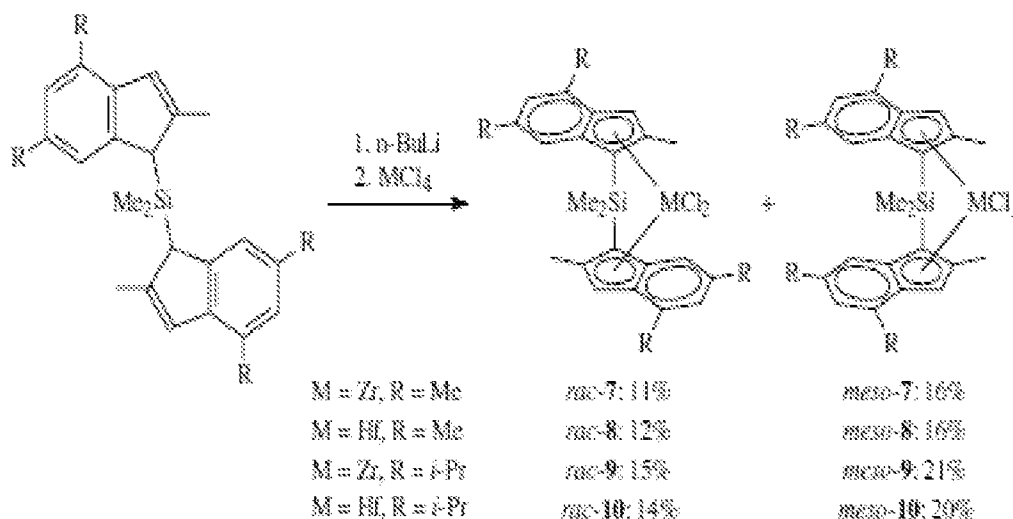
[0006] Also see WO 2011/051705 which discloses substituted indenyl compounds, but no cyclic bridging groups. Also see Ransom, et al. Organometallics (2011), 30(4), pp. 800-814
25 where a series of ansa-bridged ethylene-bis(hexamethylindenyl)zirconium and hafnium complexes were explored. Likewise, see CN 2006-10080838 (also referred to as CN 101074276 B) which appears to use $\text{Me}_2\text{Si}(2\text{-Me-4-}i\text{PrInd})_2\text{HfCl}_2$ to make isotactic polypropylene with branching by adding in functionalized styrene where the functional group is a vinyl group. See also US 7,741,417, US 7,220,695, and WO 2008/027116 where the
30 processes are disclosed to produce isotactic polypropylene by contacting propylene and optionally one or more monomers with a bis-indenyl Group 4 metallocene compound supported on a silica treated with organoaluminum compound(s) and heterocyclic compound(s), under slurry conditions in the presence of hydrogen at a temperature of about 50°C. to about 160°C. and a pressure of from about 3 MPa to about 5 MPa to provide a
35 catalyst activity of greater than 30,000lb of product per lb of catalyst (note that rac-dimethylsilyl-bis(2-methyl-4,6-diisopropyl-indenyl)hafnium (or zirconium) dimethyl (or dichloride) are listed in the text).

[0007] Also see US 7,385,015 where certain bis-indenyl compounds are supported on a

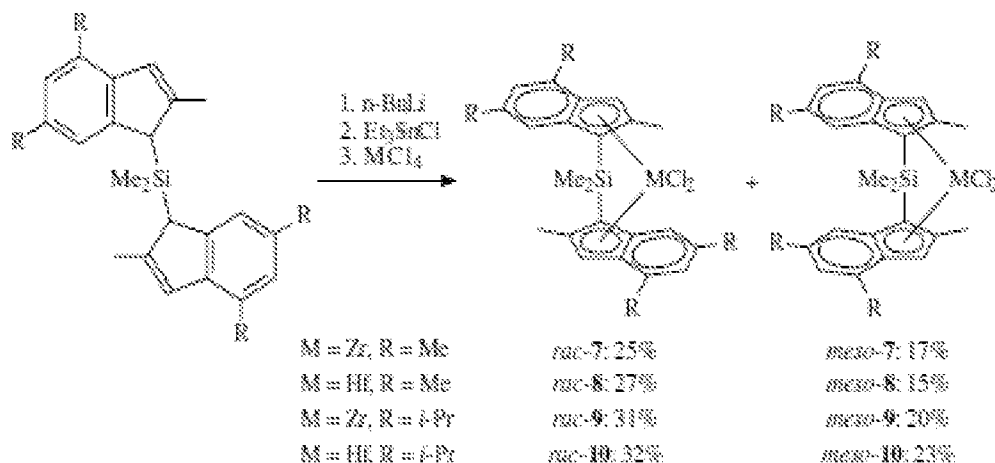
support that has been combined with a first trialkylaluminum, calcined, then combined with a second trialkylaluminum compound(s), where the alkyl groups have two or more carbon atoms and the first and second trialkylaluminum compound(s) may be the same or different. Note that *rac*-dimethylsilyl-bis(2-methyl-4,6-diisopropyl-indenyl)hafnium (or zirconium) dimethyl (or dichloride) are listed in the text as catalysts that can be supported and dimethylsilylbis(2-methyl-4-phenyl)hafnium dimethyl is used in the examples.

[0008] US 7,220,695 and US 7,741,417 disclose supported activators of an ion-exchanged layered silicate, an organoaluminum compound, and a heterocyclic compound, which may be substituted or unsubstituted. Note that *rac*-dimethylsilyl-bis(2-methyl-4,6-diisopropyl-indenyl)hafnium (or zirconium) dimethyl (or dichloride) are listed in the text as catalysts that can be supported and dimethylsilylbis(2-methyl-4-phenyl)hafnium dimethyl is used in the examples.

[0009] See also "Synthesis and molecular structures of zirconium and hafnium complexes bearing dimethylsilyl-bis-2,4,6-trimethylindenyl and dimethylsilyl-bis-2-methyl-4,6-diisopropylindenyl ligands" Izmer et al., Journal of Organometallic Chemistry (2005), 690(4), pp. 1067-1079 which describes zirconium and hafnium ansa-complexes containing 2,4,6-trialkyl-substituted indenyl fragments, such as *rac*- and *meso*-Me₂Si(2-Me-4,6-R₂C₉H₃-η⁵)₂MCl₂ (R = Me, *i*Pr; M = Zr, Hf) The complexes reproduced below were disclosed. No polymerizations using these compounds were performed.



Scheme 6.



Scheme 7.

[0010] EP 1 209 165 A2 and US 5,739,366 disclose a type of 4-isopropyl-7-methylindenyl substituted zirconium complex where the 2 position can be H or C_{1-3} .

[0011] US 5,767,033 mentions dimethylsilyl-bis{1-(2-methyl-4-*i*-propyl-7-methylindenyl)}hafnium dichloride at column 11, line 43 and uses *rac*-dimethylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride and *rac*-diphenylsilyl-bis{1-(2,7-dimethyl-4-isopropylindenyl)}zirconium dichloride in the examples. Cyclic bridging groups do not appear to be mentioned.

[0012] None of the above disclose hafnium based indenyl metallocene compounds where the 4 position is substituted, the 3 position is not substituted, and the bridge is a cyclic group, preferably used in combination with a non-coordinating anion activator.

[0013] 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 melting point, high molecular weights, to increase conversion or comonomer incorporation, to alter comonomer distribution without negatively impacting the resulting polymer's properties, increasing vinyl chain ends, particularly increasing vinyl unsaturations at the chain end while also maintaining or increasing Mw.

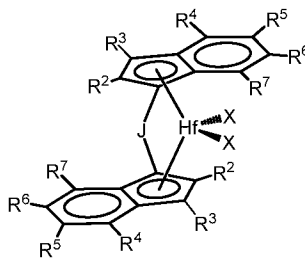
[0014] It is therefore an object of the present invention to provide novel catalyst compounds, catalysts systems comprising such compounds, and processes for the polymerization of olefins using such compounds and systems.

SUMMARY OF THE INVENTION

[0015] This invention relates to novel bridged a hafnium transition metal metallocene catalyst compounds having two indenyl ligands substituted at the 4 positions with a C_1 to C_{10} alkyl, where the 3 positions are hydrogen (assuming the bridge position is counted as the one position) and the bridging atom is carbon or silicon which is incorporated into a cyclic group comprising 3, 4, 5, or 6 silicon and/or carbon atoms that make up the cyclic ring.

[0016] This invention relates to a metallocene catalyst compound represented by the

formula:



where each R^3 is hydrogen; each R^4 is independently a C_1 - C_{10} alkyl; each R^2 and R^7 is independently hydrogen, or C_1 - C_{10} alkyl; each R^5 and R^6 is independently hydrogen, C_1 - C_{50} substituted or unsubstituted hydrocarbyl, or C_1 - C_{50} substituted or unsubstituted halocarbyl; and R^4 and R^5 , R^5 and R^6 and/or R^6 and R^7 may optionally be bonded together to form a ring structure; J is a bridging group represented by the formula R^a_2J , where J is C or Si, and each R^a is, independently, C_1 to C_{20} substituted or unsubstituted hydrocarbyl, and the two R^a form a cyclic structure incorporating J and the cyclic structure may be a saturated or partially saturated cyclic or fused ring system; and each X is a univalent anionic ligand, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.

[0017] This invention further relates to a catalyst system comprising said metallocene catalyst compound(s) and an activator.

[0018] This invention further relates to a method to polymerize olefins comprising contacting olefins with a catalyst system comprising said metallocene catalyst compound(s) described above and an activator.

[0019] This invention further relates to polymer compositions produced by the methods described herein.

20 **BRIEF DESCRIPTION OF THE FIGURES**

[0020] Figure 1 is a graph of pressure of ethylene (psi) introduced into the reactor versus amount of vinyl termination in the polymer produced. The labels within the graph correspond to the examples number in Tables 4a and 4b.

Definitions

[0021] As used herein, the numbering scheme for the Periodic Table Groups is the new notation as set out in CHEMICAL AND ENGINEERING NEWS, 63(5), 27 (1985). Therefore, a "group 4 metal" is an element from group 4 of the Periodic Table, e.g. Zr, Ti, and Hf.

[0022] The terms "hydrocarbyl radical," "hydrocarbyl" and "hydrocarbyl group" are used interchangeably throughout this document. Likewise the terms "group", "radical", and "substituent" are also used interchangeably in this document. For purposes of this disclosure, "hydrocarbyl radical" is defined to be a radical, which contains hydrogen atoms and up to 50 carbon atoms and which may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic.

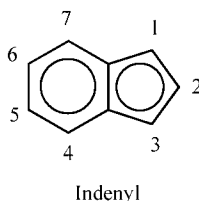
[0023] Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom has been substituted with at least one functional group such as NR^*_2 , OR^* , SeR^* , TeR^* , PR^*_2 , AsR^*_2 , SbR^*_2 , SR^* , BR^*_2 , SiR^*_3 , GeR^*_3 , SnR^*_3 , PbR^*_3 and the like or where at least one non-hydrocarbon atom or group has been inserted within the hydrocarbyl radical, such as -O-, -S-,
 5 -Se-, -Te-, -N(R*)-, =N-, -P(R*)-, =P-, -As(R*)-, =As-, -Sb(R*)-, =Sb-, -B(R*)-, =B-,
 -Si(R*)₂-, -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.

[0024] Halocarbyl radicals are radicals in which one or more hydrocarbyl hydrogen atoms
 10 have been substituted with at least one halogen (e.g. F, Cl, Br, I) or halogen-containing group (e.g. CF_3).

[0025] Substituted halocarbyl radicals are radicals in which at least one halocarbyl hydrogen or halogen 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 , SiR^*_3 , GeR^*_3 , SnR^*_3 , PbR^*_3 and
 15 the like or where at least one non-carbon atom or group has been inserted within the halocarbyl radical such as -O-, -S-, -Se-, -Te-, -N(R*)-, =N-, -P(R*)-, =P-, -As(R*)-, =As-, -Sb(R*)-, =Sb-,
 -B(R*)-, =B-, -Si(R*)₂-, -Ge(R*)₂-, -Sn(R*)₂-, -Pb(R*)₂- and the like, where R* is independently a hydrocarbyl or halocarbyl radical provided that at least one halogen atom remains on the original halocarbyl radical. Additionally, two or more R* may join together to
 20 form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.

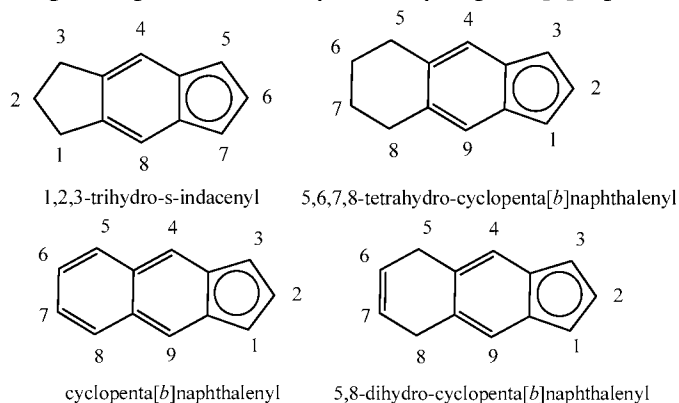
[0026] In some embodiments of the invention, the hydrocarbyl radical is independently selected from methyl, ethyl, ethenyl and isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl,
 25 octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, hexacosenyl, heptacosenyl, octacosenyl, nonacosenyl,
 30 triacontenyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, tridecynyl, tetradecynyl, pentadecynyl, hexadecynyl, heptadecynyl, octadecynyl, nonadecynyl, eicosynyl, heneicosynyl, docosynyl, tricosynyl, tetracosynyl, pentacosynyl, hexacosynyl, heptacosynyl, octacosynyl, nonacosynyl, triacontynyl, butadienyl, pentadienyl, hexadienyl, heptadienyl, octadienyl, nonadienyl, and decadienyl. Also included
 35 are isomers of saturated, partially unsaturated and aromatic cyclic and polycyclic structures wherein the radical may additionally be subjected to the types of substitutions described above. Examples include phenyl, methylphenyl, dimethylphenyl, ethylphenyl, diethylphenyl, propylphenyl, dipropylphenyl, butylphenyl, dibutylphenyl, benzyl, methylbenzyl, naphthyl,

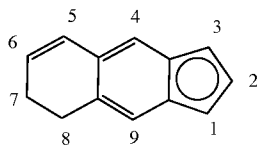
- anthracenyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, cycloheptyl, cycloheptenyl, norbornyl, norbornenyl, adamantyl and the like. For this disclosure, when a radical is listed, it indicates that radical type and all other radicals formed when that radical type is subjected to the substitutions defined above. Alkyl, alkenyl and alkynyl radicals listed include all isomers including cyclic isomers, for example, butyl includes *n*-butyl, 2-methylpropyl, 1-methylpropyl, *tert*-butyl, and cyclobutyl (and analogous substituted cyclopropyls); pentyl includes *n*-pentyl, cyclopentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, and neopentyl (and analogous substituted cyclobutyls and cyclopropyls); butenyl includes E and Z forms of 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-1-propenyl and 2-methyl-2-propenyl (and cyclobutenyls and cyclopropenyls). Cyclic compounds having substitutions include all isomer forms, for example, methylphenyl would include ortho-methylphenyl, meta-methylphenyl and para-methylphenyl; dimethylphenyl would include 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, and 3,5-dimethylphenyl.
- [0027]** For nomenclature purposes, the following numbering schemes are used for indenyl. It should be noted that indenyl can be considered a cyclopentadienyl with fused a benzene ring. The structure below is drawn and named as an anion.



- [0028]** The following ring structures are substituted indenyls, where the substitution at the 5 and 6 positions forms a ring structure. For specific compound nomenclature purposes, these ligands are described below. A similar numbering and nomenclature scheme is used for these types of substituted indenyls that include indacenyls, cyclopenta[*b*]naphthalenyls, heterocyclopentanaphthyls, heterocyclopentaindenyls, and the like, as illustrated below. Each structure is drawn and named as an anion.

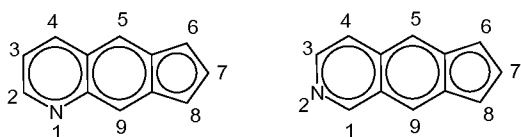
- [0029]** Non-limiting examples of indacenyls and cyclopenta[*b*]naphthalenyls include:





7,8-dihydro-cyclopenta[b]naphthalenyl.

[0030] Non-limiting examples of heterocyclopentanaphthyls include:

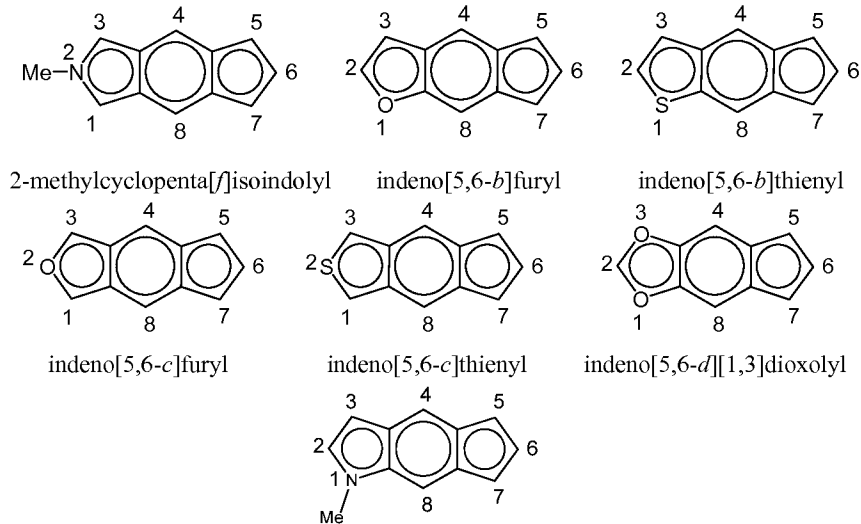


cyclopenta[g]quinolyl

cyclopenta[g]isoquinolyl.

[0031] Further non-limiting examples of heterocyclopentanaphthyls include cyclopenta[g]phosphinolyl, cyclopenta[g]isophosphinolyl, cyclopenta[g]arsinolyl, and cyclopenta[g]isoarsinolyl.

[0032] Non-limiting examples of heterocyclopentaindenyls include:



1-methylcyclopenta[f]indolyl.

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[0033] Further non-limiting examples of heterocyclopentaindenyls include 1-hydrocarbylcyclopenta[f]phosphindolyl, 2-hydrocarbylcyclopenta[f]isophosphindolyl, 1-hydrocarbylcyclopenta[f]arsindolyl, 2-hydrocarbylcyclopenta[f]isoarsindolyl, indeno[5,6-*b*]selenophenyl, indeno[5,6-*b*]tellurophenyl, indeno[5,6-*c*]selenophenyl, indeno[5,6-*c*]tellurophenyl, 2-hydrocarbylcyclopenta[f]isoindolyl, and 1-hydrocarbylcyclopenta[f]indolyl, where hydrocarbyl is a "hydrocarbyl radical" as previously defined.

[0034] A "ring carbon atom" is a carbon atom that is part of a cyclic ring structure. By this definition, an indenyl fragment has nine ring carbon atoms. It is within the scope of the invention to replace one of more of the ring carbon atoms with a heteroatom, such as a boron atom, a Group 14 atom that is not carbon, a Group 15 atom, or a Group 16 atom. Preferred heteroatoms include boron, nitrogen, oxygen, phosphorus, and sulfur.

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[0035] A "bondable ring position" is a ring position that is capable of bearing a substituent

or bridging substituent. For example, indeno[5,6-*c*]thienyl has seven bondable ring positions (at the carbon atoms) and one non-bondable ring position (the sulfur atom).

[0036] "Ring Structure" means atoms bonded together in one or more cyclic arrangements.

[0037] An "olefin," alternatively referred to as "alkene," is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an "ethylene" content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer. A "polymer" has two or more of the same or different mer units. A "homopolymer" is a polymer having mer units that are the same. A "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three mer units that are different from each other. "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. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. An oligomer is typically a polymer having a low molecular weight (such an Mn of less than 25,000 g/mol, preferably less than 2,500 g/mol) or a low number of mer units (such as 75 mer units or less). An "ethylene polymer" or "ethylene copolymer" is a polymer or copolymer comprising at least 50 mole% ethylene derived units, a "propylene polymer" or "propylene copolymer" is a polymer or copolymer comprising at least 50 mole% propylene derived units, and so on.

[0038] In the context of this document, "homopolymerization" would produce a polymer made from one type of monomer. For example, homopolymerization of propylene would produce homopolypropylene; homopolymerization of ethylene would produce homopolyethylene; and the like. Likewise, "copolymerization" would produce polymers with more than one monomer type. For example, ethylene copolymers include polymers of ethylene with α -olefins, cyclic olefins and diolefins, vinylaromatic olefins, α -olefinic diolefins, substituted α -olefins, and/or acetylenically unsaturated monomers.

[0039] Non-limiting examples of α -olefins include propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tricosene, 1-tetracosene, 1-pentacosene, 1-hexacosene, 1-heptacosene, 1-octacosene, 1-nonacosene, 1-triacontene, 4-methyl-1-pentene, 3-methyl-1-pentene, 5-methyl-1-nonene, 3,5,5-trimethyl-1-hexene, vinylcyclohexane, and vinylnorbornane.

[0040] For the purposes of this invention, ethylene shall be considered an α -olefin.

[0041] Non-limiting examples of cyclic olefins and diolefins include cyclobutene,

cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclononene, cyclodecene, norbornene, 4-methylnorbornene, 3-methylcyclopentene, 4-methylcyclopentene, vinylcyclohexane, norbornadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, vinylcyclohexene, 5-vinyl-2-norbornene, 1,3-divinylcyclopentane, 1,2-divinylcyclohexane, 1,3-divinylcyclohexane, 1,4-divinylcyclohexane, 1,5-divinylcyclooctane, 1-allyl-4-vinylcyclohexane, 1,4-diallylcyclohexane, 1-allyl-5-vinylcyclooctane, and 1,5-diallylcyclooctane.

[0042] Non-limiting examples of vinylaromatic olefins and diolefins include styrene, *para*-methylstyrene, *para*-*t*-butylstyrene, vinylnaphthylene, vinyltoluene, and divinylbenzene.

[0043] Non-limiting examples of α -olefinic dienes include 1,4-hexadiene, 1,5-hexadiene, 1,5-heptadiene, 1,6-heptadiene, 6-methyl-1,6-heptadiene, 1,7-octadiene, 7-methyl-1,7-octadiene, 1,9-decadiene, 1,11-dodecene, 1,13-tetradecene and 9-methyl-1,9-decadiene.

[0044] Substituted α -olefins (also called functional group containing α -olefins) include those containing at least one non-carbon Group 13 to 17 atom bound to a carbon atom of the substituted α -olefin where such substitution if silicon may be adjacent to the double bond or terminal to the double bond, or anywhere in between, and where inclusion of non-carbon and non-silicon atoms such as for example B, O, S, Se, Te, N, P, Ge, Sn, Pb, As, F, Cl, Br, or I, are contemplated, where such non-carbon or non-silicon moieties are sufficiently far removed from the double bond so as not to interfere with the coordination polymerization reaction with the catalyst and so to retain the generally hydrocarbyl characteristic. By sufficiently far removed from the double bond we intend that the number of carbon atoms, or the number of carbon and silicon atoms, separating the double bond and the non-carbon or non-silicon moiety is preferably 6 or greater, e.g. 7, or 8, or 9, or 10, or 11, or 12, or 13, or 14 or more. The number of such carbon atoms, or carbon and silicon atoms, is counted from immediately adjacent to the double bond to immediately adjacent to the non-carbon or non-silicon moiety. Examples include allyltrimethylsilane, divinylsilane, 8,8,8-trifluoro-1-octene, 8-methoxyoct-1-ene, 8-methylsulfanyloct-1-ene, 8-dimethylaminooct-1-ene, or combinations thereof. The use of functional group-containing α -olefins where the functional group is closer to the double bond is also within the scope of embodiments of the invention when such olefins may be incorporated in the same manner as are their α -olefin analogs. See, "Metallocene Catalysts and Borane Reagents in The Block/Graft Reactions of Polyolefins", T.C. Chung, *et al*, *Polym. Mater. Sci. Eng.*, v. 73, p. 463 (1995), and the masked α -olefin monomers of US 5,153,282. Such monomers permit the preparation of both functional-group containing copolymers capable of subsequent derivatization, and of functional macromers which may be used as graft and block type polymeric segments.

[0045] An α -olefin may also include α -olefinic macromonomers of up to 2000 mer units.

[0046] The term "catalyst system" is defined to mean a catalyst precursor/activator pair, and optional co-activator, and an optional support material. When "catalyst system" is used to describe such a pair before activation, it means the unactivated catalyst (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 catalyst and the activator or other charge-balancing moiety. 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.

[0047] A transition metal compound may be neutral as in a precatalyst, or a charged species with a counter ion as in an activated catalyst system.

[0048] Catalyst precursor is also often referred to as precatalyst, catalyst, catalyst compound, catalyst precursor, transition metal compound or transition metal complex. These words are used interchangeably. Activator and cocatalyst are also used interchangeably. A scavenger is a compound that is typically added to facilitate oligomerization or 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 the transition metal compound to form an alkylated transition metal compound.

[0049] A polymerization catalyst system is a catalyst system that can polymerize monomers to polymer. An “anionic ligand” is a negatively charged ligand which donates one or more pairs of electrons to a metal ion. A “neutral donor ligand” is a neutrally charged ligand which donates one or more pairs of electrons to a metal ion.

[0050] A metallocene catalyst is defined as an organometallic compound with at least one π -bound cyclopentadienyl moiety (or substituted cyclopentadienyl moiety such as indenyl) and more frequently two π -bound cyclopentadienyl moieties or substituted cyclopentadienyl moieties.

[0051] Noncoordinating anion (NCA) is defined to mean an anion either that does not coordinate to the catalyst metal cation or that does coordinate to the metal cation, but only weakly. An NCA coordinates weakly enough that a neutral Lewis base, such as an olefinically or acetylenically unsaturated monomer can displace it from the catalyst center. Any metal or metalloid that can form a compatible, weakly coordinating complex may be used or contained in the noncoordinating anion. Suitable metals include, but are not limited to, aluminum, gold, and platinum. Suitable metalloids include, but are not limited to, boron, aluminum, phosphorus, and silicon.

[0052] A stoichiometric activator can be either neutral or ionic. The terms ionic activator, and stoichiometric ionic activator can be used interchangeably. Likewise, the terms neutral stoichiometric activator, and Lewis acid activator can be used interchangeably.

[0053] As used herein, Mn is number average molecular weight, Mw is weight average molecular weight, and Mz is z average molecular weight, wt% is weight percent, and mol% is mole percent. Molecular weight distribution (MWD), also referred to as polydispersity (PDI),

is defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (e.g., Mw, Mn, Mz) are g/mol. 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, Bn is benzyl, THF or thf is tetrahydrofuran, MAO is methylalumoxane.

[0054] 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.

[0055] For purposes of this invention and claims thereto, "alkoxides" include those where the alkyl group is a C₁ to C₁₀ hydrocarbyl. The alkyl group may be straight chain, branched, or cyclic.

[0056] For purposes of this invention, an "alkyl" group is a linear, branched, or cyclic radical of carbon and hydrogen. In a preferred embodiment, "alkyl" refers to linear alkyls.

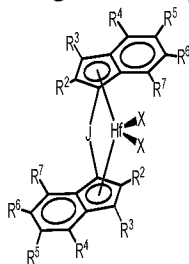
[0057] Room temperature is 22 °C, unless otherwise indicated.

DETAILED DESCRIPTION

Metallocene Catalyst Compounds

[0058] This invention relates to novel bridged a hafnium transition metal metallocene catalyst compounds having two indenyl ligands substituted at the 4 positions with a C₁ to C₁₀ alkyl, where the 3 positions are hydrogen (assuming the bridge position is counted as the one position) and the bridge is carbon or silicon which is incorporated into a cyclic group comprising 3, 4, 5 or 6 silicon and/or carbon atoms that make up the cyclic ring, preferably the 2, 4 positions, 4, 7 positions, 2, 4, 5 positions, 2, 4, 6 positions, 2, 4, 7 positions, or 2, 4, 5, 6, 7 positions are substituted, preferably by a C₁ to C₁₀ alkyl group, and optionally, if alkyl substituted, the 4 and 5, 5 and 6, and/or 6 and 7 positions may be bonded together to form a ring structure.

[0059] In a preferred embodiment this invention is related to metallocene catalyst compounds, and catalyst systems comprising such compounds, represented by the formula:



where each R³ is hydrogen; each R⁴ is independently a C₁-C₁₀ alkyl (preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof); each R², and R⁷ are independently hydrogen, or C₁-C₁₀ alkyl (preferably hydrogen, methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof); each R⁵ and R⁶ are independently hydrogen, or C₁-C₅₀ substituted or unsubstituted hydrocarbyl (preferably

hydrogen, methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof); and R^4 and R^5 , R^5 and R^6 and/or R^6 and R^7 may optionally be bonded together to form a ring structure; J is a bridging group represented by the formula R^a_2J , where J is C or Si, and each R^a is, independently C_1 to C_{20} substituted or unsubstituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof), and two R^a form a cyclic structure incorporating J and the cyclic structure may be a saturated or partially saturated cyclic or fused ring system; and each X is a univalent anionic ligand, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.

10 [0060] In a preferred embodiment of the invention, each R^2 is independently a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof.

[0061] In a preferred embodiment of the invention, each R^2 and R^4 are, independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof. Each R^2 and R^4 may be the same or different.

15 [0062] In a preferred embodiment of the invention, each R^2 , R^4 and R^5 are, independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof. Each R^2 , R^4 and R^5 may be the same or different.

[0063] In a preferred embodiment of the invention, each R^2 , R^4 and R^6 are, independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof. Each R^2 , R^4 and R^6 may be the same or different.

[0064] In a preferred embodiment of the invention, each R^2 , R^4 and R^7 are, independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof. Each R^2 , R^4 and R^7 may be the same or different.

25 [0065] In a preferred embodiment of the invention, each R^2 , R^4 , R^5 and R^6 are, independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof. Each R^2 , R^4 , R^5 and R^6 may be the same or different.

[0066] In a preferred embodiment of the invention, each R^2 , R^4 , R^5 and R^7 are, independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof. Each R^2 , R^4 , R^5 and R^7 may be the same or different.

[0067] In a preferred embodiment of the invention, each R^2 , R^4 , R^5 , R^6 and R^7 are, independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof. Each R^2 , R^4 , R^5 , R^6 and R^7 may be the same or different.

35 [0068] In a preferred embodiment of the invention, each R^2 , R^4 and R^7 are the same and are selected from the group consisting of C_1 to C_{10} alkyl group, preferably methyl, ethyl,

propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl and isomers thereof. In a preferred embodiment of the invention, each R², R⁴ and R⁷ are the same and are selected from the group consisting of C₁ to C₅ alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, and isomers thereof.

5 [0069] In a preferred embodiment of the invention, each R² is independently a C₁ to C₃ alkyl group, preferably methyl, ethyl, n-propyl, isopropyl or cyclopropyl.

[0070] In a preferred embodiment of the invention, each R² is independently a C₁ to C₃ alkyl group, preferably methyl or ethyl.

10 [0071] In a preferred embodiment of the invention each R⁴ is independently a C₁ to C₄ alkyl group, preferably methyl, ethyl, propyl, butyl and isomers thereof.

[0072] In a preferred embodiment of the invention each R⁴ is independently a C₁ to C₄ alkyl group, preferably methyl, ethyl, n-propyl, cyclopropyl, or n-butyl.

[0073] In a preferred embodiment of the invention, each R⁴ and R⁷ are, independently, a C₁ to C₄ alkyl group, preferably methyl, ethyl, propyl, butyl and isomers thereof.

15 [0074] In a preferred embodiment of the invention, each R⁴ and R⁷ are, independently, a C₁ to C₄ alkyl group, preferably methyl, ethyl, n-propyl, cyclopropyl, or n-butyl.

[0075] In a preferred embodiment of the invention, each R⁵ and R⁶ are independently a C₁ to C₁₀ alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof, and R⁵ and R⁶ may optionally be bonded together to form a ring structure.

[0076] In a preferred embodiment of the invention, each R⁵ and R⁶ are independently a C₁ to C₅ alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, or an isomer thereof, and R⁵ and R⁶ may optionally be bonded together to form a ring structure.

25 [0077] In a preferred embodiment of the invention, each R² is independently a C₁ to C₃ alkyl group, preferably methyl, ethyl, n-propyl, isopropyl or cyclopropyl, each R³, R⁵, R⁶, and R⁷ are hydrogen, and each R⁴ is independently a C₁ to C₄ alkyl group, preferably methyl, ethyl, propyl, butyl, or an isomer thereof.

[0078] In a preferred embodiment of the invention, each R² is independently a C₁ to C₃ alkyl group, preferably methyl, ethyl, n-propyl, isopropyl or cyclopropyl, each R³, R⁵, R⁶, and R⁷ are hydrogen, and each R⁴ is independently a C₁ to C₄ alkyl group, preferably methyl, ethyl, n-propyl, cyclopropyl, or n-butyl.

30 [0079] In a preferred embodiment of the invention, each R² is a C₁ to C₃ alkyl group, preferably methyl, ethyl, n-propyl, isopropyl or cyclopropyl, each R³, R⁵, and R⁶ are hydrogen, and R⁴ and R⁷ are, independently, a C₁ to C₄ alkyl group, preferably methyl, ethyl, propyl, butyl, or an isomer thereof.

35 [0080] In a preferred embodiment of the invention, each R² is a C₁ to C₃ alkyl group, preferably methyl, ethyl, n-propyl, isopropyl or cyclopropyl, each R³, R⁵, and R⁶ are hydrogen, and R⁴ and R⁷ are, independently, a C₁ to C₄ alkyl group, preferably methyl, ethyl, n-propyl,

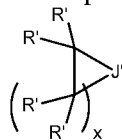
cyclopropyl, or n-butyl.

[0081] In a preferred embodiment of the invention, each R^2 , R^4 , R^5 , R^6 and R^7 are, independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof, R^3 is hydrogen, and R^5 and R^6 are joined together to form a 5-membered partially unsaturated ring.

[0082] In a preferred embodiment of the invention, each R^2 , R^4 , and R^7 are independently methyl, ethyl, or n-propyl, each R^5 and R^6 are independently, a C_1 to C_{10} alkyl group, preferably methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl or an isomer thereof, R^3 is hydrogen, and R^5 and R^6 are joined together to form a 5-membered partially unsaturated ring.

[0083] In a preferred embodiment of the invention, each R^2 , R^4 and R^7 are the same and are selected from the group consisting of C_1 to C_3 alkyl group, preferably methyl, ethyl, propyl, and isomers thereof, and R^3 , R^5 and R^6 are hydrogen.

[0084] In a preferred embodiment of the invention, J is preferably represented by the



formula:

wherein J' is a carbon or silicon atom, x is 1, 2, 3, or 4, preferably 2 or 3, and each R' is, independently, hydrogen or C_1 - C_{10} hydrocarbyl, preferably hydrogen. Particularly preferred J groups include cyclopentamethylenesilylene, cyclotetramethylenesilylene, cyclotrimethylenesilylene, and the like.

[0085] In a preferred embodiment of the invention, each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X 's may form a part of a fused ring or a ring system), preferably each X is independently selected from halides and C_1 to C_5 alkyl groups, preferably each X is a methyl, ethyl, propyl, butyl or pentyl group, preferably a methyl group;

[0086] In a preferred embodiment of the invention, R^4 is not an aryl group (substituted or unsubstituted). An aryl group is defined to be a single or multiple fused ring group where at least one ring is aromatic. A substituted aryl group is an aryl group where a hydrogen has been replaced by a heteroatom or heteroatom containing group. Examples of aryl groups include phenyl, benzyl, carbazolyl, naphthyl, and the like.

[0087] In a preferred embodiment of this invention, R^2 , R^4 and R^7 are not a substituted or unsubstituted aryl group.

[0088] In a preferred embodiment of this invention, R^2 , R^4 , R^5 , R^6 and R^7 are not a substituted or unsubstituted aryl group.

[0089] Metallocene compounds that are particularly useful in this invention include one or

more of:

- cyclotetramethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dimethyl,
5 cyclotetramethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dimethyl,
10 cyclotrimethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dimethyl,
15 cyclopentamethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dichloride,
20 cyclotetramethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2-methyl-4-cyclopropylindenyl)hafnium dichloride,
25 cyclotrimethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dichloride,
30 cyclopentamethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dimethyl,
35 cyclotetramethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dimethyl,

cyclopentamethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dimethyl,
cycloctetramethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dichloride,
5 cyclotrimethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dichloride,
cycloctetramethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dimethyl,
cycloctetramethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dichloride,
10 cyclopentamethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dichloride,
cycloctetramethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dimethyl,
15 cycloctetramethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dichloride,
cycloctetramethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dimethyl,
20 cyclotrimethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dimethyl,
cycloctetramethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride,
cycloctetramethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dimethyl,
25 cyclopentamethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dimethyl,
cycloctetramethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dichloride,
30 cycloctetramethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium
dimethyl,
cyclopentamethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium
dimethyl,
cyclotrimethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium dimethyl,
35 cycloctetramethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium
dichloride,
cyclopentamethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium
dichloride,

cyclotrimethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium dichloride.

[0090] In a preferred embodiment, the dimethyl in any of the compounds listed above may be replaced with dialkyl (such as diethyl, dipropyl, diphenyl, dibenzyl) or a dihalide (such as difluoride, dibromide, or diiodide). In a preferred embodiment of the invention, the catalyst compound is in the *rac* form. In a preferred embodiment of the invention, at least 90 wt% of the catalyst compound is in the *rac* form, based upon the weight of the *rac* and *meso* forms present, preferably from 92 to 100 wt%, preferably from 95 to 100 wt%, preferably from 98 to 100 wt%. In a preferred embodiment of the invention, the ratio of *rac* to *meso* in the catalyst compound is from 1:100 to 100:1, preferably 1:1 to 100:1, preferably 50:1 to 100:1, preferably 85:1 to 100:1. In a preferred embodiment of the invention, the catalyst compound is greater than 90% *rac*, preferably greater than 95% *rac*, preferably greater than 98% *rac*.

[0091] Amounts of *rac* and *meso* isomers are determined by proton NMR. ¹H NMR data are collected at ambient temperature (22°C) in a 5 mm probe using a 400 MHz Bruker spectrometer with deuterated solvent in which the precatalyst compound is completely soluble. Data is recorded using a maximum pulse width of 45°, 8 seconds between pulses and signal averaging 16 transients.

[0092] In a preferred embodiment in any of the processes described herein one metallocene catalyst compound is used, e.g. the metallocene catalyst compounds are not different. For purposes of this invention one metallocene catalyst compound is considered different from another if they differ by at least one atom. For example "bis-indenyl zirconium dichloride" is different from (indenyl)(2-methylindenyl) zirconium dichloride" which is different from "(indenyl)(2-methylindenyl) hafnium dichloride." Metallocene catalyst compounds that differ only by isomer are considered the same for purposes of determining whether they are the "same", e.g., *rac*-dimethylsilylbis(2-methyl-4-phenyl)hafnium dimethyl and *meso*-dimethylsilylbis(2-methyl-4-phenyl)hafnium dimethyl are isomers of dimethylsilylbis(2-methyl-4-phenyl)hafnium dimethyl. Furthermore for hafnium compounds, the Zr analog may be present at up to 3 wt% and still be considered the "same." Preferably, the zirconium analog is present at less than 2 wt% Zr, more preferably less than 1 wt% Zr, even more preferably less than 0.5 wt% Zr, more preferably less than 0.1 wt%. Amount of Zr and Hf present is determined by using ICPES (Inductively Coupled Plasma Emission Spectrometry), which is described in J. W. Olesik, "Inductively Coupled Plasma-Optical Emission Spectroscopy," in Encyclopedia of Materials Characterization, C. R. Brundle, C. A. Evans, Jr. and S. Wilson, eds., Butterworth-Heinemann, Boston, Mass., 1992, pp. 633-644).

[0093] In some embodiments, two or more different metallocene catalyst compounds are present in the catalyst system used herein. In some embodiments, two or more different metallocene 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 should be chosen such that the two are compatible. A simple screening method such as by ^1H or ^{13}C NMR, known to those of ordinary skill in the art, can be used to determine which transition metal compounds 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 ligand which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the alumoxane or aluminum alkyl (such as triisobutyl aluminum) are typically contacted with the transition metal compounds prior to addition of the non-coordinating anion activator.

[0094] 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.

[0095] In a preferred embodiment, the hafnium bis-indenyl metallocene compound used herein is at least 90% rac isomer and is the indenyl groups are substituted at the 4 position with a C_1 to C_{10} alkyl group, the 3 position is hydrogen, the bridge is carbon or silicon which is incorporated into a 4, 5 or 6 membered ring.

[0096] The metallocene compounds described herein are synthesized according to procedures known in the art.

Activators

[0097] The terms "cocatalyst" and "activator" are used herein interchangeably and are defined to be any compound which can activate any one of the catalyst compounds described above by converting the neutral catalyst compound to a catalytically active catalyst compound cation. Non-limiting activators, for example, include alumoxanes, aluminum alkyls, 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, σ -bound, metal ligand making the metal complex cationic and providing a charge-balancing noncoordinating or weakly coordinating anion.

[0098] In one embodiment, alumoxane activators are utilized as an activator in the catalyst composition. Alumoxanes are generally oligomeric compounds containing $-\text{Al}(\text{R}^1)-\text{O}-$ sub-units, where R^1 is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO),

modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is an alkyl, halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution. A useful alumoxane is a modified methyl alumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under patent number U.S. Patent No. 5,041,584).

10 **[0099]** When the activator is an alumoxane (modified or unmodified), some embodiments select the maximum amount of activator at a 5000-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.

15 **[00100]** 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.

[00101] 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. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral by-product from the anion. Non-coordinating anions useful in accordance with 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.

25 **[00102]** It is within the scope of this invention to use an ionizing or stoichiometric activator, neutral or ionic, such as tri (n-butyl) ammonium tetrakis (pentafluorophenyl) borate, a tris perfluorophenyl boron metalloid precursor or a tris perfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (U.S. Patent No. 5,942,459), or combination thereof. It is also within the scope of this invention to use neutral or ionic activators alone or in combination with alumoxane or modified alumoxane activators.

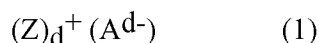
30 **[00103]** Examples of neutral stoichiometric activators include tri-substituted boron, tellurium, aluminum, gallium, and indium, or mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogens, substituted alkyls, aryls, arylhalides, alkoxy, and halides. Preferably, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds,

and mixtures thereof, preferred are alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls). More preferably, the three groups are alkyls having 1 to 4 carbon groups, phenyl, naphthyl, or mixtures thereof. Even more preferably, the three groups are halogenated, preferably fluorinated, aryl groups. A preferred neutral stoichiometric activator is tris perfluorophenyl boron or tris perfluoronaphthyl boron.

[00104] Ionic stoichiometric activator compounds may contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP 0 570 982 A; EP 0 520 732 A; EP 0 495 375 A; EP 0 500 944 B1; EP 0 277 003 A; EP 0 277 004 A; U.S. Patent Nos. 5,153,157; 5,198,401; 5,066,741; 5,206,197; 5,241,025; 5,384,299; 5,502,124; and U.S. Patent Application Serial No. 08/285,380, filed August 3, 1994; all of which are herein fully incorporated by reference.

[00105] Preferred compounds useful as an activator in the process of this invention comprise a cation, which is preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4 cation) which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases, such as ethers, amines, and the like. Two classes of useful compatible non-coordinating anions have been disclosed in EP 0 277,003 A1, and EP 0 277,004 A1: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core; and 2) anions comprising a plurality of boron atoms such as carboranes, metallacarboranes, and boranes.

[00106] In a preferred embodiment, the stoichiometric activators include a cation and an anion component, and are preferably represented by the following formula (1):



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 integer from 1 to 3.

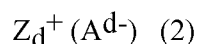
[00107] When Z is (L-H) such that the cation component is (L-H)_d⁺, the cation component may include Bronsted acids such as protonated Lewis bases capable of protonating a moiety, such as an alkyl or aryl, from the bulky ligand metallocene containing transition metal catalyst precursor, resulting in a cationic transition metal species. Preferably, the activating cation (L-H)_d⁺ is a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, preferably ammoniums of methylamine, aniline,

dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers, such as dimethyl ether diethyl ether, 5 tetrahydrofuran, and dioxane, sulfoniums from thioethers, such as diethyl thioethers and tetrahydrothiophene, and mixtures thereof.

[00108] When Z is a reducible Lewis acid it is preferably represented by the formula: (Ar_3C^+) , where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl, preferably the reducible Lewis acid is represented by the 10 formula: (Ph_3C^+) , where Ph is phenyl or phenyl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl. In a preferred embodiment, the reducible Lewis acid is triphenyl carbenium.

[00109] The anion component A^{d-} include 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 3, 4, 5 or 6; $n - k = d$; M is an element selected from 15 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 one occurrence is Q a halide, and two Q groups may form a ring structure. Preferably, 20 each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a pentafluoro aryl group. Examples of suitable A^{d-} components also include diboron compounds as disclosed in U.S. Patent No. 5,447,895, which is fully incorporated herein by reference.

[00110] In a preferred embodiment, this invention relates to a method to polymerize olefins 25 comprising contacting olefins (preferably ethylene) with metallocene catalyst compound described herein, a chain transfer agent and a boron containing NCA activator represented by the formula (2):



where: Z is (L-H) or a reducible Lewis acid; L is a neutral Lewis base (as further described 30 above); H is hydrogen; (L-H) is a Bronsted acid (as further described above); A^{d-} is a boron containing non-coordinating anion having the charge d^- (as further described above); d is 1, 2, or 3.

[00111] In a preferred embodiment in any NCA's represented by Formula 2 described above, the reducible Lewis acid is represented by the formula: (Ar_3C^+) , where Ar is aryl or 35 aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl, preferably the reducible Lewis acid is represented by the formula: (Ph_3C^+) , where Ph is phenyl or phenyl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl.

[00112] In a preferred embodiment in any of the NCA's represented by Formula 2 described above, Z_d^+ is represented by the formula: $(L-H)_d^+$, wherein L is a neutral Lewis base; H is hydrogen; (L-H) is a Bronsted acid; and d is 1, 2, or 3, preferably $(L-H)_d^+$ is a Bronsted acid selected from ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof.

5 **[00113]** In a preferred embodiment in any of the NCA's represented by Formula 2 described above, the anion component A^{d-} is represented by 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 boron; and Q^* is independently selected from hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and
10 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.

[00114] This invention also relates to a method to polymerize olefins comprising contacting olefins (such as ethylene) with a metallocene catalyst compound described herein, a chain transfer agent and an NCA activator represented by the formula (3):



where R is a monoanionic ligand; M^{**} is a Group 13 metal or metalloid; $ArNHal$ is a halogenated, nitrogen-containing aromatic ring, polycyclic aromatic ring, or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together; and n is 0, 1, 2, or 3. Typically the NCA comprising an anion of Formula 3 also
20 comprises a suitable cation that is essentially non-interfering with the ionic catalyst complexes formed with the transition metal compounds, preferably the cation is Z_d^+ as described above.

[00115] In a preferred embodiment in any of the NCA's comprising an anion represented by Formula 3 described above, R is selected from the group consisting of substituted or unsubstituted C_1 to C_{30} hydrocarbyl aliphatic or aromatic groups, where substituted means that
25 at least one hydrogen on a carbon atom is replaced with a hydrocarbyl, halide, halocarbyl, hydrocarbyl or halocarbyl substituted organometaloid, dialkylamido, alkoxy, aryloxy, alkylsulfido, arylsulfido, alkylphosphido, arylphosphide, or other anionic substituent; fluoride; bulky alkoxides, where bulky means C_4 to C_{20} hydrocarbyl groups; $--SR^1$, $--NR^2$, and $--PR^3$, where each R^1 , R^2 , or R^3 is independently a substituted or unsubstituted hydrocarbyl
30 as defined above; or a C_1 to C_{30} hydrocarbyl substituted organometaloid.

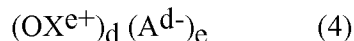
[00116] In a preferred embodiment in any of the NCA's comprising an anion represented by Formula 3 described above, the NCA also comprises cation comprising a reducible Lewis acid represented by the formula: (Ar_3C^+) , where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl, preferably the reducible Lewis
35 acid represented by the formula: (Ph_3C^+) , where Ph is phenyl or phenyl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl.

[00117] In a preferred embodiment in any of the NCA's comprising an anion represented by Formula 3 described above, the NCA also comprises a cation represented by the formula, (L-

$H)_d^+$, wherein L is a neutral Lewis base; H is hydrogen; (L-H) is a Bronsted acid; and d is 1, 2, or 3, preferably $(L-H)_d^+$ is a Bronsted acid selected from ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof.

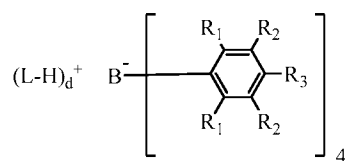
[00118] Further examples of useful activators include those disclosed in U.S. Patent Nos. 7,297,653 and 7,799,879.

[00119] Another activator useful herein comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula (4):



wherein OX^{e+} is a cationic oxidizing agent having a charge of $e+$; e is 1, 2, or 3; d is 1, 2 or 3; and A^{d-} is a non-coordinating anion having the charge of d- (as further described above). Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+ , or Pb^{+2} . Preferred embodiments of A^{d-} include tetrakis(pentafluorophenyl)borate.

[00120] In another embodiment, metallocene catalyst compounds described herein can be used with Bulky activators. A "Bulky activator" as used herein refers to anionic activators represented by the formula:



where:

each R_1 is, independently, a halide, preferably a fluoride;

each R_2 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_2 is a fluoride or a perfluorinated phenyl group);

each R_3 is a halide, 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_3 is a fluoride or a C_6 perfluorinated aromatic hydrocarbyl group); wherein R_2 and R_3 can form one or more saturated or unsaturated, substituted or unsubstituted rings (preferably R_2 and R_3 form a perfluorinated phenyl ring);

L is a neutral Lewis base; (L-H)⁺ is a Bronsted acid; d is 1, 2, or 3;

wherein the anion has a molecular weight of greater than 1020 g/mol; and

wherein at least three of the substituents on the B atom each have a molecular volume of greater than 250 cubic Å, alternately greater than 300 cubic Å, or alternately greater than 500 cubic Å.

[00121] "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.

[00122] 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, , Vol. 71, No. 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 the following table of relative volumes. For fused rings, the V_s is decreased by 7.5% per fused ring.

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

[00123] Exemplary bulky substituents of activators suitable herein and their respective scaled volumes and molecular volumes are shown in the table below. The dashed bonds indicate binding to boron, as in the general formula above.

Activator	Structure of boron substituents	Molecular Formula of each substituent	MV Per subst. (Å ³)	Total MV (Å ³)
Dimethylanilinium tetrakis(perfluoronaphthyl)borate		C ₁₀ F ₇	261	1044
Dimethylanilinium tetrakis(perfluorobiphenyl)borate		C ₁₂ F ₉	349	1396
[4-tButyl-PhNMe ₂ H] [(C ₆ F ₃ (C ₆ F ₅) ₂) ₄ B]		C ₁₈ F ₁₃	515	2060

[00124] Exemplary bulky activators useful in catalyst systems herein include: trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate, tri(t-butyl)ammonium

tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
 N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-
 trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium
 tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
 5 triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium
 tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
 trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium
 tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate, tri(n-
 butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(t-butyl)ammonium
 10 tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
 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, triethylsilylium
 15 tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, [4-t-
 butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B], and the types disclosed in U.S. Patent No. 7,297,653.

[00125] Illustrative, but not limiting, examples of boron compounds which may be used as an activator in the processes of this invention are:

trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate,
 20 tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, tri(t-
 butyl)ammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate, N,N-
 diethylanilinium tetraphenylborate, 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,
 tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium
 tetrakis(pentafluorophenyl)borate, N,N-diethylanilinium tetrakis(pentafluorophenyl)borate,
 30 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, benzene(diazonium) tetrakis(pentafluorophenyl)borate,
 trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, triethylammonium tetrakis-
 35 (2,3,4,6-tetrafluorophenyl)borate, tripropylammonium tetrakis-(2,3,4,6-
 tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate,
 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,
 triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylphosphonium tetrakis-
 (2,3,4,6-tetrafluorophenyl)borate, triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 5 benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trimethylammonium
 tetrakis(perfluoronaphthyl)borate, triethylammonium tetrakis(perfluoronaphthyl)borate,
 tripropylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium
 tetrakis(perfluoronaphthyl)borate, tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
 N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium
 10 tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)
 tetrakis(perfluoronaphthyl)borate, tropillium tetrakis(perfluoronaphthyl)borate,
 triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylphosphonium
 tetrakis(perfluoronaphthyl)borate, triethylsilylium tetrakis(perfluoronaphthyl)borate,
 benzene(diazonium) tetrakis(perfluoronaphthyl)borate, trimethylammonium
 15 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, N,N-diethylanilinium
 tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium)
 20 tetrakis(perfluorobiphenyl)borate, tropillium tetrakis(perfluorobiphenyl)borate,
 triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylphosphonium
 tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate,
 benzene(diazonium) tetrakis(perfluorobiphenyl)borate, trimethylammonium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, triethylammonium tetrakis(3,5-
 25 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, N,N-diethylanilinium tetrakis(3,5-
 30 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, triethylsilylium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, benzene(diazonium) tetrakis(3,5-
 35 bis(trifluoromethyl)phenyl)borate, and dialkyl ammonium salts, such as: di-(i-
 propyl)ammonium tetrakis(pentafluorophenyl)borate, and dicyclohexylammonium
 tetrakis(pentafluorophenyl)borate; and additional tri-substituted phosphonium salts, such as
 tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate, and tri(2,6-

dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate.

[00126] Preferred activators include N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, $[\text{Ph}_3\text{C}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$, $[\text{Me}_3\text{NH}^+][\text{B}(\text{C}_6\text{F}_5)_4^-]$; 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium; and tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine.

[00127] In a preferred embodiment, the activator comprises a triaryl carbonium (such as triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

[00128] In another embodiment, the activator comprises one or more of trialkylammonium tetrakis(pentafluorophenyl)borate, N,N-dialkylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate, trialkylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate, N,N-dialkylanilinium tetrakis(2,3,4,6-tetrafluorophenyl)borate, trialkylammonium tetrakis(perfluoronaphthyl)borate, N,N-dialkylanilinium tetrakis(perfluoronaphthyl)borate, trialkylammonium tetrakis(perfluorobiphenyl)borate, N,N-dialkylanilinium tetrakis(perfluorobiphenyl)borate, trialkylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, (where alkyl is methyl, ethyl, propyl, n-butyl, sec-butyl, or t-butyl).

[00129] In a particularly preferred embodiment, the activator used in combination with any catalyst compound(s) described herein is N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate.

[00130] In a preferred embodiment, any of the activators described herein may be mixed together before or after combination with the catalyst compound, preferably before being mixed with the catalyst compound.

[00131] In some embodiments two NCA activators may be used in the polymerization and the molar ratio of the first NCA activator to the second NCA activator can be any ratio. In some embodiments, the molar ratio of the first NCA activator to the second NCA activator is 0.01:1 to 10,000:1, preferably 0.1:1 to 1000:1, preferably 1:1 to 100:1.

[00132] Further, the typical activator-to-catalyst ratio, e.g., all NCA activators-to-catalyst ratio is 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.

[00133] It is also within the scope of this invention that the catalyst compounds can be combined with combinations of alumoxanes and NCA's (see for example, US 5,153,157, US 5,453,410, EP 0 573 120 B1, WO 94/07928, and WO 95/14044 which discuss the use of an alumoxane in combination with an ionizing activator).

Optional Scavengers or Co-Activators

[00134] In addition to the activator compounds, scavengers or co-activators may be used. Aluminum alkyl or organoaluminum compounds which may be utilized as scavengers or co-activators include, for example, trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like. Other oxophilic species such as diethyl zinc may be used.

Optional Support Materials

[00135] In embodiments herein, the catalyst system may comprise an inert support material. Preferably the supported material is a porous support material, for example, talc, and inorganic oxides. Other support materials include zeolites, clays, organoclays, or any other organic or inorganic support material and the like, or mixtures thereof.

[00136] Preferably, the support material is an inorganic oxide in a finely divided form. Suitable inorganic oxide materials for use in metallocene catalyst systems herein include Groups 2, 4, 13, and 14 metal oxides, such as silica, alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins, such as finely divided polyethylene. Particularly useful supports include magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania, and the like. Preferred support materials include Al_2O_3 , ZrO_2 , SiO_2 , and combinations thereof, more preferably SiO_2 , Al_2O_3 , or $\text{SiO}_2/\text{Al}_2\text{O}_3$.

[00137] It is preferred that the support material, most preferably an inorganic oxide, has a surface area in the range of from about 10 to about 700 m^2/g , pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 5 to about 500 μm . More preferably, the surface area of the support material is in the range of from about 50 to about 500 m^2/g , pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 10 to about 200 μm . Most preferably the surface area of the support material is in the range is from about 100 to about 400 m^2/g , pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 5 to about 100 μm . The average pore size of the support material useful in the invention is in the range of from 10 to 1000 Å, preferably 50 to about 500 Å, and most preferably 75 to about 350 Å. In some embodiments, the support

material is a high surface area, amorphous silica (surface area=300 m²/gm; pore volume of 1.65 cm³/gm). Preferred silicas are marketed under the tradenames of DAVISON 952 or DAVISON 955 by the Davison Chemical Division of W.R. Grace and Company. In other embodiments DAVISON 948 is used.

5 **[00138]** The support material should be dry, that is, free of absorbed water. Drying of the support material can be effected by heating or calcining at about 100°C to about 1000°C, preferably at least about 600°C. When the support material is silica, it is heated to at least 200°C, preferably about 200°C to about 850°C, and most preferably at about 600°C; and for a time of about 1 minute to about 100 hours, from about 12 hours to about 72 hours, or from
10 about 24 hours to about 60 hours. The calcined support material must have at least some reactive hydroxyl (OH) groups to produce supported catalyst systems of this invention. The calcined support material is then contacted with at least one polymerization catalyst comprising at least one metallocene compound and an activator.

[00139] The support material, having reactive surface groups, typically hydroxyl groups, is
15 slurried in a non-polar solvent and the resulting slurry is contacted with a solution of a metallocene compound and an activator. In some embodiments, the slurry of the support material is first contacted with the activator for a period of time in the range of from about 0.5 hours to about 24 hours, from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours. The solution of the metallocene compound is then contacted with the isolated
20 support/activator. In some embodiments, the supported catalyst system is generated in situ. In alternate embodiment, the slurry of the support material is first contacted with the catalyst compound for a period of time in the range of from about 0.5 hours to about 24 hours, from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours. The slurry of the supported metallocene compound is then contacted with the activator solution.

25 **[00140]** The mixture of the metallocene, activator and support is heated to about 0°C to about 70°C, preferably to about 23°C to about 60°C, preferably at room temperature. Contact times typically range from about 0.5 hours to about 24 hours, from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours.

[00141] Suitable non-polar solvents are materials in which all of the reactants used herein,
30 i.e., the activator, and the metallocene compound, are at least partially soluble and which are liquid at reaction temperatures. Preferred non-polar solvents are alkanes, such as isopentane, hexane, n-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as cyclohexane, aromatics, such as benzene, toluene, and ethylbenzene, may also be employed.

35 Polymerization Processes

[00142] In embodiments herein, the invention relates to polymerization processes where monomer (such as ethylene), and optionally comonomer, are contacted with a catalyst system comprising an activator and at least one metallocene 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.

[00143] Monomers useful herein include substituted or unsubstituted C₂ to C₄₀ alpha olefins, preferably C₂ to C₂₀ alpha olefins, preferably C₂ to C₁₂ alpha olefins, preferably ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In a preferred embodiment, the monomer comprises ethylene and an optional comonomers comprising one or more C₃ to C₄₀ olefins, preferably C₄ to C₂₀ olefins, or preferably C₆ to C₁₂ olefins. The C₃ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₃ to C₄₀ cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups.

[00144] In another preferred embodiment, the monomer comprises propylene and an optional comonomers comprising one or more of ethylene or 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 a particularly preferred embodiment of the invention, the monomer is propylene and no comonomer is present.

[00145] In another preferred embodiment, the monomer comprises 1-butene, or 1-pentene, or 1-hexene, or 1-heptene, or 1-octene, or 1-nonene, or 1-decene, or 1-undecene, or 1-dodecene, and the polymerization is a homopolymerization. Optionally, small amounts of ethylene may be added.

[00146] Exemplary C₂ to C₄₀ olefin monomers and optional comonomers include ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof, preferably hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, norbornene, norbornadiene, and their respective homologs and derivatives, preferably norbornene, norbornadiene, and dicyclopentadiene.

[00147] In a preferred 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.

[00148] Preferred diolefin monomers useful in this invention include any hydrocarbon structure, preferably C₄ to C₃₀, having at least two unsaturated bonds, wherein at least two of

the unsaturated bonds are readily incorporated into a polymer by either a stereospecific or a non-stereospecific catalyst(s). It is further preferred that the diolefin monomers be selected from alpha, omega-diene monomers (i.e. di-vinyl monomers). More preferably, the diolefin monomers are linear di-vinyl monomers, most preferably those containing from 4 to 30 carbon atoms. Examples of preferred 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, particularly preferred 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 low molecular weight polybutadienes (Mw less than 1000 g/mol). Preferred cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, ethylidene norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

[00149] In some embodiments, where butene is the comonomer, the butene source may be a mixed butene stream comprising various isomers of butene. The 1-butene monomers are expected to be preferentially consumed by the polymerization process. Use of such mixed butene streams will provide an economic benefit, as these mixed streams are often waste streams from refining processes, for example, C₄ raffinate streams, and can therefore be substantially less expensive than pure 1-butene.

[00150] Preferably the comonomer(s) are present in the copolymer at less than 50 mol%, preferably from 0.5 to 45 mol%, preferably from 1 to 30 mol%, preferably from 3 to 25 mol%, preferably from 5 to 20 mol%, preferably from 7 to 15 mol%, with the balance of the copolymer being made up of the main monomer (such as ethylene or propylene).

[00151] Polymerization processes of this invention can be carried out in any manner known in the art. Any suspension, homogeneous, bulk, solution, slurry, or gas phase 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 and slurry processes are preferred. (A homogeneous polymerization process is defined to be a process where at least 90 wt% of the product is soluble in the reaction media.) A bulk homogeneous process is particularly preferred. (A bulk process is defined to be a process where monomer concentration in all feeds to the reactor is 70 volume % or more.) 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). In another embodiment, the process is a slurry process. As used herein the term "slurry polymerization process" means a polymerization process where a supported catalyst is employed and monomers are polymerized on the supported catalyst particles. At least 95 wt% of polymer products derived from the supported catalyst are in granular form as solid particles

(not dissolved in the diluent).

[00152] 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™); perhalogenated hydrocarbons, such as perfluorinated C₄₋₁₀ alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In 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.

[00153] In a preferred embodiment, the feed concentration of the monomers and comonomers 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. Preferably the polymerization is run in a bulk process.

[00154] Preferred polymerizations can be run at any temperature and/or pressure suitable to obtain the desired polymers. 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 20 MPa, preferably from about 0.45 MPa to about 16 MPa, or preferably from about 0.5 MPa to about 12 MPa.

[00155] 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.

[00156] 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).

[00157] In an alternate embodiment, the activity of the catalyst is at least 50 g/mmol/hour, preferably 500 or more g/mmol/hour, preferably 5000 or more g/mmol/hr, preferably 50,000 or more g/mmol/hr, preferably 100,000 or more g/mmol/hr. 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.

[00158] In an embodiment of the invention, little or no alumoxane is used in the process to produce the polymers. Preferably, alumoxane is present at zero mol%, alternately the alumoxane is present at a molar ratio of aluminum to transition metal 500:1 or less, preferably 300:1 or less, preferably 100:1 or less.

[00159] In an embodiment of the invention, little or no scavenger is used in the process to produce the polymer. - The scavenger may be present at a molar ratio of scavenger metal to transition metal of less than 100:1, preferably less than 50:1, preferably less than 20:1, preferably less than 10:1.

[00160] In a preferred embodiment, the polymerization: 1) is conducted at temperatures of 0 to 300°C (preferably 25 to 150°C, preferably 40 to 120°C, preferably 45 to 80°C); 2) is conducted at a pressure of atmospheric pressure to 20 MPa (preferably 0.35 to 16 MPa, preferably from 0.45 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 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) or aromatic solvents such as toluene, benzene or xylenes; 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 500:1 or less, preferably 300:1 or less, preferably 100:1 or less,) the polymerization preferably occurs in one reaction zone; 6) the productivity of the catalyst compound is at least 80,000 g/mmol/hr (preferably at least 150,000 g/mmol/hr, preferably at least 200,000 g/mmol/hr, preferably at least 250,000 g/mmol/hr, preferably at least 300,000 g/mmol/hr); 7) optionally scavengers (such as trialkyl aluminum compounds) are absent (e.g. present at zero mol%, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, preferably less than 50:1, preferably less than 20:1, 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. 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. Room temperature is 23°C unless otherwise noted.

[00161] Other additives may also be used in the polymerization, as desired, such as one or more scavengers, promoters, modifiers, chain transfer agents (such as diethyl zinc), reducing agents, oxidizing agents, hydrogen, aluminum alkyls, or silanes.

5 [00162] In a preferred embodiment of the invention, higher reactor temperatures, such as 70 to 150°C and Bulky activators, such N,N-dimethylanilinium tetrakis (perfluoronaphthyl)borate are used.

[00163] In a preferred embodiment of the invention, the polymerization occurs in a supercritical or supersolution state.

10 [00164] 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.

[00165] 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.

[00166] A super solution polymerization or supersolution polymerization system is one where the polymerization occurs at a temperature of 65°C to 150°C and a pressure of between
20 250 to 5,000 psi (1.72 to 34.5 MPa), preferably the super solution polymerization polymerizes a C₂ 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 ethylene and 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
25 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
30 a temperature below the critical temperature of the polymerization system, or (2) at a pressure below the critical pressure of the polymerization system.

[00167] In a preferred embodiment of the invention, the polymerization process is conducted under homogeneous (such as solution, supersolution, or supercritical) conditions preferably including a temperature of about 60°C to about 200°C, preferably for 65°C to
35 195°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 conducted at a pressure in excess of 1.7 MPa, especially under supersolution 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 1500 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.

[00168] In a preferred embodiment of the invention, the polymerization process is conducted under supersolution 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.

[00169] 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 1500 MPa, preferably between 20 MPa and 140 MPa.

[00170] 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 2175 psi) to 1500 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.

[00171] 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 ethylene and 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.

[00172] 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.

[00173] 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.

[00174] 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.

[00175] In another embodiment, the polymerization system is preferably a homogeneous, single phase polymerization system, preferably a homogeneous dense fluid polymerization system.

[00176] 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.

[00177] 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.

[00178] 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.

[00179] 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 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.

[00180] In another embodiment, the polymerization process temperature is above the solid-fluid phase transition temperature of the polymer-containing fluid polymerization system at the 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 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 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.

Polyolefin Products

[00181] This invention also relates to compositions of matter produced by the methods described herein.

[00182] In a preferred embodiment of the invention, the process described herein produces propylene homopolymers or propylene copolymers, such as propylene-alphaolefin (preferably ethylene and or C₄ to C₂₀) copolymers (such as propylene-ethylene copolymers, propylene-hexene copolymers or propylene-octene copolymers) having: a Mw/Mn of greater than 1 to 4 (preferably greater than 1 to 3).

[00183] In a preferred embodiment of the invention, the process described herein produces ethylene homopolymers or ethylene copolymers, such as ethylene-alphaolefin (preferably C₃ to C₂₀) copolymers (such as ethylene-propylene copolymers, ethylene-hexene copolymers or ethylene-octene copolymers) having: a Mw/Mn of greater than 1 to 4 (preferably greater than 1 to 3).

[00184] In a preferred embodiment of the invention, the process described herein produces 1-decene, 1-octene, 1-hexene or 1-butene homopolymers having: a Mw/Mn of greater than 1 to 4 (preferably greater than 1 to 3).

[00185] In a preferred embodiment of the invention, the process described herein produces polymers or oligomers comprising 1-dodecene, 1-decene, 1-octene, 1-hexene and/or 1-butene wherein the polymers or oligomers have a Mw/Mn of greater than 1 to 4 (preferably greater than 1 to 3).

[00186] Generally, the process of this invention produces olefin polymers, preferably polyethylene and polypropylene homopolymers and copolymers. In a preferred embodiment,

the polymers produced herein are homopolymers of ethylene or propylene, are copolymers of ethylene preferably having from 0 to 25 mole% (alternately from 0.5 to 20 mole%, alternately from 1 to 15 mole%, preferably from 3 to 10 mole%) of one or more C₃ to C₂₀ olefin comonomer (preferably C₃ to C₁₂ alpha-olefin, preferably propylene, butene, hexene, octene, decene, dodecene, preferably propylene, butene, hexene, octene), or are copolymers of propylene preferably having from 0 to 25 mole% (alternately from 0.5 to 20 mole%, alternately from 1 to 15 mole%, preferably from 3 to 10 mole%) of one or more of C₂ or C₄ to C₂₀ olefin comonomer (preferably ethylene or C₄ to C₁₂ alpha-olefin, preferably ethylene, butene, hexene, octene, decene, dodecene, preferably ethylene, butene, hexene, octene).

10 **[00187]** In a preferred embodiment, the monomer is ethylene and the comonomer is hexene, preferably from 1 to 30 mole% hexene, alternately 1 to 20 mole%, alternatively 1 to 10 mole%.

[00188] In a preferred embodiment, the monomer is ethylene and the comonomer is octene, preferably from 1 to 30 mole% octene, alternately 1 to 20 mole%, alternatively 1 to 10 mole%.

15 **[00189]** In a preferred embodiment, the monomer is ethylene and the comonomer is decene, preferably from 1 to 30 mole% decene, alternately 1 to 20 mole%, alternatively 1 to 10 mole%.

[00190] In a preferred embodiment, the monomer is ethylene and the comonomer is propylene, preferably from 1 to 50 mole% propylene, alternately 5 to 45 mole%, alternately, 5 to 40 mole%, alternately 10 to 40 mole%, alternately 10 to 30 mole%, alternately 20 to 40 mole%. In a preferred embodiment, the ethylene-propylene copolymer contains greater than 20 50% vinyl unsaturation, alternately greater than 60% vinyl unsaturation, alternately greater than 70% vinyl unsaturation, alternately greater than 80% vinyl unsaturation, alternately greater than 90% vinyl unsaturation, alternately greater than 95% vinyl unsaturation.

[00191] In a preferred embodiment, the monomer is propylene and the comonomer is ethylene, preferably from 1 to 50 mole% ethylene, alternately 1 to 40 mole%, alternately 1 to 25 mole 20%, alternately 1 to 10 mole%. In a preferred embodiment, the propylene-ethylene copolymer contains greater than 50% vinyl unsaturation, alternately greater than 60% vinyl unsaturation, alternately greater than 70% vinyl unsaturation, alternately greater than 80% vinyl unsaturation, alternately greater than 90% vinyl unsaturation, alternately greater than 95% vinyl unsaturation.

30 **[00192]** In a preferred embodiment, the monomer is propylene and the comonomer is hexene, preferably from 0.1 to 50 mole% hexene, alternately 1 to 40 mole%, alternately 1 to 30 mole%, alternately 1 to 20 mol%, alternately 1 to 10 mol%, alternately 1 to 5 mol%. In a preferred embodiment, the propylene-hexene copolymer contains greater than 50% vinyl unsaturation, alternately greater than 60% vinyl unsaturation, alternately greater than 70% vinyl unsaturation, alternately greater than 80% vinyl unsaturation, alternately greater than 90% vinyl unsaturation, alternately greater than 95% vinyl unsaturation.

35 **[00193]** In a preferred embodiment, the monomer is propylene and the comonomer is octene, preferably from 0.1 to 50 mole% octene, alternately 1 to 40 mole%, alternately 1 to 30

mole%, alternately 1 to 20 mol%, alternately 1 to 10 mol%, alternately 1 to 5 mol%. In a preferred embodiment, the propylene-octene copolymer contains greater than 50% vinyl unsaturation, alternately greater than 60% vinyl unsaturation, alternately greater than 70% vinyl unsaturation, alternately greater than 80% vinyl unsaturation, alternately greater than 90% vinyl unsaturation, alternately greater than 95% vinyl unsaturation.

[00194] In a preferred embodiment, the monomer is propylene and the comonomer is decene, preferably from 0.1 to 50 mole% decene, alternately 1 to 40 mole%, alternately 1 to 30 mole%, alternately 1 to 20 mol%, alternately 1 to 10 mol%, alternately 1 to 5 mol%. In a preferred embodiment, the propylene-decene copolymer contains greater than 50% vinyl unsaturation, alternately greater than 60% vinyl unsaturation, alternately greater than 70% vinyl unsaturation, alternately greater than 80% vinyl unsaturation, alternately greater than 90% vinyl unsaturation, alternately greater than 95% vinyl unsaturation.

[00195] In a preferred embodiment, the monomer is propylene and no comonomer is present.

[00196] In a preferred embodiment, the monomer is propylene and no comonomer is present, and the polymer is isotactic.

[00197] In a preferred embodiment, the propylene homopolymer contains greater than 50% vinyl unsaturation, alternately greater than 60% vinyl unsaturation, alternately greater than 70% vinyl unsaturation, alternately greater than 80% vinyl unsaturation, alternately greater than 90% vinyl unsaturation, alternately greater than 95% vinyl unsaturation.

[00198] Typically, the polymers produced herein have an Mw of 3,000 to 3,000,000 g/mol (preferably 5,000 to 2,000,000 g/mol, preferably 10,000 to 1,000,000 g/mol, preferably 15,000 to 175,000 g/mol, preferably 15,000 to 100,000 g/mol, preferably 15,000 to 75,000 g/mol, preferably 15,000 to 50,000 g/mol), and/or an Mw/Mn 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).

[00199] In a preferred embodiment the polymer produced herein has a unimodal or multimodal molecular weight distribution (MWD=Mw/Mn) 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).

[00200] In a preferred embodiment the copolymers produced herein have a composition distribution breadth index (CDBI) of 50% or more, preferably 60% or more, preferably 70% or more. CDBI is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO 93/03093, published February 18, 1993, specifically columns 7 and 8 as well as in Wild et al, J. Poly. Sci., Poly. Phys. Ed., Vol. 20, p. 441 (1982) and U.S. Patent No. 5,008,204, including that fractions having a weight average molecular weight (Mw) below 10,000 g/mol are ignored

when determining CDBI.

[00201] 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 ^{13}C -NMR. Preferably isotactic polymers have at least 25% (preferably at least 50%, 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.

[00202] In an embodiment of the invention, the polymer produced herein has an mm triad tacticity index of 75% or greater (preferably 80% or greater, preferably 85% or greater, preferably 90% or greater, preferably 95% or greater, as determined by Carbon 13 NMR as described below.

[00203] In a preferred embodiment of the invention, the polymer produced herein is isotactic, and contains 2,1- or 1,3-regiodefects (1,3-regiodefects are also sometimes called 3,1-regiodefects, and the term regiodefect is also called regioerror). In some embodiments of the invention, regiodefects are desired and advantageous, and in particular 1,3-regiodefects are desired. Isotactic polymers with high levels of regiodefects have properties similar to propylene-ethylene copolymers containing low levels of ethylene. In some embodiments of the invention, the polymer produced herein has 20 to 300 total regiodefects/10,000 propylene units (defined as the sum of 2,1-erythro and 2,1-threo insertions, and 3,1-isomerizations as measured by ^{13}C -NMR) (preferably 30 to 200 total regiodefects/10,000 propylene units, preferably, 50 to 150 total regiodefects/10,000 propylene units).

[00204] In a preferred embodiment of the invention, the polymer produced herein is an ethylene- α -olefin copolymer, preferably an ethylene-propylene, an ethylene-butene, an ethylene-hexene, an ethylene-octene or an ethylene-decene copolymer, and the copolymer is blocky. A blocky copolymer is one in which the product of the reactivity ratios ($r_1 r_2$) is greater than 1. A copolymerization between monomers “E” and “P” in the presence of catalyst “M” can be represented by the following reaction schemes and rate equations where R_{11} is the rate of “E” insertion after “E”, R_{12} is the rate of “P” insertion after “E”, R_{21} is the rate of “E” insertion after “P”, R_{22} is the rate of “P” insertion after “P”, and k_{11} , k_{12} , k_{21} , and k_{22} are the corresponding rate constants for each. The reactions scheme and rate equations are illustrated below.



[00205] The reactivity ratios r_1 and r_2 are:

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

$$\Gamma_1 \Gamma_2 = \frac{k_{11} k_{22}}{k_{12} k_{21}}$$

[00206] The product of $r_1 \times r_2$ provides information on how the different monomers distribute themselves along the polymer chain. Below, are illustrations of alternating, random and blocky copolymers and how the product of $r_1 \times r_2$ relates to each:

$r_1 r_2 = 0$	alternating copolymerization	EPEPEPEPEPEPEPEPEPEPEP
$r_1 r_2 = 1$	random copolymerization	PPEPEPEPEPPPEEPEEEPE
$r_1 r_2 > 1$	blocky copolymerization	PPPPEEEEEEPPEESSSSSPP

5

¹³C-NMR Spectroscopy on Polyolefins

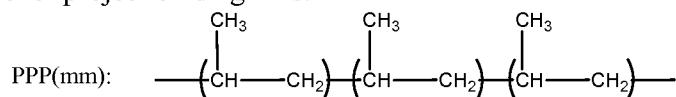
[00207] Polypropylene microstructure is determined by ^{13}C -NMR spectroscopy, including the concentration of isotactic and syndiotactic diads ([m] and [r]), triads ([mm] and [rr]), and pentads ([mmmm] and [rrrr]). The designation “m” or “r” describes the stereochemistry of pairs of contiguous propylene groups, “m” referring to meso and “r” to racemic. Samples are dissolved in d_2 -1,1,2,2-tetrachloroethane, and spectra recorded at 125°C using a 100 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, ^{13}C -NMR METHOD (Academic Press, New York, 1977).

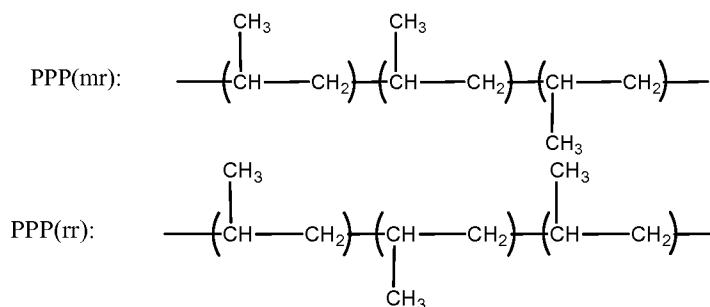
[00208] The “propylene tacticity index”, expressed herein as $[m/r]$, is calculated as defined in H.N. Cheng, *Macromolecules*, 17, p. 1950 (1984). When $[m/r]$ is 0 to less than 1.0, the polymer is generally described as syndiotactic, when $[m/r]$ is 1.0 the polymer is atactic, and when $[m/r]$ is greater than 1.0 the polymer is generally described as isotactic.

[00209] 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:

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

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:





[00210] The calculation of the mm Fraction of a propylene polymer is described in U.S. 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 ^{13}C -NMR spectrum, see 1) J. A. Ewen, CATALYTIC POLYMERIZATION OF OLEFINS: PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON FUTURE ASPECTS OF OLEFIN POLYMERIZATION, T. Keii and K. Soga, Eds. (Elsevier, 1986), pp. 271-292; and 2) U.S. Patent Application Publication No. US2004/054086 (paragraphs [0043] to [0054]).

[00211] Similarly m diads and r diads can be calculated as follows where mm, mr and rr are defined above.

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

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

[00212] ^{13}C NMR was used to determine monomer content and sequence distribution for the ethylene-propylene copolymers using the procedure from J.C. Randall's paper: Polymer Reviews, **1989**, 29:2, 201-317. The calculations of mole % C_3 , run number, average sequence length, and diad/triad distributions were all calculated per the method established in the above paper. Calculations for r_1r_2 were based on the equation $r_1r_2 = 4*[\text{EE}][\text{PP}]/[\text{EP}]^2$; where [EE], [EP], [PP] are the diad molar concentrations; E is ethylene, P is propylene. For other copolymers of ethylene, a similar methodology is used.

[00213] In another embodiment of the invention, the propylene polymers produced herein (preferably a homopolypropylene) have regiodefects (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, L. Cavallo, A. Fait, and F. Piemontesi, Chem. Rev. 2000, 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.

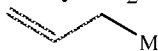
Regio defect	Chemical shift range (ppm)
2,1-erythro	42.3, 38.6, 36.0, 35.9, 31.5, 30.6, 17.6, 17.2
2,1-threo	43.4, 38.9, 35.6, 34.7, 32.5, 31.2, 15.4, 15.0
3,1 insertion	37.6, 30.9, 27.7

[00214] 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 10000 to determine the defect concentration per 10000 monomers.

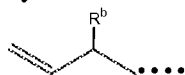
[00215] The polymers produced herein typically have at least 50% allyl chain ends or 3-alkyl chain ends (preferably at least 60%, at least 70%, at least 80%, at least 90%, at least 95%,
5 at least 98%, or at least 99% allyl chain ends and/or 3-alkyl chain ends).

[00216] An allyl chain end is represented by $\text{CH}_2\text{CH}=\text{CH}_2$, as shown in the formula:



where M represents the polymer chain. “Allylic vinyl group,” “allyl chain end,” “vinyl chain end,” “vinyl termination,” “allylic vinyl group,” and “vinyl terminated” are used
10 interchangeably in the following description. The number of allyl chain ends, vinylidene chain ends, vinylene chain ends, and other unsaturated chain ends is determined using ^1H NMR at 120°C using deuterated tetrachloroethane as the solvent on an at least 250 MHz NMR spectrometer, and in selected cases, confirmed by ^{13}C NMR. Resconi has reported proton and carbon assignments (neat perdeuterated tetrachloroethane used for proton spectra, while a
15 50:50 mixture of normal and perdeuterated tetrachloroethane was used for carbon spectra; all spectra were recorded at 100°C on a BRUKER spectrometer operating at 500 MHz for proton and 125 MHz for carbon) for vinyl terminated oligomers in *J. American Chemical Soc.*, 114, 1992, pp. 1025-1032 that are useful herein. Allyl chain ends are reported as a molar
20 percentage of the total number of moles of unsaturated groups (that is, the sum of allyl chain ends, vinylidene chain ends, vinylene chain ends, and the like).

[00217] A 3-alkyl chain end (where the alkyl is a C_1 to C_{38} alkyl), also referred to as a “3-alkyl vinyl end group” or a “3-alkyl vinyl termination”, is represented by the formula:



3-alkyl vinyl end group

where “...” represents the polyolefin chain and R^b is a C_1 to C_{38} alkyl group, or a C_1 to C_{20}
25 alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and the like. The amount of 3-alkyl chain ends is determined using ^{13}C NMR as set out below.

[00218] 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
30 be used) in a 5 mm probe using a Varian spectrometer with a ^1H frequency of 250 MHz, 400 MHz, or 500 MHz (for the purpose of the claims, a proton frequency of 500 MHz is used and the polymer sample is dissolved in 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2) and transferred into a 5 mm glass NMR tube). Data are recorded using a maximum pulse width of 45°C , 5 seconds between pulses and signal averaging 120 transients. Spectral signals are integrated and the number of
35 unsaturation types per 1000 carbons is calculated by multiplying the different groups by 1000

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

[00219] In a preferred embodiment of the invention, the polymer produced herein is an ethylene homopolymer, a propylene homopolymer, or a copolymer of ethylene and propylene, or a copolymer of ethylene and a C4 or higher α -olefin, or a copolymer of propylene and a C4 or higher α -olefin where in the copolymers comprises from 0.1 to 50 mol% comonomer) and having: 1) at least 50% allyl chain ends; and 2) an Mw of 5000 g/mol or more.

[00220] In a preferred embodiment of the invention, the polymer produced herein is a propylene homopolymer or copolymer (comprising from 0.1 to 50 mol% comonomer) having: 1) at least 50% allyl chain ends; and 2) an Mw of 5000 g/mol or more.

[00221] In a preferred embodiment of the invention, the polymer produced herein is a has a branching index (g'_{vis}) of 0.95 or less, preferably 0.90 or less, preferably 0.85 or less, preferably 0.80 or less, preferably 0.75 or less, preferably 0.70 or less, as determined by GPC, as described in the Examples section below.

[00222] In a preferred embodiment of the invention, the polymer produced herein (preferably an ethylene polymer or a propylene polymer) is a has a branching index (g'_{vis}) of 0.95 or less (preferably 0.90 or less, preferably 0.85 or less, preferably 0.80 or less, preferably 0.75 or less, preferably 0.70 or less, as determined by GPC), and has at least 50% allyl chain ends or 3-alkyl chain ends (preferably at least 60%, at least 70%, at least 80%, at least 90%, at least 95%, at least 98%, or at least 99% allyl chain ends or 3-alkyl chain ends), preferably having an Mw from 5,000 to 1,000,000 g/mol, alternately from 20,000 to 1,000,000 g/mol, alternately 100,000 to 800,000 g/mol, alternately 200,000 to 600,000 g/mol, alternately from 300,000 to 550,000 g/mol, alternately from 330,000 g/mol to 500,000 g/mol.

[00223] In another embodiment of the invention, the polymer produced herein is a octene polymer, e.g. having at least 50 mol% octene (preferably at least 60 mol%, at least 70 mol%, at least 80 mol%, at least 90 mol%, at least 95 mol%, at least 98 mol%, or at least 99 mol% octene). Preferred polyoctene polymers comprise up to 50 mol% C6 to C20 alphaolefins, preferably hexane, decene, and dodecene. Preferably the polyoctene has a kinematic viscosity at 100°C of 5 cSt or more (ASTM D 445), a viscosity index of 100 or more (ASTM D 2270), a pour point of -20°C or less (ASTM D 97), a specific gravity less than 0.86 (ASTM D 4052 (15.6/15.6°C)), and a flash point greater than 200°C (ASTM D 92).

[00224] In another embodiment of the invention, the polymer produced herein is a decene polymer, e.g. having at least 50 mol% decene (preferably at least 60 mol%, at least 70 mol%,

at least 80 mol%, at least 90 mol%, at least 95 mol%, at least 98 mol%, or at least 99 mol% decene). Preferred polydecene polymers comprise up to 50 mol% C8 to C20 alphaolefins, preferably octene and dodecene. Preferably the polydecene has a kinematic viscosity at 100°C of 5 cSt or more (ASTM D 445), a viscosity index of 100 or more (ASTM D 2270), a pour point of -20°C or less (ASTM D 97), a specific gravity less than 0.86 (ASTM D 4052 (15.6/15.6°C)), and a flash point greater than 200°C (ASTM D 92).

[00225] Alternately, the polydecene has a kinematic viscosity at 100°C of 4 cSt or more (preferably 6 cSt or more, preferably 8 cSt or more, preferably 10 cSt or more), a viscosity index of 100 or more (preferably 110 or more, preferably 120 or more, preferably 130 or more), a pour point of -15°C or less (preferably -20°C or less, preferably -25°C or less, preferably -30°C or less), a flash point of 200°C or more (preferably 220°C or more, preferably 240°C or more, preferably 260°C or more), and a specific gravity of 0.88 or less (preferably 0.87 or less, preferably 0.86 or less).

[00226] The polymers prepared herein may be functionalized by reacting a heteroatom containing group with the polymer with or without a catalyst. Examples include catalytic hydrosilylation, ozonolysis, hydroformylation, or hydroamination, sulfonation, halogenation, hydrohalogenation, hydroboration, epoxidation, or Diels-Alder reactions with polar dienes, Friedel-Crafts reactions with polar aromatics, maleation with activators such as free radical generators (e.g. peroxides). The functionalized polymers can be used in oil additives, as anti-fogging or wetting additives, adhesion promoters and many other applications. Preferred uses include additives for lubricants and or fuels. Preferred heteroatom containing groups include, amines, aldehydes, alcohols, acids, anhydrides, sulphonates, particularly succinic acid, maleic acid and maleic anhydride.

[00227] Other uses of the functionalized polymers include as plasticizers, surfactants for soaps, detergents, fabric softeners, antistatics, etc. Preferred heteroatom containing groups include, amines, aldehydes, alcohols, acids, anhydrides, and sulphonates, particularly succinic acid, maleic acid and maleic anhydride.

[00228] In some embodiments the polymers produced herein are functionalized as described in U.S. Patent No. 6,022,929; A. Toyota, T. Tsutsui, and N. Kashiwa, Polymer Bulletin 48, 213-219, 2002; and J. Am. Chem. Soc., 1990, 112, 7433-7434.

Blends

[00229] In another embodiment, the polymer (preferably the polyethylene or polypropylene) produced herein is combined with one or more additional polymers prior to being formed into a film, molded part or other article. Other useful polymers include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene, polybutene, ethylene vinyl acetate, LDPE, LLDPE, HDPE, ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free

radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and/or polyisobutylene.

[00230] In a preferred embodiment, the polymer (preferably the polyethylene or polypropylene) 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%.

[00231] 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.

[00232] 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 IRGANOXTM 1010 or IRGANOXTM 1076 available from Ciba-Geigy); phosphites (e.g., IRGAFOSTM 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.

Films

[00233] Any of the foregoing polymers, including 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 process 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.

[00234] 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.

[00235] 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.

Molded Products

[00236] The polymers described herein (preferably propylene polymers) and blends thereof may also be used to prepare molded products in any molding process, including but not limited to, injection molding, gas-assisted injection molding, extrusion blow molding, injection blow molding, injection stretch blow molding, compression molding, rotational molding, foam molding, thermoforming, sheet extrusion, and profile extrusion. The molding processes are well known to those of ordinary skill in the art.

[00237] Further, the polymers described herein (preferably propylene polymers) may be shaped into desirable end use articles by any suitable means known in the art. Thermoforming, vacuum forming, blow molding, rotational molding, slush molding, transfer molding, wet lay-up or contact molding, cast molding, cold forming matched-die molding, injection molding, spray techniques, profile co-extrusion, or combinations thereof are typically used methods.

[00238] Thermoforming is a process of forming at least one pliable plastic sheet into a desired shape. Typically, an extrudate film of the composition of this invention (and any other layers or materials) is placed on a shuttle rack to hold it during heating. The shuttle rack

indexes into the oven which pre-heats the film before forming. Once the film is heated, the shuttle rack indexes back to the forming tool. The film is then vacuumed onto the forming tool to hold it in place and the forming tool is closed. The tool stays closed to cool the film and the tool is then opened. The shaped laminate is then removed from the tool. The thermoforming is accomplished by vacuum, positive air pressure, plug-assisted vacuum forming, or combinations and variations of these, once the sheet of material reaches thermoforming temperatures, typically of from 140°C to 185°C or higher. A pre-stretched bubble step is used, especially on large parts, to improve material distribution.

[00239] Blow molding is another suitable forming means for use with the compositions of this invention, which includes injection blow molding, multi-layer blow molding, extrusion blow molding, and stretch blow molding, and is especially suitable for substantially closed or hollow objects, such as, for example, gas tanks and other fluid containers. Blow molding is described in more detail in, for example, CONCISE ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING, pp. 90-92 (Jacqueline I. Kroschwitz, ed., John Wiley & Sons 1990).

[00240] Likewise, molded articles may be fabricated by injecting molten polymer into a mold that shapes and solidifies the molten polymer into desirable geometry and thickness of molded articles. Sheets may be made either by extruding a substantially flat profile from a die, onto a chill roll, or alternatively by calendaring. Sheets are generally considered to have a thickness of from 10 mils to 100 mils (254 μm to 2540 μm), although any given sheet may be substantially thicker.

Non-Wovens and Fibers

[00241] The polymers produced herein may also be used to prepare nonwoven fabrics and fibers in any nonwoven fabric and fiber making process, including but not limited to, melt blowing, spunbonding, film aperturing, and staple fiber carding. A continuous filament process may also be used. Preferably a spunbonding process is used. The spunbonding process is well known in the art. Generally it involves the extrusion of fibers through a spinneret. These fibers are then drawn using high velocity air and laid on an endless belt. A calender roll is generally then used to heat the web and bond the fibers to one another although other techniques may be used such as sonic bonding and adhesive bonding.

Experimental

Gel Permeation Chromatography

[00242] M_w , M_n , M_z , number of carbon atoms and g'_{vis} are determined by using a High Temperature Size Exclusion Chromatograph (either from Waters Corporation or Polymer Laboratories), equipped with three in-line detectors, a differential refractive index detector (DRI), a light scattering (LS) detector, and a viscometer. Experimental details, including detector calibration, are described in: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, Macromolecules, Volume 34, Number 19, 6812-6820, (2001) and references therein. Three Polymer Laboratories PLgel 10mm Mixed-B LS columns are used. The nominal flow rate is

0.5 cm³/min, and the nominal injection volume is 300 µL. The various transfer lines, columns and differential refractometer (the DRI detector) are contained in an oven maintained at 145°C. Solvent for the experiment is prepared by dissolving 6 grams of butylated hydroxy toluene as an antioxidant in 4 liters of Aldrich reagent grade 1, 2, 4 trichlorobenzene (TCB). The TCB mixture is then filtered through a 0.7 µm glass pre-filter and subsequently through a 0.1 µm Teflon filter. The TCB is then degassed with an online degasser before entering the Size Exclusion Chromatograph. Polymer solutions are prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160°C with continuous agitation for about 2 hours. All quantities are measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/ml at room temperature and 1.324 g/ml at 145°C. The injection concentration is from 0.75 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples. Prior to running each sample the DRI detector and the injector are purged. Flow rate in the apparatus is then increased to 0.5 ml/minute, and the DRI is allowed to stabilize for 8 to 9 hours before injecting the first sample. The LS laser is turned on 1 to 1.5 hours before running the samples. The concentration, *c*, at each point in the chromatogram is calculated from the baseline-subtracted DRI signal, *I*_{DRI}, using the following equation:

$$c = K_{DRI} I_{DRI} / (dn/dc)$$

where *K*_{DRI} is a constant determined by calibrating the DRI, and (dn/dc) is the refractive index increment for the system. The refractive index, *n* = 1.500 for TCB at 145°C and *λ* = 690 nm. For purposes of this invention and the claims thereto (dn/dc) = 0.104 for propylene polymers, 0.098 for butene polymers and 0.1 otherwise. Units on parameters throughout this description of the SEC method are such that concentration is expressed in g/cm³, molecular weight is expressed in g/mole, and intrinsic viscosity is expressed in dL/g.

[00243] The LS detector is a Wyatt Technology High Temperature mini-DAWN. The molecular weight, *M*, at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M.B. Huglin, LIGHT SCATTERING FROM POLYMER SOLUTIONS, Academic Press, 1971):

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

[00244] Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , *c* is the polymer concentration determined from the DRI analysis, *A*₂ is the second virial coefficient [for purposes of this invention, *A*₂ = 0.0006 for propylene polymers, 0.0015 for butene polymers and 0.001 otherwise], (dn/dc) = 0.104 for propylene polymers, 0.098 for butene polymers and 0.1 otherwise, *P*(θ) is the form factor for a monodisperse random coil, and *K*_o is the optical constant for the system:

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

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system. The refractive index, $n = 1.500$ for TCB at 145°C and $\lambda = 690\text{ nm}$.

[00245] A high temperature 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 following equation:

$$\eta_s = c[\eta] + 0.3(c[\eta])^2$$

where c is concentration and was determined from the DRI output.

[00246] The branching index (g'_{vis}) is calculated using the output of the SEC-DRI-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{\text{avg}}$, of the sample is calculated by:

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

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

$$g'_{\text{vis}} = \frac{[\eta]_{\text{avg}}}{kM_v^\alpha}$$

where, for purpose of this invention and claims thereto, $\alpha = 0.695$ and $k = 0.000579$ for linear ethylene polymers, $\alpha = 0.705$ $k = 0.000262$ for linear propylene polymers, and $\alpha = 0.695$ and $k = 0.000181$ for linear butene polymers. M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis.

EXAMPLES

Starting materials

[00247] All manipulations with air and moisture sensitive compounds were performed either in an atmosphere of thoroughly purified argon using standard Schlenk techniques or in a controlled atmosphere glove box (Vacuum Atmospheres Co.). Tetrahydrofuran (THF, Merck = Merck KGaA, Darmstadt, Germany) and diethyl ether (Merck) for synthesis were purified by distillation over LiAlH_4 , and stored over sodium benzophenone ketyl under an inert atmosphere; prior to use, the solvents were distilled from the benzophenone ketyl. Hydrocarbon solvents such as benzene (Merck), toluene (Merck), *p*-xylene (Merck), and hexanes (Merck) were typically distilled over CaH_2 , and were stored over Na/K alloy under an inert atmosphere; prior to use, the solvents were distilled from the Na/K alloy. Methylene chloride (and CCl_2D_2 for NMR measurements) was distilled and stored over CaH_2 under an inert atmosphere; prior to use, the solvent was distilled from the CaH_2 . Celite (Aldrich) was dried in a vacuum oven at 180°C . *p*-Toluenesulfonic acid (TsOH, Aldrich), 2.5 M $n\text{-BuLi}$ in

hexanes (Chemetall GmbH), MeMgBr in ether (Aldrich), ethylmagnesium bromide in THF (Aldrich), isopropylmagnesium bromide in THF (Aldrich), tert-butylmagnesium chloride in THF (Aldrich), HfCl₄ and HfCl₄(THF)₂ (Strem), bis(dibenzylideneacetone)palladium(0) (pd(dba)₂, Strem), P^tBu₃ (Strem), Na₂SO₄ (Akzo Nobel), nickel (II) acetylacetonate (Merck), azobisisobutyronitrile (AIBN, Merck), P₄O₁₀ (Merck), anhydrous ethanol (Merck), 96% ethanol (Merck), methanol (Merck), sodium lump (Merck), ZnCl₂ (Merck), diethyl malonate (Acros), lithium tert-butoxide (Acros), 2-bromotoluene (Acros), 3-chloropropanoyl chloride (Acros), potassium hydroxide (Merck), thionyl chloride (Merck), AlCl₃ (Merck), 12 M HCl (diluted as needed; Reachim, Moscow, Russia), 96% H₂SO₄ (Reachim), ethyl acetate (Merck), ethyl bromide (Acros Organics), NH₄Cl (Merck), NaBH₄ (Aldrich), anhydrous K₂CO₃ (Merck), MgSO₄ (Merck), CuCN (Merck), N-bromosuccinimide (Alfa Aesar), 2-bromobenzyl bromide (Aldrich), 2-bromo-2-methylpropionyl bromide (Aldrich), 1,3-dicyclohexylimidazolium tetrafluoroborate (Aldrich), methylcyclohexane (Merck), hydrazine hydrate (Merck), silica gel 60 (40-63 μm; Merck), NaHCO₃ (Merck), carbon tetrachloride (Reakhim, Moscow, Russia), 85% orthophosphoric acid (Reachim), and CDCl₃ (Deutero GmbH) were used as received. Cyclopropylmagnesium bromide (^cPrMgBr) was obtained from cyclopropylbromide (Aldrich), and magnesium turnings (Acros) in THF.

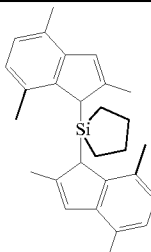
[00248] 2,4,7-Trimethylindene was obtained as described in [Kaminsky, W.; Rabe, O.; Schauwienold, A.-M.; Schupfner, G. U.; Hanss, J.; Kopf, J. J. *Organomet. Chem.*, **1995**, 497, 181–194]. Diethyl (2-bromobenzyl)malonate was obtained from sodium salt of diethyl malonate and 2-bromobenzylbromide as described for diethyl (2-bromobenzyl)methylmalonate in [Izmer, V. V.; Lebedev, A. Y.; Nikulin, M. V.; Ryabov, A. N.; Asachenko, A. F.; Lygin, A. V.; Sorokin, D. A.; Voskoboynikov, A. Z. *Organometallics*, **2006**, 25, 1217–1229]. 1,1-Dichlorosilolane, 1,1-dichlorosilane and 1,1-dichlorosilene were obtained as described in [West, R. J. *Am. Chem. Soc.*, **1954**, 76, 6015–6017] and [Denmark, S. E.; Griedel, B. D.; Coe, D. M.; Schnute, M. E., *J. Am. Chem. Soc.*, **1994**, 116, 7026–7043], respectively. 7-Bromo-2-methyl-1*H*-indene (4/7-bromo-2-methyl-1*H*-indene) was obtained as described in [Izmer, V. V.; Lebedev, A. Y.; Nikulin, M. V.; Ryabov, A. N.; Asachenko, A. F.; Lygin, A. V.; Sorokin, D. A.; Voskoboynikov, A. Z. *Organometallics*, **2006**, 1217].

[00249] Analytical and semi-preparative liquid chromatography was performed using a Waters Delta 600 HPLC system including a 996 Photodiode Array Detector, Nova-Pack C18 or HR Silica (60A, 6 μm, 3.9 and 19 x 300 mm) and Symmetry C18 (5 μm, 4.6 x 250 mm) columns. MPLC (Medium Pressure Liquid Chromatography, pressure 5-15 bars) was performed using MPLC glass columns and fittings (Ace Glass), a PD5130 pump drive equipped with a J1 gear-well pump head (Heidolph), a 996 Photodiode Array Detector and a Fraction Collector II (Waters Corp.). ¹H and ¹³C spectra were recorded with a Bruker Avance-400 spectrometer. Chemical shifts for ¹H and ¹³C were measured relative to tetramethylsilane (TMS). ¹H NMR spectral assignments were made on the basis of double

resonance and Nuclear Overhauser Effect (NOE) experiments. CHN microanalyses were done using a CHN-O-Rapid analyzer (Heraecus Ltd., Banau, Germany).

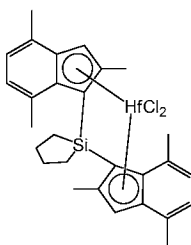
Example 1: Synthesis of 1,1-Silolanediyl-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride otherwise named cyclotetramethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride (1)

1,1-Bis(2,4,7-trimethyl-1*H*-inden-1-yl)silolane



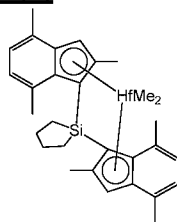
[00250] To a solution of 39.6 g (0.25 mol) of 2,4,7-trimethylindene in 350 ml of ether, 100 ml (0.25 mol) of 2.5 M ⁿBuLi in hexanes was slowly added. The resulting suspension was stirred for 30 min at room temperature, and then 50 ml of THF was added that resulted in dissolution of the precipitate. The resulting mixture was stirred for 1 h, then cooled to -60°C, and 1.12 g (12.5 mmol) of CuCN was added. The formed mixture was stirred 40 min at room temperature, and then 19.4 g (0.125 mmol) of 1,1-dichlorosilolane was added in one portion. This mixture was stirred at room temperature overnight, then 200 ml of cold water was added. The organic layer was separated. The aqueous layer was extracted with 2 x 50 ml of dichloromethane. The combined organic extract was washed by 3 x 100 ml of water, dried over Na₂SO₄, and evaporated to dryness. The starting indene was distilled off using Kugelrohr apparatus. Crude product was purified using flash chromatography on silica gel 60 (40-63 μm; eluent: hexanes-dichloromethane = 10:1, vol.). Yield 46.1 g (92%) of yellowish oil of a ca. 4 to 3 mixture of *rac*- and *meso*-compounds. Calcd. for C₂₈H₃₄Si: C, 84.36; H, 8.60. Found: C, 84.59; H, 8.85. ¹H NMR (CDCl₃): *meso*-product, δ 6.89 (d, J = 7.5 Hz, 2H, 5-H in indenyl), 6.78 (d, J = 7.5 Hz, 2H, 6-H in indenyl), 6.58 (s, 2H, 3-H in indenyl), 3.38 (s, 2H, 1-H in indenyl), 2.37 (s, 6H, 7-Me in indenyl), 2.35 (s, 6H, 4-Me in indenyl), 1.89 (s, 6H, 2-Me in indenyl), 1.15 (m, 2H, 2,2'-H in silacyclopentane), 0.89 (m, 2H, m, 2H, 5,5'-H in silacyclopentane), 0.55 (m, 2H, m, 2H, 3,3'-H in silacyclopentane), 0.27 (m, 2H, m, 2H, 4,4'-H in silacyclopentane); *rac*-product, δ 6.87 (d, J = 7.5 Hz, 2H, 5-H in indenyl), 6.75 (d, J = 7.5 Hz, 2H, 6-H in indenyl), 6.64 (s, 2H, 3-H in indenyl), 3.45 (s, 2H, 1-H in indenyl), 2.34 (s, 6H, 7-Me in indenyl), 2.32 (s, 6H, 4-Me in indenyl), 2.14 (s, 6H, 2-Me in indenyl), 1.03 (m, 2H, m, 2H, 2,5-H in silacyclopentane), 0.69 (m, 2H, m, 2H, 2',5'-H in silacyclopentane), 0.52 (m, 4H, m, 2H, 3,3',4,4'-H in silacyclopentane).

1,1-Silolanediyl-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride otherwise named cyclotetramethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride (1)



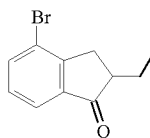
[00251] To a solution of 19.9 g (50 mmol) of the above-obtained bridging ligand in 350 ml of ether, 40.0 ml (100 mmol) of 2.5 M ⁿBuLi in hexanes was slowly added. This mixture was stirred for 12 h at room temperature, then cooled to -50°C, and 23.2 g (50 mmol) of HfCl₄(THF)₂ was added. The resulting mixture was stirred for 12 h at room temperature. The formed yellow precipitate was filtered off on glass frit (G3), washed by 100 ml of ether, and dried in vacuum. This procedure gave 28.5 g of a mixture of *rac*- and *meso*-hafnocene dichlorides as well as LiCl. ¹H NMR (CD₂Cl₂): δ 6.96 (m), 6.74-6.80 (m), 6.59 (m), 2.70 (s), 2.63 (s), 2.60 (s), 2, 2.27 (s), 2.06 (m), 1.90-1.98 (m), 1.58-1.66 (m).

10 **Example 2: Synthesis of *rac*-1,1-Silolanediyl-bis(2,4,7-trimethylinden-1-yl)dimethylhafnium otherwise named *rac*-cyclotetramethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dimethyl (2)**

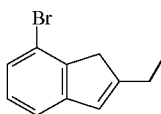


[00252] To a suspension of 18.2 g (28.2 mmol) of the above-obtained mixture of *rac*-, *meso*-hafnocenes and LiCl (1, from example 1) in 250 ml of THF, 35 ml (107 mmol) of 3.05 M MeMgBr in ether was added. This mixture was stirred overnight at 60°C and then evaporated to dryness. The residue was treated with 250 ml of hot toluene, then toluene was stripped off in vacuum. The formed products were extracted from the residue using 300 ml of hot methylcyclohexane. Crystals precipitated from this extract at -30°C were collected, and the mother liquor was used again for extraction of the products. This procedure was repeated until no solid material precipitated from the extract at -30°C. The combined precipitate was washed by 2 x 40 ml of THF and then dried in vacuum. This procedure gave 10.2 g (60%) of pure *rac*-zirconocene dimethyl complex. Calcd. for C₃₀H₃₈HfSi: C, 59.54; H, 6.33. Found: C, 59.45; H, 6.24. ¹H NMR (C₆D₆): δ 6.91 (dd, J = 6.8 Hz, J = 1.0 Hz, 2H, 5-H in indenyl), 6.70 (d, J = 6.8 Hz, 2H, 6-H in indenyl), 6.68 (m, 2H, 3-H in indenyl), 2.46 (s, 6H, 7-Me in indenyl), 2.30 (s, 6H, 4-Me in indenyl), 1.98 (s, 6H, 2-Me in indenyl), 1.93-2.01 (m, 4H, 3,3',4,4'-H in silacyclopentane), 1.67-1.77 (m, 2H, 2,5-H in silacyclopentane), 1.23-1.33 (m, 2H, 2',5'-H in silacyclopentane), -1.00 (s, 6H, HfMe₂).

30 **Example 3: Synthesis of *rac*-1,1-Silolanediyl-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride otherwise named *rac*-cyclotetramethylenesilylenen-bis(2-ethyl-4-methylinden-**

1-yl)hafnium dichloride (3)**4-Bromo-2-ethylindan-1-one**

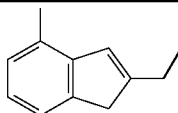
[00253] To a solution of sodium ethoxide prepared from 30.4 g (1.32 mol) of sodium metal and 830 ml of dry ethanol, 364 g (1.10 mol) of diethyl (2-bromobenzyl)malonate was added. This solution was stirred for 10 min, and then 98.5 ml (1.32 mol) of bromoethane was added in small portions by vigorous stirring for 15 min. The obtained mixture was refluxed for 4 h, and then a solution of 185 g (3.30 mol) of KOH in 450 ml of water was added. This mixture was refluxed for 4 h, and then ethanol was distilled off under atmospheric pressure. The resulting solution was extracted with diethyl ether, then the aqueous layer was acidified by 12 M HCl to pH 1-2 and then extracted with 3 x 300 ml of ethyl acetate. The combined organic extract was washed with 2 x 100 ml of water, dried over Na₂SO₄, and then evaporated to dryness. The resulting oil was decarboxylated at 160-200°C. Further on, 280 ml (3.85 mol) of thionyl chloride was added, and the resulting mixture was stirred overnight at room temperature. An excess of thionyl chloride was distilled off at atmospheric pressure, and the residue was distilled in vacuum to give 216 g of the respective acid chloride, b.p. 102-125°C/4 mbar. To a stirred suspension of 130 g (975 mmol) of AlCl₃ in 500 ml of dichloromethane, a solution of 216 g (780 mmol) of 2-(2-bromobenzyl)butanoyl chloride in 100 ml of dichloromethane was added dropwise at -10°C. The resulting mixture was stirred overnight at room temperature and then poured into 2000 g of ice. The organic layer was separated, the aqueous layer was extracted with 2 x 200 ml of dichloromethane. The combined organic extract was washed with aqueous NaHCO₃, water, dried over Na₂SO₄, and then evaporated to dryness. The residue was distilled in vacuum to give 158 g (60%) of colorless oil which solidified upon standing at room temperature, b.p. 126°C/1 mm Hg. Calcd. for C₁₁H₁₁BrO: C, 55.25; H, 4.64. Found: C, 55.03; H, 4.90. ¹H NMR (CDCl₃): δ 7.70 (d, J=7.8 Hz, 1H), 7.64 (d, J=7.6 Hz, 1H), 7.22 (m, 1H), 3.22 (dd, J=17.6 Hz, J=7.9 Hz, 1H), 2.70 (dd, J=17.6 Hz, J=3.9 Hz, 1H), 2.61 (m, 1H), 1.89-1.99 (m, 1H), 1.47-1.58 (m, 1H), 0.99 (t, J=7.3 Hz, 3H).

7-Bromo-2-ethyl-1H-indene (also called 2-ethyl-4/7-bromoindene)

[00254] To a solution of 195 g (816 mmol) of 4-bromo-2-ethylindan-1-one in 800 ml THF, 37.2 g (980 mmol) of NaBH₄ was added at 0°C, and then 450 ml of MeOH was added dropwise at 0°C. The resulting mixture was additionally stirred for 1 h and then evaporated to dryness. The residue was poured into 1000 ml of hot water, the formed mixture was cooled to room temperature, and crude product was extracted with 3 x 300 ml of dichloromethane. The

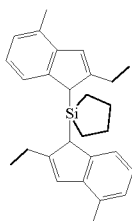
organic layer was separated, dried over Na_2SO_4 and then evaporated to dryness. To a solution of the residue in 800 ml of toluene 0.8 g of TsOH was added, and the formed mixture was refluxed until the reaction was complete (TLC). After that the reaction mixture was passed through a pad of silica gel 60 (40-63 μm) and evaporated to dryness. Yield 180 g (98%) of colorless liquid. Calcd. for $\text{C}_{11}\text{H}_{11}\text{Br}$: C, 59.22; H, 4.97. Found: C, 59.53; H, 5.20. ^1H NMR (CDCl_3): δ 7.19-7.25 (m, 2H), 7.09-7.12 (m, 1H), 6.53 (m, 1H), 3.31 (s, 2H), 2.53 (q, $J=7.5$ Hz, 2H), 1.24 (t, $J=7.5$ Hz, 3H).

2-Ethyl-4/7-methyl-1H-indene



[00255] To a mixture of 30.0 g (0.132 mol) of 2-ethyl-4/7-bromoindene, 1.53 g (2.64 mmol) of $\text{Pd}(\text{dba})_2$, and 1.00 g (5.28 mmol) of $t\text{Bu}_3\text{P}$ in 700 ml of THF, 66.0 ml (0.198 mol) of 3.05 M methylmagnesium bromide in THF was added dropwise at room temperature. This mixture was stirred overnight at 60°C , cooled to room temperature, and then 150 ml of saturated aqueous NH_4Cl was added. Further on, THF was evaporated in vacuum, and crude product was extracted with 3 x 200 ml of ethyl acetate. The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The product was isolated by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexane). Yield 20.9 g (99%) of colorless oil of a mixture of two isomeric indenenes. Calcd. for $\text{C}_{12}\text{H}_{14}$: C, 91.08; H, 8.92. Found: C, 91.23; H, 8.80. ^1H NMR (CDCl_3): δ 7.14-7.19 (m, 2H), 6.95 (m, 1H), 6.54 (m, 1H), 3.24 (s, 2H), 2.55 (q, $J=7.6$ Hz, 2H), 2.36 (s, 3H), 1.26 (t, $J=7.6$ Hz, 3H).

1,1-Bis(2-ethyl-4-methyl-1H-inden-1-yl)silolane

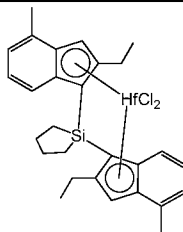


[00256] To a solution of 7.00 g (44.0 mmol) of 2-ethyl-4/7-methyl-1H-indene in 250 ml of ether cooled to 0°C , 17.6 ml (44.0 mmol) of 2.5 M $n\text{BuLi}$ in hexanes was added. The resulting mixture was stirred overnight at room temperature. Further on, 50 ml of THF was added, the obtained mixture was cooled to -60°C , and 0.394 g (4.40 mmol) of CuCN was added. This mixture was allowed to warm to -30°C , stirred for 2 h at this temperature, then cooled to -60°C , and 2.91 ml (22.0 mmol) of 1,1-dichlorosilolane was added. The resulting mixture was stirred for 12 h at room temperature, then 20 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 50 ml of ethyl acetate. The combined organic extract was dried over MgSO_4 and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexanes). Yield 6.80 g (78%) of

yellow glassy solid of a ca. 1 to 1 mixture of *rac*- and *meso*-compounds.

Calcd. for C₂₈H₃₄Si: C, 84.36; H, 8.60. Found: C, 84.53; H, 8.72. ¹H NMR (CDCl₃): δ 6.96-7.11 (m), 6.66 (s), 6.53 (s), 3.43 (s), 3.40 (s), 2.44-2.60 (m), 2.41 (s), 2.40 (s), 2.16-2.33 (m), 1.05-1.33 (m), 0.85-0.92 (m), 0.50-0.71 (m), 0.31 (m).

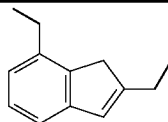
5 **rac-1,1-Silolanediyl-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride otherwise named rac-cyclotetramethylenesilylenen-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride (3)**



[00257] To a solution of 3.40 g (8.00 mmol) of 1,1-bis(2-ethyl-4-methyl-1*H*-inden-1-yl)silane in 100 ml of ether cooled to 0°C, 6.80 ml (16.0 mmol) of 2.5 M ^{*n*}BuLi in hexanes was added. The resulting mixture was stirred for 12 h at room temperature, then cooled to -70°C, and 3.96 g (8.00 mmol) of HfCl₄(THF)₂ was added. The obtained mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was dissolved in 50 ml of toluene, and this solution was heated to 80°C and then filtered through a Celite pad. The filtrate was left for crystallization. The resulting precipitate was additionally (3 times) re-crystallized from toluene. This procedure gave 1.05 g (20%) of pure *rac*-complex as yellow crystalline solid. Calcd. for C₂₈H₃₂Cl₂HfSi: C, 52.06; H, 4.99. Found: C, 52.10; H, 5.12. ¹H NMR (CD₂Cl₂): δ 7.46 (d, J= 8.5 Hz, 2H), 7.05 (d, J= 6.4 Hz, 2H), 6.89 (dd, J= 8.5 Hz, J= 6.4 Hz, 2H), 6.67 (s, 2H), 2.78 (m, 2H), 2.38 (m, 2H), 2.32 (s, 6H), 2.16 (m, 2H), 1.95 (m, 2H), 1.87 (m, 4H), 1.11 (t, J=7.4 Hz, 6H).

20 **Example 4: Synthesis of rac-1,1-Siletanediyl-bis(2,4-diethylinden-1-yl)hafnium dichloride otherwise named rac-cyclotrimethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dichloride (4)**

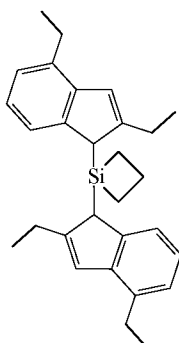
2,7-Diethyl-1*H*-indene



25 [00258] A solution of 23.4 g (172 mmol) of ZnCl₂ in 100 ml of THF was added to 150 ml (158 mmol) of 1.03 M ethylmagnesium bromide in THF at -30°C. The resulting mixture was stirred for 30 min at room temperature and then diluted with 400 ml of THF. Further on, 30.0 g (0.132 mol) of 2-ethyl-4/7-bromoindene, 1.53 g (2.64 mmol) of Pd(dba)₂, and 1.05 g (5.28 mmol) of ^{*t*}Bu₃P were added. This mixture was stirred overnight at 60°C, cooled to room temperature, and then 150 ml of saturated aqueous NH₄Cl was added. Tetrahydrofuran was evaporated in vacuum, and crude product was extracted from the residue by 3 x 200 ml of ethyl acetate. The combined organic extract was dried over Na₂SO₄ and then evaporated to

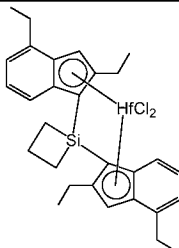
dryness. The product was isolated by flash chromatography on silica gel 60 (40-63 μ m; eluent: hexane). Yield 22.6 g (98%) of colorless oil. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.43; H, 9.50. 1H NMR ($CDCl_3$): δ 7.20-7.24 (m, 1H), 7.14-7.16 (m, 1H), 6.98-7.01 (m, 1H), 6.54 (m, 1H), 3.29 (s, 2H), 2.72 (q, J = 7.7 Hz, 2H), 2.55 (q, J = 7.5 Hz, 2H), 1.31 (t, J = 7.7 Hz, 3H), 1.26 (t, J = 7.5 Hz, 3H).

1,1-Bis(2,4-diethyl-1H-inden-1-yl)siletane



[00259] To a solution of 9.10 g (53.0 mmol) of 2,4-diethyl-1H-indene in 250 ml of ether cooled to 0°C, 21.0 ml (53.0 mmol) of 2.5 M n BuLi in hexanes was added. The resulting mixture was stirred overnight at room temperature. Further on, 50 ml of THF was added, the obtained mixture was cooled to -60°C, and 0.238 g (2.65 mmol) of CuCN was added. This mixture was allowed to warm to -30°C, stirred for 2 h at this temperature, then cooled to -60°C, and 3.73 ml (26.5 mmol) of 1,1-dichlorosiletane was added. The resulting mixture was stirred for 12 h at room temperature, then 20 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 50 ml of ethyl acetate. The combined organic extract was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μ m; eluent: hexanes). Yield 9.51 g (87%) of yellow glassy solid of a ca. 1 to 1 mixture of *rac*- and *meso*-compounds. Calcd. for $C_{29}H_{36}Si$: C, 84.40; H, 8.79. Found: C, 84.63; H, 8.92. 1H NMR ($CDCl_3$): δ 7.13 (m), 6.97-7.06 (m), 6.76 (m), 6.71 (s), 6.60 (s), 3.29 (s), 3.24 (s), 2.76 (m), 2.32-2.53 (m), 2.09 (m), 1.92 (m), 1.82 (m), 1.24 (m), 1.17 (m), 1.06(m).

rac-1,1-Siletanediyl-bis(2,4-diethylinden-1-yl)hafnium dichloride otherwise named rac-cyclotrimethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dichloride (4)



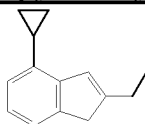
[00260] To a solution of 8.60 g (20.8 mmol) of 1,1-bis(2,4-diethyl-1H-inden-1-yl)siletane in 250 ml of ether cooled to 0°C, 16.7 ml (41.6 mmol) of 2.5 M n BuLi in hexanes was added. The resulting mixture was stirred for 12 h at room temperature, then cooled to -70°C, and 9.68 g

(20.8 mmol) of $\text{HfCl}_4(\text{THF})_2$ was added. The obtained mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was dissolved in 150 ml of toluene, and the obtained mixture was filtered through a Celite pad. The filtrate was evaporated to ca. 90 ml. Crystals precipitated at room temperature were collected and then re-crystallized from 50 ml of toluene. This procedure gave 2.48 g (18%) of pure *rac*-complex as orange crystals.

Calcd. for $\text{C}_{29}\text{H}_{34}\text{Cl}_2\text{HfSi}$: C, 52.77; H, 5.19. Found: C, 52.53; H, 5.09. ^1H NMR (CD_2Cl_2): δ 7.36 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 6.9 Hz, 2H), 6.92 (dd, J = 8.6 Hz, J = 6.9 Hz, 2H), 6.72 (s, 2H), 2.68-2.85 (m, 8H), 2.38 (m, 2H), 2.15 (m, 4H), 1.30 (t, J = 7.6 Hz, 6H), 1.14 (t, J = 7.4 Hz, 6H).

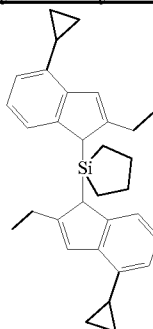
Example 5: Synthesis of *rac*-1,1-Silolanediyl-bis(4-cyclopropyl-2-ethylinden-1-yl)hafnium dichloride otherwise named *rac*-cyclotetramethylenesilylene-bis(4-cyclopropyl-2-ethylinden-1-yl)hafnium dichloride (5)

4/7-Cyclopropyl-2-ethyl-1*H*-indene



[00261] To a solution of 35.0 g (157 mmol) of 2-ethyl-4/7-bromoindene, 1.80 g (3.14 mmol) of $\text{Pd}(\text{dba})_2$ and 1.27 g (6.28 mmol) of $t\text{Bu}_3\text{P}$ in 400 ml of THF, 310 ml (235 mmol) of 0.76 M cyclopropylmagnesium bromide in THF was added dropwise at room temperature. This mixture was stirred overnight at 60°C , cooled to room temperature, and then 250 ml of saturated aqueous NH_4Cl was added. Tetrahydrofuran was evaporated in vacuum, and crude product was extracted with 3 x 200 ml of ethyl acetate. The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The product was isolated by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexane). Yield 28.3 g (98%) of colorless oil of a ca. **7** to **1** mixture of two isomeric indenenes. Calcd. for $\text{C}_{14}\text{H}_{16}$: C, 91.25; H, 8.75. Found: C, 91.10; H, 8.81. ^1H NMR (CDCl_3): δ 7.19-7.20 (m, 1H, **B**), 7.14-7.16 (m, 1H, **A**), 7.09-7.10 (m, 1H, **A**), 7.02 (m, 1H, **B**), 6.81 (m, 1H, **B**), 6.78 (m, 1H, **B**), 6.65 (d, J = 7.7 Hz, 1H, **A**), 6.51 (m, 1H, **A**), 3.37 (s, 3H, **A**), 3.32 (s, 3H, **B**), 2.53 (m, 2H+2H, **A+B**), 2.08 (m, 1H, **B**), 1.95 (m, 1H, **A**), 1.25 (t, J = 7.5 Hz, 3H, **B**), 1.24 (t, J = 7.5 Hz, 3H, **A**), 0.93-0.96 (m, 2H+2H, **A+B**), 0.71-0.75 (m, 2H+2H, **A+B**).

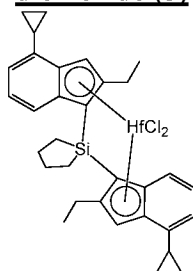
1,1-Bis(4-cyclopropyl-2-ethyl-1*H*-inden-1-yl)silolane



[00262] To a solution of 9.00 g (49.0 mmol) of 4/7-cyclopropyl-2-ethyl-1*H*-indene in 250 ml of ether cooled to 0°C, 19.6 ml (49.0 mmol) of 2.5 M ⁿBuLi in hexanes was added. The resulting mixture was stirred overnight at room temperature. Further on, 50 ml of THF was added, the obtained mixture was cooled to -60°C, and 0.22 g (2.45 mmol) of CuCN was added. This mixture was allowed to warm to -30°C, stirred for 2 h at this temperature, then cooled to -60°C, and 3.22 ml (24.5 mmol) of 1,1-dichlorosilolane was added. The resulting mixture was stirred for 12 h at room temperature, then 200 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 50 ml of ethyl acetate. The combined organic extract was dried over MgSO₄ and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm; eluent: hexanes). Yield 9.77 g (89%) of yellow glassy solid of a ca. 1 to 1 mixture of *rac*- and *meso*-compounds. Calcd. for C₃₂H₃₈Si: C, 85.27; H, 8.50. Found: C, 85.03; H, 8.31. ¹H NMR (CDCl₃): δ 7.19 (m), 6.95-7.04 (m), 6.85 (s), 6.76-6.78 (m), 6.72 (s), 3.43 (s), 3.39 (s), 2.48-2.55 (m), 2.36-2.44 (m), 2.21-2.27 (m), 2.06-2.12 (m), 1.35-1.40 (m), 1.29-1.33 (m), 1.13-1.17 (m), 1.03-1.08 (m), 0.90-0.98 (m), 0.71-0.78 (m), 0.64-0.69 (m), 0.58 (m), 0.32 (m).

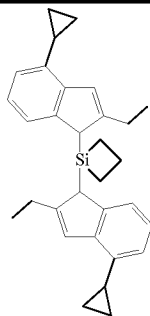
rac-1,1-Silolanediyl-bis(4-cyclopropyl-2-ethylinden-1-yl)hafnium dichloride otherwise named rac-cyclotetramethylenesilylene-bis(4-cyclopropyl-2-ethylinden-1-yl)hafnium

dichloride (5)



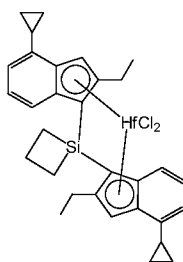
[00263] To a solution of 8.30 g (18.4 mmol) of 1,1-bis(4-cyclopropyl-2-ethyl-1*H*-inden-1-yl)silolane in 250 ml of ether cooled to 0°C, 14.7 ml (36.8 mmol) of 2.5 M ⁿBuLi in hexanes was added. The resulting mixture was stirred for 12 h at room temperature, then cooled to -70°C, and 8.55 g (18.4 mmol) of HfCl₄(THF)₂ was added. The obtained mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was dissolved in 150 ml of toluene, and the obtained mixture was filtered through a Celite pad. The filtrate was evaporated to ca. 100 ml, and this solution was left for crystallization. Crystals precipitated at room temperature were collected and dried in vacuum. This procedure gave 1.55 g (12%) of pure *rac*-complex as yellow crystals. Calcd. for C₃₂H₃₆Cl₂HfSi: C, 55.05; H, 5.20. Found: C, 55.17; H, 5.33. ¹H NMR (CD₂Cl₂): δ 7.45 (d, J = 7.8 Hz, 2H), 6.88-6.94 (m, 6H), 2.80 (m, 2H), 2.42 (m, 2H), 2.15 (m, 2H), 1.87-1.98 (m, 8H), 1.13 (t, J = 7.3 Hz, 6H), 0.84-0.93 (m, 6H), 0.73 (m, 2H).

Example 6: Synthesis of rac-1,1-Siletanediyl-bis(4-cyclopropyl-2-ethylinden-1-yl)hafnium dichloride otherwise named rac-cyclotrimethylenesilylene-bis(4-cyclopropyl-2-

ethylinden-1-yl)hafnium dichloride (6)**1,1-Bis(4-cyclopropyl-2-ethyl-1*H*-inden-1-yl)siletane**

[00264] To a solution of 9.05 g (49.0 mmol) of 4/7-cyclopropyl-2-ethyl-1*H*-indene in 250 ml of ether cooled to 0°C, 19.7 ml (49.0 mmol) of 2.5 M ⁿBuLi in hexanes was added. The resulting mixture was stirred overnight at room temperature. Further on, 50 ml of THF was added, the obtained mixture was cooled to -60°C, and 0.22 g (2.45 mmol) of CuCN was added. This mixture was allowed to warm to -30°C, stirred for 2 h at this temperature, then cooled to -60°C, and 3.45 g (24.5 mmol) of 1,1-dichlorosiletane was added. The resulting mixture was stirred for 12 h at room temperature, then 200 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 100 ml of ethyl acetate. The combined organic extract was dried over MgSO₄ and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm; eluent: hexanes). Yield 9.46 g (88%) of yellow glassy solid of a ca. 1 to 1 mixture of *rac*- and *meso*-compounds. Calcd. for C₃₁H₃₆Si: C, 85.26; H, 8.31. Found: C, 85.01; H, 8.17. ¹H NMR (CDCl₃): δ 7.11 (m), 7.02 (m), 6.95 (m), 6.88 (s), 6.72-6.79 (m), 3.30 (s), 3.25 (s), 2.33-2.56 (m), 2.05-2.13 (m), 1.95 (m), 1.84 (m), 1.17-1.22 (m), 1.07 (m), 0.90-0.97 (m), 0.64-0.75(m).

rac-1,1-Siletanediyl-bis(4-cyclopropyl-2-ethylinden-1-yl)hafnium dichloride otherwise named rac-cyclotrimethylenesilylene-bis(4-cyclopropyl-2-ethylinden-1-yl)hafnium dichloride (6)



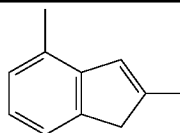
[00265] To a solution of 8.30 g (19.0 mmol) of 1,1-bis(4-cyclopropyl-2-ethyl-1*H*-inden-1-yl)siletane in 250 ml of ether cooled to 0°C, 15.2 ml (38.0 mmol) of 2.5 M ⁿBuLi in hexanes was added. The resulting mixture was stirred for 12 h at room temperature, then cooled to -70°C, and 8.83 g (19.0 mmol) of HfCl₄(THF)₂ was added. The obtained mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was dissolved in 150 ml of toluene, and the obtained solution was filtered through a Celite pad. The filtrate was

evaporated to ca. 100 ml and then left for crystallization. Crystals precipitated at room temperature were collected and re-crystallized from 50 ml of toluene. This procedure gave 1.43 g (11%) of pure *rac*-complex as yellow crystals. Calcd. for $C_{31}H_{34}Cl_2HfSi$: C, 54.43; H, 5.01. Found: C, 54.32; H, 4.94. 1H NMR (CD_2Cl_2): δ 7.34 (d, J = 8.1 Hz, 2H), 6.88-6.94 (m, 6H), 2.69-2.83 (m, 4H), 2.35-2.43 (m, 2H), 2.06-2.24 (m, 4H), 1.92-1.96 (m, 2H), 1.15 (t, J = 7.3 Hz, 6H), 0.85-0.93 (m, 6H), 0.74 (m, 2H).

Example 7: Synthesis of *rac*-1,1-Silolanediyl-bis(2,4-dimethylinden-1-yl)hafnium dichloride otherwise named *rac*-cyclotetramethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride (7)

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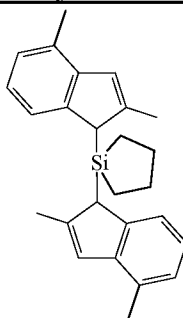
2,4/7-Dimethyl-1*H*-indene



[00266] To a solution of 10.0 g (48 mmol) of 4/7-bromo-2-methyl-1*H*-indene, 0.55 g (0.96 mmol) of $Pd(dba)_2$, and 0.39 g (1.92 mmol) of tBu_3P in 200 ml of THF, 19.0 ml (57.0 mmol) of 3.05 M methylmagnesium bromide in THF was added dropwise at room temperature. This mixture was stirred overnight at 60°C, cooled to room temperature, and then 100 ml of saturated aqueous NH_4Cl was added. Further on, THF was evaporated in vacuum, and crude product was extracted with 3 x 100 ml of ethyl acetate. The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. The product was isolated by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexane). Yield 6.45 g (94%) of colorless oil of a mixture of two isomeric indenenes. Calcd. for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.83; H, 8.34. 1H NMR ($CDCl_3$): δ 7.14-7.21 (m, 2H), 6.96 (d, J = 7.2 Hz, 1H), 6.53 (m, 1H), 3.22 (s, 2H), 2.37 (s, 3H), 2.20 (s, 3H).

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1,1-Bis(2,4-dimethyl-1*H*-inden-1-yl)silolane

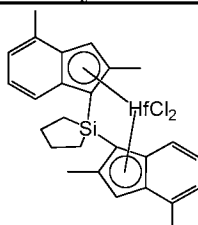


[00267] To a solution of 6.29 g (44.0 mmol) of 2,4/7-dimethyl-1*H*-indene in 150 ml of ether cooled to 0°C, 17.5 ml (44.0 mmol) of 2.5 M $nBuLi$ in hexanes was added. The resulting mixture was stirred overnight at room temperature. Further on, 30 ml of THF was added, the obtained mixture was cooled to -60°C, and 0.20 g (2.20 mmol) of $CuCN$ was added. This mixture was allowed to warm to -30°C, stirred for 2 h at this temperature, then cooled to -60°C, and 3.41 g (22.0 mmol) of 1,1-dichlorosilolane was added. The resulting mixture was

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stirred for 12 h at room temperature, then 100 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 100 ml of ethyl acetate. The combined organic extract was dried over MgSO_4 and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexanes). Yield 2.88 g (38%) of yellow oil of a ca. 1 to 1 mixture of *rac*- and *meso*-compounds. Calcd. for $\text{C}_{26}\text{H}_{30}\text{Si}$: C, 84.26; H, 8.16. Found: C, 84.07; H, 8.01. ^1H NMR (CDCl_3): δ 7.20-7.23 (m), 7.04-7.07 (m), 6.93-6.99 (m), 6.64 (s), 6.54 (s), 3.37 (s), 3.35 (s), 2.39 (s), 2.38 (s), 2.16 (s), 2.05 (s), 1.27-1.33 (m), 1.04-1.18 (m), 0.46-0.64 (m), 0.36 (m).

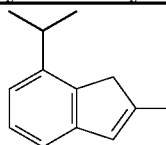
rac-1,1-Silolanediyl-bis(2,4-dimethylinden-1-yl)hafnium dichloride otherwise named rac-cyclotetramethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride (7)



[00268] To a solution of 1.70 g (4.60 mmol) of 1,1-bis(2,4-dimethyl-1*H*-inden-1-yl)silolane in 50 ml of ether cooled to 0°C , 3.70 ml (9.20 mmol) of 2.5 M $n\text{BuLi}$ in hexanes was added. The resulting mixture was stirred for 12 h at room temperature, then cooled to -70°C , and 2.10 g (4.60 mmol) of $\text{HfCl}_4(\text{THF})_2$ was added. The obtained mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was dissolved in 50 ml of toluene and filtered through a Celite pad. The filtrate was evaporated to ca. 20 ml, and the obtained solution was left for crystallization. Crystals precipitated at room temperature were collected and dried in vacuum. This procedure gave 0.23 g (8%) of pure *rac*-complex as yellow crystals. Calcd. for $\text{C}_{26}\text{H}_{28}\text{Cl}_2\text{HfSi}$: C, 50.53; H, 4.57. Found: C, 50.38; H, 4.60. ^1H NMR (CD_2Cl_2): δ 7.48 (d, $J = 8.7$ Hz), 7.07 (d, $J = 6.8$ Hz, 2H), 6.90 (dd, $J = 8.7$ Hz, $J = 6.8$ Hz, 2H), 6.63 (s, 2H), 2.32 (s, 6H), 2.28 (s, 6H), 2.10-2.19 (m, 2H), 1.87-1.92 (m, 6H).

Example 8: Synthesis of rac-1,1-Silolanediyl-bis(4-isopropyl-2-methylinden-1-yl)hafnium dichloride otherwise named rac-cyclotetramethylenesilylene-bis(4-isopropyl-2-methylinden-1-yl)hafnium dichloride (8)

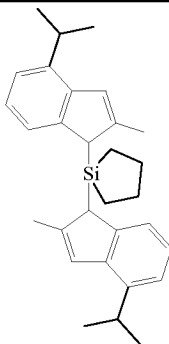
7-Isopropyl-2-methyl-1*H*-indene



[00269] To a solution of 35.1 g (0.167 mol) of 4/7-bromo-2-methyl-1*H*-indene, 413 ml (0.252 mol) of 0.61 M isopropylmagnesium bromide in THF was added dropwise at room temperature. Further on, a solution of 1.92 g (3.34 mmol) of $\text{Pd}(\text{dba})_2$ and 1.35 g (6.68 mmol) of $t\text{Bu}_3\text{P}$ in 700 ml THF was added. This mixture was stirred overnight at 60°C , cooled to room temperature, and then 150 ml of saturated aqueous NH_4Cl was added. Further on, THF was

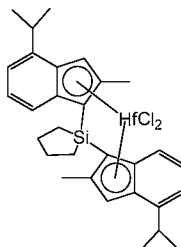
evaporated in vacuum, and crude product was extracted with 3 x 200 ml of ethyl acetate. The combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The product was isolated by flash chromatography on silica gel 60 (40-63 μ m; eluent: hexane). Yield 28.7 g (99%) of colorless oil. Calcd. for C₁₃H₁₆: C, 90.64; H, 9.36. Found: C, 90.81; H, 9.54. ¹H NMR (CDCl₃), δ : 7.25 (m, 1H, 5-H), 7.14 (m, 1H, 4-H), 7.06 (m, 1H, 6-H), 6.53 (m, 1H, 3-H), 3.31 (m, 2H, 1,1'-H), 3.12 (sept, J = 6.94 Hz, 1H, CHMe₂), 2.20 (s, 3H, 2-Me), 1.33 (d, J = 6.94 Hz, 6H, CHMe₂).

1,1-Bis(4-isopropyl-2-methyl-1H-inden-1-yl)silolane



[00270] To a solution of 7.50 g (44.0 mmol) of 7-isopropyl-2-methyl-1H-indene in 250 ml of ether cooled to 0°C, 17.6 ml (44.0 mmol) of 2.5 M ⁿBuLi in hexanes was added. The resulting mixture was stirred overnight at room temperature. Further on, 50 ml of THF was added, the obtained mixture was cooled to -60°C, and 0.40 g (4.40 mmol) of CuCN was added. This mixture was allowed to warm to -30°C, stirred for 2 h at this temperature, then cooled to -60°C, and 3.40 g (22.0 mmol) of 1,1-dichlorosilolane was added. The resulting mixture was stirred for 12 h at room temperature, then 100 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 100 ml of ethyl acetate. The combined organic extract was dried over MgSO₄ and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μ m; eluent: hexanes). Yield 3.43 g (38%) of yellow oil of a ca. 3 to 2 mixture of *rac*- and *meso*-compounds. Calcd. for C₃₀H₃₈Si: C, 84.44; H, 8.98. Found: C, 84.37; H, 9.13. ¹H NMR (CDCl₃): δ 7.20-7.23 (m), 7.01-7.07 (m), 6.71 (s), 6.66 (s), 3.36 (s), 3.35 (s), 3.15-3.23 (m), 2.14 (s), 2.01 (s), 1.25-1.29 (m), 1.04-1.18 (m), 0.84-0.89 (m), 0.55 (m), 0.39 (m).

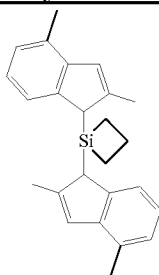
rac-1,1-Silolanediyl-bis(4-isopropyl-2-methylinden-1-yl)hafnium dichloride otherwise named rac-cyclotetramethylenesilylene-bis(4-isopropyl-2-methylinden-1-yl)hafnium dichloride (8)



[00271] To a solution of 2.00 g (4.70 mmol) of 1,1-bis(4-isopropyl-2-methyl-1*H*-inden-1-yl)silolane in 50 ml of ether cooled to 0°C, 3.80 ml (9.40 mmol) of 2.5 M ⁿBuLi in hexanes was added. The resulting mixture was stirred for 12 h at room temperature, then cooled to -70°C, and 2.17 g (4.70 mmol) of HfCl₄(THF)₂ was added. The obtained mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was dissolved in 100 ml of toluene and filtered through a Celite pad. The filtrate was evaporated to ca. 40 ml, and the obtained solution was left for crystallization. Crystals precipitated at room temperature were collected and dried in vacuum. This procedure gave 0.60 g (19%) of pure *rac*-complex as yellow crystals. Calcd. for C₃₀H₃₆Cl₂HfSi: C, 53.45; H, 5.38. Found: C, 53.41; H, 5.55. ¹H NMR (CD₂Cl₂): δ 7.49 (d, J= 8.7 Hz, 2H), 7.14 (d, J= 7.1 Hz, 2H), 6.95 (dd, J= 8.7 Hz, J= 7.1 Hz, 2H), 6.73 (s, 2H), 3.03 (sept, J= 6.9 Hz, 2H), 2.31 (s, 6H), 2.12 (m, 2H), 1.82-2.00 (m, 6H), 1.32 (d, J= 6.9 Hz, 6H), 1.25 (d, J= 6.9 Hz, 6H).

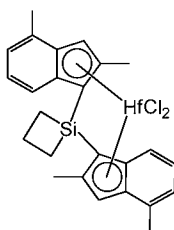
Example 9: Synthesis of *rac*-1,1-Siletanediyl-bis(2,4-dimethylinden-1-yl)hafnium dichloride otherwise named *rac*-cyclotrimethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride (9)

1,1-Bis(2,4-dimethyl-1*H*-inden-1-yl)siletane



[00272] To a solution of 6.40 g (44.0 mmol) of 2,4/7-dimethyl-1*H*-indene in 250 ml of ether cooled to 0°C, 17.6 ml (44.0 mmol) of 2.5 M ⁿBuLi in hexanes was added. The resulting mixture was stirred overnight at room temperature. Further on, 50 ml of THF was added, the obtained mixture was cooled to -60°C, and 0.40 g (4.40 mmol) of CuCN was added. This mixture was allowed to warm to -30°C, stirred for 2 h at this temperature, then cooled to -60°C, and 3.10 g (22.0 mmol) of 1,1-dichlorosiletane was added. The resulting mixture was stirred for 12 h at room temperature, then 100 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 100 ml of ethyl acetate. The combined organic extract was dried over MgSO₄ and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm; eluent: hexanes). Yield 6.19 g (79%) of yellow oil of a ca. 2 to 1 mixture of *rac*- and *meso*-compounds. Calcd. for C₂₅H₂₈Si: C, 84.21; H, 7.91. Found: C, 84.37; H, 8.18. ¹H NMR (CDCl₃): δ 7.13 (m), 6.94-7.03 (m), 6.78 (m), 6.68 (s), 6.58 (s), 3.21 (s), 3.16 (s), 2.41 (s), 2.39 (s), 2.13 (s), 1.95 (s), 1.87 (m), 1.15-1.30 (m), 0.97-1.07 (m), 0.79-0.90 (m).

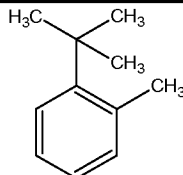
***rac*-1,1-Siletanediyl-bis(2,4-dimethylinden-1-yl)hafnium dichloride otherwise named *rac*-cyclotrimethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride (9)**



[00273] To a solution of 2.00 g (5.60 mmol) of 1,1-bis(2,4-dimethyl-1*H*-inden-1-yl)siletane in 50 ml of ether cooled to 0°C, 4.50 ml (11.2 mmol) of 2.5 M ⁿBuLi in hexanes was added. The resulting mixture was stirred for 12 h at room temperature, then cooled to -70°C, and 2.60 g (5.60 mmol) of HfCl₄(THF)₂ was added. The obtained mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was dissolved in 100 ml of toluene, and the resulting solution was filtered through a Celite pad. The filtrate was evaporated to ca. 40 ml in volume, and the obtained solution was left for crystallization. Crystals precipitated at room temperature were collected and re-crystallized from a mixture of toluene-methylcyclohexane (ca. 10:1, vol.). This procedure gave 0.24 g (15%) of pure *rac*-complex as yellow crystals. Calcd. for C₂₅H₂₆Cl₂HfSi: C, 49.72; H, 4.34. Found: C, 49.81; H, 4.48. ¹H NMR (CD₂Cl₂): δ 7.36 (d, J= 8.5 Hz, 2H), 7.06 (d, J= 6.8 Hz, 2H), 6.88 (dd, J= 8.5 Hz, J= 6.8 Hz, 2H), 6.62 (s, 2H), 2.82 (m, 2H), 2.32 (s, 6H), 2.23 (s, 6H), 2.07-2.18 (m, 4H).

Example 10: Synthesis of *rac*-1,1-Siletanediyl-bis(4-*tert*-butyl-2-methylinden-1-yl)hafnium dichloride otherwise named *rac*-cyclotrimethylenesilylene-bis(4-*tert*-butyl-2-methylinden-1-yl)hafnium dichloride (10)

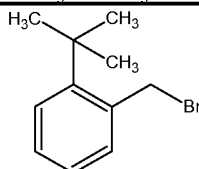
2-*tert*-Butyltoluene



[00274] To a mixture of 3.30 g (13.0 mmol) of nickel (II) acetylacetonate, 4.16 g (13.0 mmol) of 1,3-dicyclohexylimidazolium tetrafluoroborate, 20.6 g (0.258 mol) of lithium *tert*-butoxide, and 100 ml of THF cooled to -10°C, 300 ml (0.258 mol) of 0.86 M *tert*-butylmagnesium chloride in THF was added dropwise by vigorous stirring for 15 min at -10°C. Further on, 29.4 g (0.172 mol) of 2-bromotoluene was added dropwise at -10°C. The resulting mixture was stirred for additional 3 h at this temperature, then stirred overnight at room temperature, and finally quenched by pouring into a solution of ammonium chloride. Crude product was extracted with 3 x 100 ml of ether. The combined organic extract was dried over Na₂SO₄ and then evaporated to dryness. The residue was distilled in vacuum to obtain colorless oil with b.p. 116-123°C/100 mm Hg. Yield 10.1 g (43%) of a ca. 10:3 mixture of 2-*tert*-butyltoluene and 2-isobutyltoluene. This mixture was used on the next step without an additional purification. Calcd. for C₁₁H₁₆: C, 89.12; H, 10.88. Found: C, 89.04; H, 10.95. ¹H NMR (CDCl₃), δ: 7.41 (m, 1H, 3-H in phenyl), 7.12-7.19 (m, 3H, 4,5,6-H in phenyl), 2.58 (s,

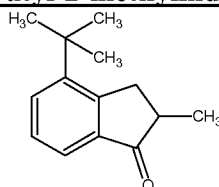
3H, 1-Me in phenyl), 1.45 (s, 9H, ^tBu).

2-tert-Butylbenzyl bromide



[00275] A mixture of 77.4 g (0.435 mol) of N-bromosuccinimide, 46.0 g (0.311 mol) of the
 5 above-obtained mixture of 2-tert-butyltoluene and 2-isobutyltoluene (with ratio equal to ca.
 10:3), 0.9 g of AIBN, and 550 ml of tetrachloromethane was refluxed for 1 h. The resulting
 mixture was filtered through glass frit (G3), the filtrate was evaporated to dryness. The residue
 was distilled in vacuum to give 37.0 g (53%) of a ca. 13.2:1 mixture of 2-tert-butylbenzyl
 bromide and 2-isobutylbenzyl bromide, b.p 77-82°C/4 mm Hg. Calcd. for C₁₁H₁₅Br: C, 58.17;
 10 H, 6.66. Found: C, 58.31; H, 6.80. ¹H NMR (CDCl₃), δ: 7.48 (m, 1H, 4-H in phenyl), 7.40 (m,
 1H, 5-H in phenyl), 7.22-7.29 (m, 2H, 3,6-H in phenyl), 4.86 (s, 2H, CH₂Br), 1.49 (s, 9H, ^tBu).

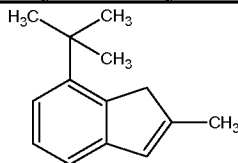
4-tert-Butyl-2-methylindanone-1



[00276] To a solution of sodium ethoxide prepared from 3.75 g (0.163 mol) of sodium metal
 15 and 120 ml of dry ethanol, 28.4 g (0.163 mol) of diethyl methylmalonate was added. This
 solution was stirred for 10 min, and then 37.0 g (0.163 mol) of the above-obtained mixture of
 2-tert-butylbenzyl bromide and 2-isobutylbenzyl bromide (with ratio equal to 13.2:1) was
 added in small portions by vigorous stirring for 15 min. The obtained mixture was refluxed for
 4 h, and then a solution of 27.5 g of KOH in 100 ml of water was added. This mixture was
 20 refluxed for 4 h, and then ethanol was distilled off under atmospheric pressure. The resulting
 solution was extracted with 2 x 300 ml of ether, then the aqueous layer was acidified to pH 1-2
 by 12 M HCl and extracted with 3 x 100 ml of ether. The combined organic extract was
 washed with 2 x 100 ml of water, dried over Na₂SO₄, and then evaporated to dryness. The
 residue was washed with 250 ml of n-hexane. The resulting white solid was decarboxylated at
 25 160-200°C. This procedure gave 21.7 g (61%) of an orange solid. To polyphosphoric acid
 obtained from 154 g of P₄O₁₀ and 102 g of 85% orthophosphoric acid, 25.6 g (0.116 mol) of 2-
 methyl-3-(2-tertbutylphenyl)propionic acid was added in one portion by vigorous stirring at
 80°C. The obtained mixture was stirred for 1.5 h at 80°C and then poured into 1000 cm³ of
 cold water. The product was extracted with 3 x 150 ml of ether. The combined organic extract
 30 was dried over Na₂SO₄ and then evaporated to dryness. The residue was passed through a pad
 of silica gel 60 (40-63 μm; eluent: n-hexane:ethyl acetate = 6:1, vol.). This procedure gave
 15.6 g (66%) of yellowish oil. Thus, the total yield of the title product obtained from 2-tert-

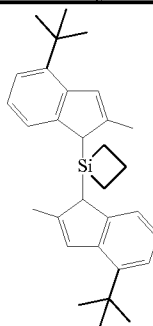
butylbenzyl bromide was 40%. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.27; H, 9.11. 1H NMR ($CDCl_3$), δ : 7.63 (m, 1H, 7-H), 7.60 (m, 1H, 5-H), 7.32 (m, 1H, 6-H), 3.65 (dd, $J = 16.7$ Hz, $J = 7.7$ Hz, 1H, 3-H), 2.89 (dd, $J = 16.7$ Hz, $J = 4.2$ Hz, 1H, 3'-H), 2.69 (m, 1H, 2-H), 1.43 (s, 9H, t Bu), 1.31 (d, $J = 7.5$ Hz, 3H, 2-Me).

7-tert-Butyl-2-methyl-1H-indene



[00277] To a flask containing 15 g (74 mmol) of 4-tertbutyl-2-methylindanone-1 in 80 ml THF, 2.80 g (74 mmol) of $NaBH_4$ was added at $0^\circ C$. Further on, 40 ml of MeOH was added dropwise for 1 h at $0^\circ C$. The resulting mixture was stirred for 1 h, and then solvents were evaporated. The residue was poured into 500 ml of water, and crude product was extracted with 3 x 70 ml of dichloromethane. The combined organic extract was passed through a pad of silica gel 60 (40-63 μm). The obtained elute was evaporated to dryness. The residue was dissolved in 250 ml of toluene, 1 g of TsOH was added, and the obtained mixture was refluxed for 1 h. After that the reaction mixture was washed with aqueous potassium carbonate and passed through a pad of silica gel 60 (40-63 μm). The obtained elute was evaporated to dryness to give 13 g (96%) of yellowish crystalline product. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.51; H, 9.65. 1H NMR ($CDCl_3$), δ : 7.14-7.23 (m, 3H, 4,5,6-H), 6.50 (m, 1H, 3-H), 3.53 (s, 2H, 1,1'-H), 2.18 (m, 3H, 2-Me), 1.46 (s, 9H, t Bu).

1,1-Bis(4-tert-butyl-2-methyl-1H-inden-1-yl)siletane



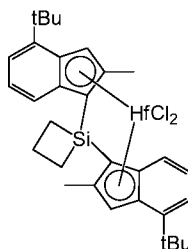
20

[00278] To a solution of 8.00 g (43.0 mmol) of 7-tert-butyl-2-methyl-1H-indene in 250 ml of ether cooled to $0^\circ C$, 17.2 ml (43.0 mmol) of 2.5 M n BuLi in hexanes was added. The resulting mixture was stirred for at room temperature overnight. Further on, 50 ml of THF was added, the obtained mixture was cooled to $-60^\circ C$, and 0.39 g (4.30 mmol) of CuCN was added. This mixture was allowed to warm to $-30^\circ C$, stirred for 2 h at this temperature, then cooled to $-60^\circ C$, and 3.03 g (21.5 mmol) of 1,1-dichlorosiletane was added. The resulting mixture was stirred for 12 h at room temperature, then 100 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 100 ml of ethyl acetate. The combined organic extract was dried over $MgSO_4$ and evaporated to dryness. The residue was

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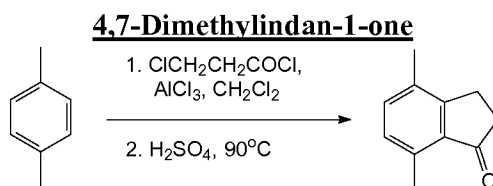
purified by flash chromatography on silica gel 60 (40-63 μ m; eluent: hexanes/ether 20/1). Yield 9.40 g (98%) of yellow crystalline solid of a ca. 1 to 1 mixture of *rac*- and *meso*-compounds. Calcd. for $C_{31}H_{40}Si$: C, 84.48; H, 9.15. Found: C, 84.22; H, 9.00. 1H NMR ($CDCl_3$): δ 7.13-7.17 (m), 7.03-7.07 (m), 6.95-6.98 (m), 6.70 (s), 6.68 (s), 3.14 (s), 3.13 (s), 2.17 (s), 1.90 (s), 1.73-1.79 (m), 1.41 (s), 1.40 (s), 1.15 (m), 1.02-1.10 (m), 0.85-0.92 (m), 0.72 (m).

rac-1,1-Siletanediyl-bis(4-*tert*-butyl-2-methylinden-1-yl)hafnium dichloride otherwise named rac-cyclotrimethylenesilylene-bis(4-*tert*-butyl-2-methylinden-1-yl)hafnium dichloride (10)



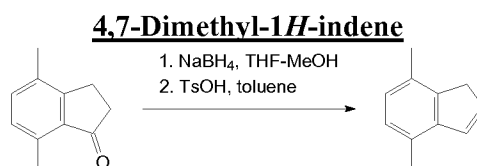
[00279] To a solution of 2.00 g (4.50 mmol) of 1,1-bis(4-*tert*-butyl-2-methyl-1*H*-inden-1-yl)siletane in 60 ml of ether cooled to 0°C, 3.60 ml (9.10 mmol) of 2.5 M n BuLi in hexanes was added. The resulting mixture was stirred for 12 h at room temperature, then cooled to -70°C, and 2.10 g (4.50 mmol) of $HfCl_4(THF)_2$ was added. The obtained mixture was stirred overnight at room temperature and then evaporated to dryness. The residue was dissolved in 50 ml of toluene, and the obtained solution was filtered through a Celite pad. The filtrate was evaporated to ca. 10 ml, and this solution was left for crystallization. Crystals precipitated at room temperature were collected and dried in vacuum. This procedure gave 0.20 g (6.4%) of pure *rac*-complex as yellow crystals. Calcd. for $C_{31}H_{38}Cl_2HfSi$: C, 54.11; H, 5.57. Found: C, 54.02; H, 5.41. 1H NMR (CD_2Cl_2): δ 7.40 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 7.2 Hz, 2H), 6.92 (dd, J = 8.6 Hz, J = 7.2 Hz, 2H), 6.90 (s, 2H), 2.80 (m, 2H), 2.29 (s, 6H), 2.18-2.23 (m, 2H), 2.10-2.15 (m, 2H), 1.38 (s, 18H).

Example 11: Synthesis of rac-1,1-silinanediyl-bis[4,7-dimethylinden-1-yl]hafnium dichloride otherwise named rac-cyclopentamethylenesilylene-bis[4,7-dimethylinden-1-yl]hafnium dichloride (11)



[00280] To a stirred suspension of 224 g (1.68 mol) of $AlCl_3$ in 900 ml of dichloromethane, a mixture of 186 g (1.5 mol) of 3-chloropropanoyl chloride, 148 g (1.4 mol) of *p*-xylene, and 175 ml of dichloromethane was added dropwise for 3 h at room temperature. This mixture was stirred for 2 h at room temperature and then poured on 1000 g of crushed ice. The organic

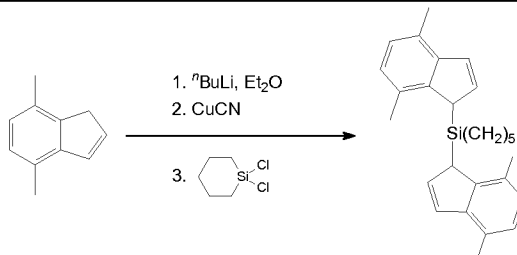
layer was separated, the aqueous layer was extracted with 3 x 200 ml of dichloromethane. The combined organic extract was washed by aqueous K₂CO₃, dried over K₂CO₃, passed through a short pad of silica gel 60 (40-63 μ m), and then evaporated to dryness to give 284 g of dark oily liquid. This liquid was added to 2000 ml of 96% sulfuric acid at room temperature, the
 5 obtained mixture then was stirred at room temperature. The resulting dark solution was heated for 40 min to 90°C and stirred for 1 h at this temperature. After cooling to room temperature the reaction mixture was poured on 4000 g of crushed ice, and 4000 ml of cold water and 2000 ml of dichloromethane were added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (100 ml per 900 ml of the aqueous phase). The combined
 10 organic extract was washed by the water, then by aqueous K₂CO₃, dried over K₂CO₃, and passed through a short pad of silica gel 60 (40-63 μ m). The elute was evaporated to dryness to give a slightly yellowish solid mass. Re-crystallization of the later from 500 ml of n-hexane (hot→r.t.→0°C, overnight) gave 195 g (87%) of 4,7-dimethylindan-1-one as a white crystalline material. Anal. calc. for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.54; H, 7.65. ¹H
 15 NMR (CDCl₃): δ 7.22 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 2.93 (m, 2H), 2.63 (m, 2H), 2.58 (s, 3H), 2.28 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 208.18, 154.63, 135.73, 134.23, 134.02, 132.65, 129.05, 36.49, 24.12, 17.81, 17.23.



20 **[00281]** To a solution of 181 g (1.13 mol) of 4,7-dimethylindan-1-one in 1100 ml of THF cooled to 5°C, 64 g (1.69 mol) of NaBH₄ was added. Further on, 550 ml of methanol was added dropwise to this mixture by vigorous stirring for ca. 5 h at 5°C. This mixture was stirred overnight at room temperature and then evaporated to dryness. To the obtained white mass 1500 ml of dichloromethane and 1000 ml of water were added, the resulting mixture was
 25 acidified by 2 M HCl to pH~4. The organic layer was separated, the aqueous layer was extracted with 2 x 250 ml of dichloromethane. The combined organic extract was dried over Na₂SO₄ and then evaporated to dryness to give a white solid mass. To a solution of this mass in 2000 ml of toluene 2 g of TsOH was added, this mixture was rapidly heated to reflux, refluxed with Dean-Stark head for 15 min, and then cooled to room temperature using water
 30 bath. The resulting solution was washed by 10% aqueous Na₂CO₃. The organic layer was separated, the aqueous layer was extracted with 2 x 150 ml of dichloromethane. The combined organic extract was dried over K₂CO₃ and then passed through a short pad of silica gel 60 (40-63 μ m). The silica gel pad was additionally washed by 250 ml of dichloromethane. The combined elute was evaporated to dryness to give a slightly yellowish liquid which was then
 35 distilled in vacuum to give 134 g (83%) of a colorless liquid, b.p. 100–110°C/12 mm Hg. Anal. calc. for C₁₁H₁₂: C, 91.61; H, 8.39. Found: C, 91.48; H, 8.42. ¹H NMR (CDCl₃): δ 6.95–7.02

(m, 2H), 6.91 (d, $J = 7.6$ Hz, 1H), 6.54 (dt, $J = 5.6$ Hz, $J = 1.8$ Hz, 1H), 3.26 (s, 2H), 2.41 (s, 3H), 2.32 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 143.19, 142.11, 133.22, 130.48, 130.12, 127.67, 127.53, 125.76, 38.23, 18.40, 18.26.

1,1-Bis(4,7-dimethyl-1*H*-inden-1-yl)silinane

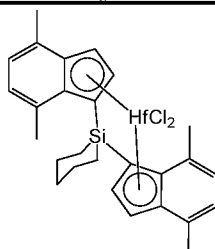


5

[00282] To a solution of 10.8 g (75.0 mmol) of 4,7-dimethyl-1*H*-indene in 250 ml of ether, 30.0 ml (75.0 mmol) of 2.5 M $n\text{BuLi}$ in hexanes was added in one portion at -50°C . This mixture was stirred at room temperature for 5 h, then the resulting suspension was cooled to -50°C , and 1.70 g (19.0 mmol) of CuCN was added. This mixture was stirred for 30 min at -25°C , and 6.35 g (37.6 mmol) of 1,1-dichlorosilane was added in one portion. Further on, this mixture was stirred overnight at ambient temperature, then filtered through a pad of silica gel 60 (40-63 μm) which was additionally washed by 2 x 75 ml of dichloromethane. The combined filtrate was evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (eluent: hexane, then hexane/dichloromethane 10:1) yielding 12.3 g (85%) of the title compound as a slightly yellowish oil. Anal. calc. for $\text{C}_{27}\text{H}_{32}\text{Si}$: C, 84.31; H, 8.39. Found: C, 84.55; H, 8.48. ^1H NMR (CDCl_3): δ 6.82-6.99 (m), 6.45 (dd, $J = 5.3$ and 1.8 Hz), 6.10 (dd, $J = 5.3$ and 1.8 Hz), 3.42 (s), 3.34 (s), 2.39 (s), 2.34 (s), 2.24 (s), 1.46-1.55 (m), 1.35-1.46 (m), 1.13-1.23 (m), 0.82-0.94 (m), 0.66 (t, $J = 6.5$ Hz), 0.37 (t, $J = 6.6$ Hz).

rac-1,1-silanediy-bis[4,7-dimethylinden-1-yl]hafnium dichloride otherwise named rac-cyclopentamethylenesilylene-bis[4,7-dimethylinden-1-yl]hafnium dichloride (11)

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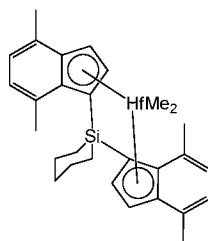


[00283] To a solution of 5.08 g (13.2 mmol) of 1,1-bis(4,7-dimethyl-1*H*-inden-1-yl)silinane in 200 ml of ether cooled to -60°C , 10.6 ml (26.5 mmol) of 2.5 M $n\text{BuLi}$ in hexanes was added in one portion. This mixture was stirred overnight at room temperature. The resulting light-orange suspension was cooled to -40°C , and 6.14 g (13.2 mmol) of $\text{HfCl}_4(\text{THF})_2$ was added. The reaction mixture was stirred for 24 h and then evaporated to dryness. The residue was treated with 200 ml of hot toluene. This mixture was filtered while hot through a glass frit (G4). The filtrate was evaporated to 100 ml. Crystals precipitated at room temperature were

25

collected and dried in vacuum. This procedure gave 4.36 g (52%) of *rac*-hafnocene dichloride contaminated with ca. 5% of *meso*-isomer. The second crop of crystals was obtained from the mother liquor by crystallization at -30°C. This procedure gave 2.39 g of a ca. 1 to 4 mixture of *rac*- and *meso*-complexes. Thus, the total yield of *rac*- and *meso*-hafnocenes isolated in this synthesis was 6.75 g (81%). *Rac*-complex contaminated with 5% of *meso*-form (4.36 g, as obtained above) was re-crystallized from 100 ml of toluene. Orange crystals precipitated from this solution at room temperature were collected and dried in vacuum. This procedure gave 2.20 g of pure *rac*-metallocene. Anal. calc. for C₂₇H₃₀Cl₂HfSi: C, 51.31; H, 4.78. Found: C, 51.45; H, 4.69. ¹H NMR (CD₂Cl₂): δ 6.88 (d, *J* = 3.5 Hz, 2H), 6.87 (d, *J* = 6.8 Hz, 2H), 6.72 (d, *J* = 6.8 Hz, 2H), 6.06 (d, *J* = 3.5 Hz, 2H), 2.48 (s, 6H), 2.25 (s, 6H), 2.03-2.17 (m, 2H), 1.89-2.03 (m, 2H), 1.65-1.80 (m, 4H), 1.51-1.61 (m, 2H). ¹³C{¹H} NMR (CDCl₃): δ 133.31, 132.41, 132.28, 128.29, 127.57, 126.32, 118.56, 117.52, 92.38, 30.37, 25.05, 22.74, 19.32, 17.75.

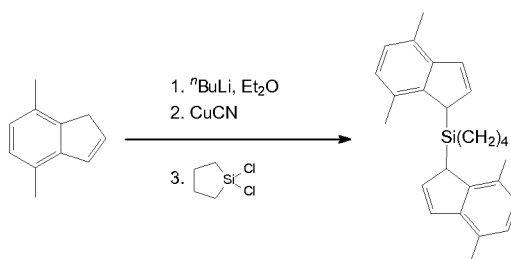
Example 12: Synthesis of *rac*-1,1-silanediy-bis[4,7-dimethylinden-1-yl]hafnium dimethyl otherwise named *rac*-cyclopentamethylenesilylene-bis[4,7-dimethylinden-1-yl]hafnium dimethyl (12)



[00284] To a suspension of 1.27 g (2.01 mmol) of *rac*-silanediy-bis[η⁵-4,7-dimethylinden-1-yl]hafnium dichloride (11) in 45 ml of toluene cooled to -30°C, 4.00 ml (8.44 mmol, 2.1 eq.) of 2.11 M methylmagnesium bromide in ether was added in one portion, and the reaction mixture was stirred overnight at room temperature. The reaction mixture was evaporated to ca. 20 ml and filtered through glass frit (G4). Yellowish crystals precipitated from this solution for 12 h at -30°C were collected, washed with 2 x 5 ml of cold (-30°C) n-hexane, and dried in vacuum. This procedure gave 1.09 g (92%) of *rac*-silanediybis[η⁵-4,7-dimethylinden-1-yl]hafnium dimethyl. Anal. calc. for C₂₉H₃₆HfSi: C, 58.92; H, 6.14. Found: C, 59.11; H, 6.30. ¹H NMR (C₆D₆): δ 6.91 (d, *J* = 3.4 Hz, 2H), 6.89 (d, *J* = 6.8 Hz, 2H), 6.70 (d, *J* = 6.8 Hz, 2H), 5.77 (d, *J* = 3.4 Hz, 2H), 2.31 (s, 6H), 2.30 (s, 6H), 1.77-2.04 (m, 4H), 1.49-1.59 (m, 2H), 1.37-1.49 (m, 2H), 1.22-1.33 (m, 2H), -1.2 (s, 6H).

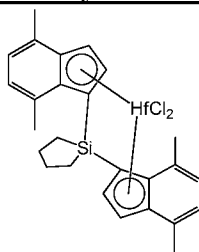
Example 13: Synthesis of 1,1-silolanediy-bis[4,7-dimethylinden-1-yl]hafnium dichloride otherwise named cyclo-tetramethylenesilylene-bis[4,7-dimethylinden-1-yl]hafnium dichloride (13)

1,1-Bis(4,7-dimethyl-1*H*-inden-1-yl)silolane



[00285] To a solution of 14.4 g (100 mmol) of 4,7-dimethyl-1*H*-indene in 250 ml of ether, 40.0 ml (100 mmol) of 2.5 M *n*-BuLi in hexanes was added in one portion at -50°C. This mixture was stirred at room temperature for 5 h, then the resulting suspension was cooled to -50°C, and 2.24 g (25.0 mmol) of CuCN was added. The resulting mixture was stirred for 30 min at -25°C, and then 7.76 g (50.0 mmol) of 1,1-dichlorosilolane was added in one portion. Further on, this mixture was stirred overnight at ambient temperature. This solution was filtered through a pad of silica gel 60 (40-63 μ m) which was additionally washed by 2 x 100 ml of dichloromethane. The combined filtrate was evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (eluent: hexane-dichloromethane = 10:1, vol.). Yield 16.4 g (89%) of 1,1-bis(4,7-dimethylinden-1-yl)silolane as a slightly yellowish oil. Anal. calc. for C₂₆H₃₀Si: C, 84.26; H, 8.16. Found: C, 86.39; H, 8.25. ¹H NMR (CDCl₃): δ 6.81-6.99 (m), 6.47 (dd, *J* = 5.3 and 1.8 Hz), 6.22 (dd, *J* = 5.3 and 1.8 Hz), 3.41 (s), 3.39 (s), 2.40 (s), 2.38 (s), 2.37 (s), 2.33 (s), 1.20-1.38 (m), 0.99-1.20 (m), 0.63-0.78 (m), 0.26-0.37 (m), 0.24 (t, *J* = 6.8 Hz).

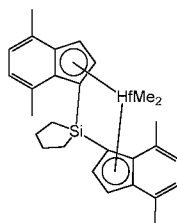
Rac-1,1-silolanediy-bis[4,7-dimethylinden-1-yl]hafnium dichloride otherwise named rac-cyclotetramethylenesilylene-bis[4,7-dimethylinden-1-yl]hafnium dichloride (13)



[00286] To a solution of 9.53 g (25.7 mmol) of 1,1-bis(4,7-dimethyl-1*H*-inden-1-yl)silolane in 250 ml of ether cooled to -78°C, 20.6 ml (51.5 mmol) of 2.5 M *n*-BuLi in hexanes was added in one portion. This mixture was stirred overnight at room temperature. The resulting light-orange solution was cooled to -50°C, and 11.95 g (25.7 mmol) of HfCl₄(THF)₂ was added. The reaction mixture was stirred for 24 h and then evaporated to dryness. The residue was treated with 200 ml of hot toluene. The obtained hot mixture was filtered through glass frit (G4). The filtrate was evaporated to 100 ml and heated to dissolve the precipitate. Crystals precipitated from this solution for 3 h at room temperature were collected and dried in vacuum. This procedure gave 7.80 g (49%) of *rac*-hafnocene dichloride. The second crop of crystals was obtained from the mother liquor after its evaporation to ca. 40 ml followed by crystallization overnight at -30°C. This procedure gave 1.76 g of a ca. 4 to 1 mixture of *rac*- and *meso*-

complexes. Thus, the total yield of *rac*- and *meso*-hafnocene dichlorides isolated in this synthesis was 9.56 g (60%). Anal. calc. for $C_{26}H_{28}Cl_2HfSi$: C, 50.53; H, 4.57. Found: C, 50.45; H, 4.68. 1H NMR (CD_2Cl_2): δ 6.96 (d, J = 3.3 Hz, 2H), 6.95 (d, J = 6.8 Hz, 2H), 6.79 (d, J = 6.8 Hz, 2H), 6.14 (d, J = 3.3 Hz, 2H), 2.57 (s, 6H), 2.34 (s, 6H), 2.17-2.29 (m, 2H), 1.74-1.91 (m, 4H), 1.61-1.74 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 133.40, 132.47, 132.05, 128.32, 127.55, 126.41, 118.74, 118.44, 92.36, 27.44, 24.10, 19.33, 17.66.

Example 14: Synthesis of *rac*-1,1-silolanediy-bis[4,7-dimethylinden-1-yl]hafnium dimethyl otherwise named *rac*-cyclotetramethylenesilylene-bis[4,7-dimethylinden-1-yl]hafnium dimethyl (14)

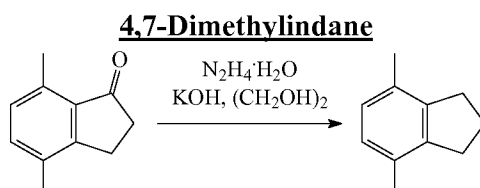


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[00287] To a suspension of 3.10 g (5.04 mmol) of *rac*-silolanediy-bis[η^5 -4,7-dimethyl-1H-inden-1-yl]hafnium dichloride (13) in 75 ml of toluene cooled to $-30^\circ C$, 10.0 ml (21.1 mmol, 2.1 eq.) of 2.11 M methylmagnesium bromide in ether was added in one portion, and the reaction mixture was stirred overnight at room temperature. Then, the reaction mixture was evaporated to ca. 40 ml, filtered through glass frit (G4), and finally evaporated to ca. 25 ml. Crystals precipitated from this solution for 12 h at $-30^\circ C$ were collected, washed with 2 x 5 ml of cold ($-30^\circ C$) n-hexane, and dried in vacuum. This procedure gave 2.47 g (85%) of *rac*-silolanediybis[η^5 -4,7-dimethylinden-1-yl]hafnium dimethyl. Anal. calc. for $C_{28}H_{34}HfSi$: C, 58.27; H, 5.94. Found: C, 58.43; H, 6.12. 1H NMR ($CDCl_3$): δ 6.88 (d, J = 3.5 Hz, 2H), 6.85 (d, J = 6.8 Hz, 2H), 6.64 (d, J = 6.8 Hz, 2H), 5.77 (d, J = 3.5 Hz, 2H), 2.38 (s, 6H), 2.32 (s, 6H), 2.03-2.15 (m, 2H), 1.58-1.72 (m, 2H), 1.38-1.58 (m, 4H), -1.79 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 132.21, 131.98, 129.14, 126.05, 125.74, 124.06, 118.45, 111.50, 86.49, 40.32, 26.96, 23.65, 19.30, 17.14.

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Example 15: Synthesis of *rac*-1,1-silolanediy-bis[4,6,8-trimethyl-1,2,3-trihydro-s-indacen-5-yl]hafnium dichloride otherwise named *rac*-cyclotetramethylenesilylene-bis[4,6,8-trimethyl-1,2,3-trihydro-s-indacen-5-yl]hafnium dichloride (15)

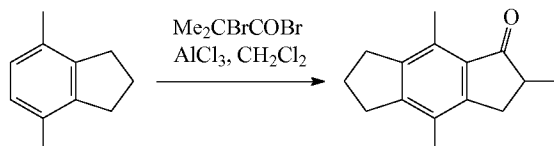


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[00288] A mixture of 124 g (2.21 mol) of KOH, 91.4 g (570.5 mmol) of 4,7-dimethylindan-1-one, and 102 ml of hydrazine hydrate in 1100 ml of ethylene glycol was refluxed for 5 h. Then, the reflux condenser was replaced with a Claisen distillation head with condenser, and a

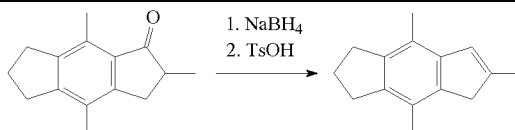
mixture of water, hydrazine hydrate, the title product, and ethylene glycol was distilled until the distillation temperature reached 195°C. To the residue cooled to room temperature, 300 ml of ethylene glycol, the second portion of 2,2-dimethylindan-1-one (182.5 g, 1.139 mol), and hydrazine hydrate (144 ml) were added, and the reduction procedure was repeated as described above. The combined distillate was diluted with 1000 ml of water, and crude product was extracted with 3 x 300 ml of dichloromethane. The combined organic extract was washed with 1 M HCl, dried over anhydrous K₂CO₃, passed through a short pad of silica gel 60 (40-63 µm), and the obtained filtrate was evaporated to dryness to give a slightly yellowish liquid. This liquid was distilled in vacuum to give 68.1 g (82%) of 4,7-dimethylindane as a colorless liquid, b.p. 88-90°C/10 mm Hg. Anal. calc. for C₁₁H₁₄: C, 90.35; H, 9.65. Found: C, 90.47; H, 9.50. ¹H NMR (CDCl₃): δ 6.86 (s, 2H), 2.82 (t, *J* = 7.6 Hz, 4H), 2.21 (s, 6H), 2.05 (quint, *J* = 7.6 Hz, 2H). ¹³C{¹H} NMR (CDCl₃): δ 142.53, 130.84, 126.99, 31.62, 24.17, 18.86.

2,4,8-Trimethyl-3,5,6,7-tetrahydro-s-indacen-1(2H)-one



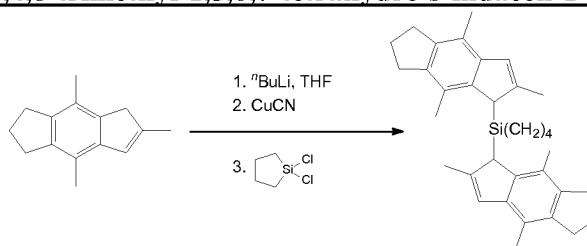
[00289] To a suspension of 333 g (2.5mol) of AlCl₃ in 300 ml of dichloromethane cooled to -30°C, 223 g (970 mmol) of 2-bromo-2-methylpropionyl bromide and a solution of 137.8 g (942 mmol) of indane in 250 ml of dichloromethane were added for 30 min. The cooling bath was then removed, and this solution was stirred for 5 h at room temperature. The reaction mixture was poured into 2 kg of crushed ice, the organic layer was separated, and the water layer was extracted with 3 x 300 ml of dichloromethane. The combined organic extract was washed with aqueous K₂CO₃, dried over anhydrous K₂CO₃, passed through a short pad of silica gel 60 (40-63 µm), and the filtrate was evaporated to dryness to give a semi-crystalline gray mass. This mass was distilled in vacuum to give 159.1 g (79%) of 2,4,8-trimethyl-3,5,6,7-tetrahydro-s-indacen-1(2H)-one as a slightly greenish oil (b.p. 175-180°C/2 mm Hg) which rapidly crystallized at room temperature. Anal. calc. for C₁₅H₁₈O: C, 84.07; H, 8.47. Found: C, 84.22; H, 8.26. ¹H NMR (CDCl₃): δ 3.19 (dd, *J* = 16.9 and 8.1 Hz, 1H, 3-CHH'), 2.90 (t, *J* = 7.8 Hz, 2H, CH₂ in indane), 2.88 (t, *J* = 7.8 Hz, 2H, CH₂ in indane), 2.66 (m, 1H, 2-H), 2.54 (s, 3H, 8-CH₃), 2.49 (dd, *J* = 16.9 and 3.3 Hz, 1H, 3-CHH'), 2.19 (s, 3H, 4-CH₃), 2.12 (quint, *J* = 7.8 Hz, CH₂ in indane), 1.29 (d, *J* = 7.3, 3H, 2-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 210.63, 152.07, 149.99, 143.11, 132.07, 131.26, 127.72, 42.69, 32.95, 32.01, 30.75, 24.56, 16.75, 14.42, 14.33.

4,6,8-Trimethyl-1,2,3,5-tetrahydro-s-indacene



[00290] To a solution of 77.6 g (362 mmol) of 2,4,8-trimethyl-3,5,6,7-tetrahydro-*s*-indacen-1(2*H*)-one in 400 ml of THF cooled to 5°C, 20.6 g (545 mmol) of NaBH₄ was added. Further on, 200 ml of methanol was added dropwise to this vigorously stirred mixture for ca. 5 h at 5°C. The resulting mixture was stirred for 3 h at room temperature and then evaporated to dryness, the residue was partitioned between 500 ml of dichloromethane and 500 ml of 2 M HCl. The organic layer was separated, and the aqueous layer was additionally extracted with 100 ml of dichloromethane. The combined organic extract was evaporated to dryness to give white solid mass. To a solution of this mass in 1000 ml of toluene 1 g of TsOH was added, and this mixture was refluxed with Dean-Stark head for 20 min, then cooled to room temperature using a water bath. The reaction mixture was washed by 10% aqueous K₂CO₃. The organic layer was separated, and the aqueous layer was extracted with 2 x 100 ml of dichloromethane. The combined organic extract was dried over K₂CO₃ and then passed through a short pad of silica gel 60 (40-63 μm). This silica gel pad was additionally washed by 100 ml of dichloromethane. The combined organic elute was evaporated to dryness to yield yellowish solid mass. The latter was re-crystallized from 200 ml of n-hexane (hot → r.t. → 0°C → -30°C, overnight). This procedure gave 58.2 g (81%) of 4,6,8-trimethyl-1,2,3,5-tetrahydro-*s*-indacene as a white fine-crystalline powder. Anal. calc. for C₁₅H₁₈: C, 90.85; H, 9.15. Found: C, 90.99; H, 9.27. ¹H NMR (CDCl₃): δ 6.56 (q, *J* = 1.3 Hz, 1H, 3-H), 3.16 (s, 2H, 1-CH₂), 2.86 (br. t, *J* = 7.3 Hz, 4H, two CH₂ in indane), 2.27 (s, 3H, CH₃), 2.20 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 2.09 (quint, *J* = 7.3 Hz, CH₂ in indane). ¹³C{¹H} NMR (CDCl₃): δ 144.10, 142.84, 141.08, 140.34, 138.51, 125.76, 125.54, 122.21, 41.55, 31.58, 31.43, 24.91, 17.00, 15.61, 15.36.

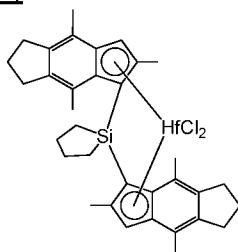
1,1-Bis(2,4,8-trimethyl-1,5,6,7-tetrahydro-*s*-indacen-1-yl)silolane



[00291] To a solution of 7.78 g (39.2 mmol) of 4,6,8-trimethyl-1,2,3,5-tetrahydro-*s*-indacene in 250 ml of THF cooled to -78°C, 15.7 ml (39.3 mmol) of 2.5 M *n*-BuLi in hexanes was added in one portion. This mixture was stirred for 5 h at room temperature, then the resulting light orange solution was cooled to -50°C, and 0.88 g (9.82 mmol, 25%) of CuCN was added. The resulting mixture was stirred for 30 min at -25°C, then 3.04 g (19.6 mmol) of 1,1-dichlorosilolane was added in one portion. Further on, this mixture was stirred overnight at ambient temperature. This solution was filtered through a pad of silica gel 60 (40-63 μm) which was additionally washed by 3 x 75 ml of dichloromethane. The combined elute was evaporated to dryness. The residue was dissolved in a mixture of hexanes-dichloromethane (1:1, vol.), and the obtained solution was filtered through glass frit (G3). The obtained yellowish powder was triturated with 30 ml of hexanes, then filtered off, and dried in vacuum.

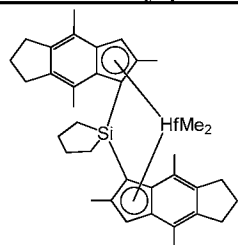
This procedure gave 8.10 g (86%) of 1,1-bis(2,4,8-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)silolane as a white powder. Anal. calc. for $C_{34}H_{42}Si$: C, 85.29; H, 8.84. Found: C, 85.40; H, 9.14. 1H NMR ($CDCl_3$): δ 6.60 (s), 6.54 (s), 3.37 (s), 2.69-2.91 (m), 2.29 (s), 2.24 (s), 1.99-2.12 (m), 2.00 (s), 1.87 (s), 1.11-1.21 (m), 0.98-1.11 (m), 0.84-0.95 (m), 0.65-0.80 (m), 0.42-0.59 (m), 0.20-0.33 (m).

rac-1,1-silolanediy-bis[4,6,8-trimethyl-1,2,3-trihydro-s-indacen-5-yl]hafnium dichloride otherwise named rac-cyclotetramethylenesilylene-bis[4,6,8-trimethyl-1,2,3-trihydro-s-indacen-5-yl]hafnium dichloride (15)



[00292] To a suspension of 3.92 g (8.19 mmol) of 1,1-bis(2,4,8-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)silolane in 200 ml of ether cooled to $-78^\circ C$, 6.60 ml (16.5 mmol) of 2.5 M $nBuLi$ in hexanes was added in one portion. This mixture was stirred overnight at room temperature: the proligand gradually dissolved completely, then a new white precipitate was formed. The resulting mixture was cooled to $-50^\circ C$, and 2.63 g (8.21 mmol) of $HfCl_4$ was added. The reaction mixture was stirred for 24 h resulting in light-orange solution with a lot of yellow precipitate. The resulting mixture was evaporated to dryness, and the residue was treated with 200 ml of hot toluene. This hot mixture was filtered through glass frit (G4). Crystals precipitated from the filtrate were collected and dried in vacuum. This procedure gave 0.94 g of *rac*-hafnocene dichloride. The second crop of crystals was obtained from the mother liquor by evaporation to ca. 50 ml followed by crystallization overnight at $-30^\circ C$. This procedure gave 1.02 g of *rac*-hafnocene. Thus, the total yield of the complex isolated in this synthesis was 1.96 g (33%). Anal. calc. for $C_{34}H_{40}Cl_2HfSi$: C, 56.24; H, 5.55. Found: C, 56.42; H, 5.51. 1H NMR ($CDCl_3$): δ 6.70 (s, 2H), 3.00-3.15 (m, 2H), 2.73-3.00 (m, 6H), 2.49 (s, 6H), 2.17-2.28 (m, 4H), 2.23 (s, 6H), 2.21 (s, 6H), 1.97-2.13 (m, 4H), 1.80-1.96 (m, 2H), 1.46-1.63 (m, 2H).

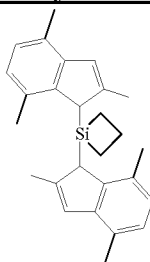
Example 16: Synthesis of rac-1,1-silolanediy-bis[4,6,8-trimethyl-1,2,3-trihydro-s-indacen-5-yl]hafnium dimethyl otherwise named rac-cyclotetramethylenesilylene-bis[4,6,8-trimethyl-1,2,3-trihydro-s-indacen-5-yl]hafnium dimethyl (16)



[00293] To a suspension of 350 mg (0.48 mmol) of *rac*-1,1-silolanediyl-bis[η⁵-4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl]hafnium dichloride (15) in a mixture of 30 ml of toluene and 10 ml of ether cooled to -30°C, 1.00 ml (2.11 mmol) of 2.11 M methylmagnesium bromide in ether was added in one portion, and the reaction mixture was stirred at room temperature for 3 days. Then, the reaction mixture was evaporated to ca. 20 ml, filtered through glass frit (G4), and the filtrate was evaporated to dryness. This procedure gave 225 mg (68%) of racemic complex contaminated with ca. 2% of *meso*-form. Anal. calc. for C₃₆H₄₆HfSi: C, 63.09; H, 6.77. Found: C, 69.21; H, 6.83. ¹H NMR (CDCl₃): δ 6.63 (s, 2H), 2.84-3.08 (m, 4H), 2.78 (t, *J* = 7.5 Hz, 4H), 2.43 (s, 6H), 2.26 (s, 6H), 2.10-2.22 (m, 4H), 1.94-2.10 (m, 4H), 2.02 (s, 6H), 1.72-1.87 (m, 2H), 1.31-1.47 (m, 2H), -1.56 (s, 6H).

Example 17: Synthesis of *rac*-1,1-siletanediyl-bis[2,4,7-trimethylinden-1-yl]hafnium dichloride otherwise named cyclotrimethylenesilylene-bis[2,4,7-trimethylinden-1-yl]hafnium dichloride (17)

1,1-Bis(2,4,7-trimethyl-1*H*-inden-1-yl)siletane

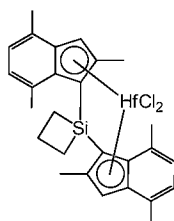


15

[00294] To a solution of 7.50 g (47.0 mmol) of 2,4,7-trimethyl-1*H*-indene in 150 ml of ether cooled to 0°C, 19.0 ml (47.0 mmol) of 2.5 M ^{*n*}BuLi in hexanes was added. The resulting mixture was stirred overnight at room temperature. Further on, 30 ml of THF was added, the obtained mixture was cooled to -60°C, and 0.42 g (4.70 mmol) of CuCN was added. This mixture was allowed to warm to -30°C, stirred for 2 h at this temperature, then cooled to -60°C, and 3.31 g (23.5 mmol) of 1,1-dichlorosiletane was added. The resulting mixture was stirred for 12 h at room temperature, then 100 ml of water was added, and the organic layer was separated. The aqueous layer was extracted with 2 x 100 ml of ethyl acetate. The combined organic extract was dried over MgSO₄ and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm; eluent: hexanes). Yield 3.20 g (36%) of yellow oil of a ca. 1 to 1 mixture of *rac*- and *meso*-compounds. Calcd. for C₂₇H₃₂Si: C, 84.31; H, 8.39. Found: C, 84.10; H, 8.47. ¹H NMR (CDCl₃): δ 6.87-6.90 (m), 6.73-6.78 (m), 6.65 (s), 6.62 (s), 3.39 (s), 3.38 (s), 2.35 (s), 2.32 (s), 2.24 (s), 2.06 (s), 1.81 (s), 1.48 (m), 1.34 (m), 0.86-1.01 (m).

***rac*-1,1-siletanediyl-bis[2,4,7-trimethylinden-1-yl]hafnium dichloride otherwise named cyclotrimethylenesilylene-bis[2,4,7-trimethylinden-1-yl]hafnium dichloride (17)**

30



[00295] To a solution of 3.27 g (8.50 mmol) of 1,1-bis(2,4,7-trimethyl-1*H*-inden-1-yl)siletane in 85 ml of ether cooled to -60°C, 6.80 ml (17.0 mmol) of 2.5 M *n*BuLi in hexanes was added in one portion. This mixture was stirred overnight at room temperature. The resulting light-red solution was cooled to -60°C, and 2.73 g (8.52 mmol) of HfCl₄ was added. The reaction mixture was stirred for 24 h resulting in light-yellow solution with a lot of yellow precipitate. The obtained mixture was evaporated to dryness, and the residue was treated with 200 ml of hot toluene. This hot mixture was filtered through a glass frit (G4). The filtrate was evaporated to ca. 50 ml and filtered off a yellow precipitate. Crystals precipitated from the obtained filtrate solution overnight at room temperature were collected and dried in vacuum. This procedure gave 198 mg of *meso*-hafnocene. The yellow precipitate on filter left after the first crystallization was treated with 100 ml of hot toluene. The obtained hot mixture was filtered through a glass frit (G4). The above-described procedure was repeated twice, each time using 100 ml of hot toluene. The combined filtrate was evaporated to 10 ml. Yellow crystals precipitated from this solution overnight at room temperature were collected and dried in vacuum. This procedure gave 415 mg of *rac*-hafnocene dichloride.

Meso-siletanediyl-bis[η^5 -2,4,7-trimethyl-1*H*-inden-1-yl]hafnium dichloride:

Anal. calc. for C₂₇H₃₀Cl₂HfSi: C, 51.31; H, 4.78. Found: C, 51.44; H, 7.90.

¹H NMR (CDCl₃): δ 6.80 (d, *J* = 6.8 Hz, 2H), 6.76 (s, 2H), 6.61 (d, *J* = 6.8 Hz, 2H), 2.61-2.74 (m, 2H), 2.66 (s, 6H), 2.51 (s, 6H), 2.31 (s, 6H), 2.19-2.39 (m, 4H).

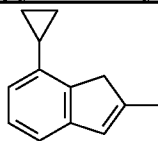
Rac-siletanediyl-bis[η^5 -2,4,7-trimethyl-1*H*-inden-1-yl]hafnium dichloride:

Anal. calc. for C₂₇H₃₀Cl₂HfSi: C, 51.31; H, 4.78. Found: C, 51.39; H, 4.69.

¹H NMR (CDCl₃): δ 7.00 (d, *J* = 6.8 Hz, 2H), 6.82 (s, 2H), 6.77 (d, *J* = 6.8 Hz, 2H), 2.59-2.72 (m, 2H), 2.59 (s, 6H), 2.32 (s, 6H), 2.25 (s, 6H), 2.22-2.37 (m, 2H), 2.07-2.20 (m, 2H).

Example 18: Synthesis of *rac*-tetramethylsilylene-bis[4-cyclopropyl-2-methylinden-1-yl]hafnium dichloride (18)

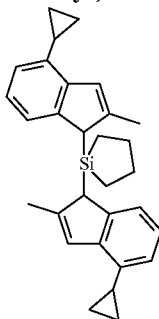
7-Cyclopropyl-2-methyl-1*H*-indene



[00296] A mixture of 2.00 g (9.57 mmol) of 4/7-bromo-2-methyl-1*H*-indene, 0.11 g (0.19 mmol) of Pd(dba)₂, 0.077 g (0.38 mmol) of *t*Bu₃P, and 15 ml of THF was stirred for 5 minutes at room temperature, and then 21.7 ml (14.4 mmol) of 0.66 M *n*PrMgBr in THF was added for 5 minutes. The obtained mixture was stirred for 12 h at 60°C and then poured into 50 ml of

aqueous NH_4Cl . The organic layer was separated, and the aqueous layer was extracted with 3 x 20 ml of ethyl acetate. The combined organic extract was washed with 30 ml of brine, dried over Na_2SO_4 , and evaporated to dryness. Crude product was purified by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexanes). Yield 1.55 g (95%) of colorless oil. Calcd. for $\text{C}_{13}\text{H}_{14}$: C, 91.71; H, 8.29. Found: C, 91.60; H, 8.43. ^1H NMR (CDCl_3): δ 7.14 (m, 1H, 5-H in indenyl), 7.07 (m, 1H, 4-H in indenyl), 6.64 (m, 1H, 7-H in indenyl), 6.49 (m, 1H, 3-H in indenyl), 3.35 (s, 2H, 1,1-H in indenyl), 2.18 (m, 3H, Me), 1.94 (m, 1H, 1-H in ^iPr), 0.94 (m, 2H, 2,3-H in ^iPr), 0.73 (m, 2H, 2',3'-H in ^iPr).

1,1-Bis(4-cyclopropyl-2-methyl-1*H*-inden-1-yl)silolane

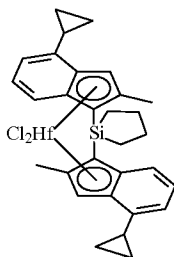


10

[00297] To a solution of 5.40 g (32.0 mmol) of 7-cyclopropyl-2-methyl-1*H*-indene in 100 ml of ether cooled to 0°C , 12.8 ml (32.0 mmol) of 2.5 M $n\text{BuLi}$ in hexanes was added. This mixture was stirred for 12 h at room temperature, and then 11 ml of THF was added. The obtained mixture was cooled to -60°C , and 0.14 g (1.60 mmol) of CuCN was added. Then, this mixture was warmed to -30°C , stirred for 30 minutes at this temperature, cooled to -60°C , and 2.10 ml (16.0 mmol) of 1,1-dichlorosilolane was added. The resulting mixture was stirred for 24 h at room temperature, and then 40 ml of water was added. The organic layer was separated, the aqueous layer was extracted with 2 x 50 ml of ethyl acetate. The combined organic extract was dried over Na_2SO_4 and then evaporated to dryness. Crude product was purified by flash chromatography on silica gel 60 (40-63 μm ; eluent: hexanes-dichloromethane = 10:1, vol.). Yield 4.73 g (70%) of yellow oil of a mixture of *rac*- and *meso*-compounds. Calcd. for $\text{C}_{30}\text{H}_{34}\text{Si}$: C, 85.25; H, 8.11. Found: C, 85.39; H, 8.27. ^1H NMR (CDCl_3): δ 7.19 (m), 6.93-7.03 (m), 6.83 (m), 6.75-6.78 (m), 3.37 (s), 3.35 (s), 2.16 (s), 2.04-2.10 (m), 1.30-1.35 (m), 1.12-1.19 (m), 1.04-1.10 (m), 0.86-0.95 (m), 0.70-0.77 (m), 0.62-0.68 (m), 0.48-0.58 (m), 0.38 (m).

25

***rac*-cyclotetramethylsilylene-bis[4-cyclopropyl-2-methylinden-1-yl]hafnium dichloride (18)**



[00298] To a solution of 1.60 g (3.78 mmol) of 1,1-bis(4-cyclopropyl-2-methyl-1*H*-inden-1-yl)silolane in 50 ml of ether cooled to 0°C, 3.05 ml (7.56 mmol) of 2.5 M ^{*n*}BuLi in hexanes was added. This mixture was stirred for 12 h at room temperature, then cooled to -50°C, and 1.75 g (3.78 mmol) of HfCl₄(THF)₂ was added. The obtained mixture was stirred overnight at room temperature and then filtered through glass frit (G4). The precipitate was poured into 100 ml of hot toluene, and the formed hot suspension was filtered through a Celite pad. The filtrate was concentrated in vacuum to 70 ml. Crystals precipitated from this solution at room temperature were collected and dried in vacuum. The obtained crystalline powder (in fact, a ca. 1 to 1 mixture of *rac*- and *meso*-complexes) was re-crystallized from 180 ml of toluene-ether (2:1, vol.) to give 0.51 g (20%) of pure *rac*-complex as yellow crystalline material. Calcd. for C₃₀H₃₂Cl₂HfSi: C, 53.77; H, 4.81. Found: C, 53.54; H, 4.69. ¹H NMR (CD₂Cl₂): δ 7.46 (m, 2H, 7-H in indenyl), 6.87-6.94 (m, 4H, 5,6-H in indenyl), 6.83 (m, 2H, 3-H in indenyl), 2.28 (s, 6H, 2-Me), 2.11 (m, 2H, 3/3'-H in silolane), 1.87-2.01 (m, 8H, 1-H in ^{*c*}Pr, 2,2'-H and 3/3'-H in silolane), 0.81-0.93 (m, 6H, 2/3-H in ^{*c*}Pr), 0.67-0.73 (m, 2H, 2/3-H in ^{*c*}Pr).

[00299] Comparative compounds used in the following polymerization examples include: *rac*-(PhC₂H₄)₂Si(4,7-Me₂Ind)₂HfMe₂ (Catalyst ID in tables 4a and 4b, C-A), *rac*-(n-C₆H₁₃)₂Si[4,7-Me₂Ind]₂HfMe₂ (Catalyst ID in tables 4a and 4b, C-B), *rac*-(Me₂Si)₂[4,7-Me₂Ind]₂HfMe₂ (Catalyst ID in tables 4a and 4b, C-C), *rac*-CH₂CH₂[5-*t*-Bu-7-MeInd]₂HfMe₂ (Catalyst ID in tables 4a and 4b, C-D), *rac*-Me₂Si[2-Me-4-PhInd]₂ZrMe₂ (Catalyst ID in tables 4a and 4b, C-E), wherein Ind = indenyl, Me = methyl, n-C₆H₁₃ = n-hexyl, Ph = phenyl, PhC₂H₄ = phenethyl, *t*Bu = tert-butyl, CH₂CH₂ = ethylene.

Polymerization Examples

[00300] Solutions of the pre-catalysts (Compounds 1 to 18, prepared above, or comparative compounds C-A to C-E) were made using toluene (ExxonMobil Chemical—anhydrous, stored under N₂) (98%). Pre-catalyst solutions were typically 0.5 mmol/L. When noted, some pre-catalysts were pre-alkylated using triisobutyl aluminum (TiBAI, neat, AkzoNobel); prealkylation was performed by first dissolving the pre-catalyst in the appropriate amount of toluene, and then adding 20 equivalents of TiBAI such that the final pre-catalyst solution was 0.5 mmol precatalyst/L and 10 mmol TiBAI/L.

[00301] Solvents, polymerization grade toluene and/or isohexanes were supplied by ExxonMobil Chemical Co. and are purified by passing through a series of columns: two 500 cc Oxyclear cylinders in series from Labclear (Oakland, Calif.), followed by two 500 cc columns in series packed with dried 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), and two 500 cc columns in series packed with dried 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company).

[00302] 1-octene (98%) (Aldrich Chemical Company) was dried by stirring over NaK overnight followed by filtration through basic alumina (Aldrich Chemical Company,

Brockman Basic 1). 1-Decene was purified by mixing 1 liter of untreated raw material with 20 grams of activated 13X molecular sieve, (which was activated by calcining at 200°C for at least four hours under a stream of purging dry nitrogen gas), and 10 grams of Oxi-Clear catalyst (purchased from Altech Associates, Inc or Deerfield, Ill. 60115) for at least two days
5 inside a glove box under a dry inert atmosphere of nitrogen. The molecular sieve and deoxygenation catalyst were then removed by filtration in the glove box to provide purified 1-decene. Alternatively, the feeds were purified by passing through a bed of activated 13X molecular sieve alone under nitrogen atmosphere.

[00303] Polymerization grade ethylene was used and further purified by passing it through a
10 series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, Calif.) followed by a 500 cc column packed with dried 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), and a 500 cc column packed with dried 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company).

[00304] Polymerization grade propylene was used and further purified by passing it through a series of columns: 2250 cc Oxiclear cylinder from Labclear followed by a 2250 cc column
15 packed with 3 Å mole sieves (8-12 mesh; Aldrich Chemical Company), then two 500 cc columns in series packed with 5 Å mole sieves (8-12 mesh; Aldrich Chemical Company), then a 500 cc column packed with Selexsorb CD (BASF), and finally a 500 cc column packed with Selexsorb COS (BASF).

[00305] Activation of the pre-catalysts was either by methylalumoxane (MAO, 10 wt% in
20 toluene, Albemarle Corp.), dimethylanilinium tetrakis(perfluorophenyl)borate (Boulder Scientific and Albemarle Corp) or dimethylanilinium tetrakis(perfluoronaphthyl)borate (Albemarle Corp). MAO was used as a 0.5 wt % or 1.0 wt % in toluene solution. Micromoles of MAO reported in the experimental section are based on the micromoles of aluminum in MAO. The formula weight of MAO is 58.0 grams/mole. Dimethylanilinium
25 tetrakis(perfluorophenyl)borate and dimethylanilinium tetrakis(perfluoronaphthyl)borate were typically used as a 5 mmol/L solution in toluene.

[00306] For polymerization runs using dimethylanilinium tetrakis(perfluorophenyl)borate or dimethylanilinium tetrakis(perfluoronaphthyl)borate, tri-n-octylaluminum (TnOAl, Neat, AkzoNobel) was also used as a scavenger prior to introduction of the activator and pre-
30 catalyst into the reactor. TnOAl was typically used as a 5 mmol/L solution in toluene.

Reactor Description and Preparation:

[00307] Polymerizations were conducted in an inert atmosphere (N₂) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal
35 volume of reactor=23.5 mL for C₂, C₂/C₈, C₂/C₁₀, C₁₀, and C₈ runs; 22.5 mL for C₃ and C₂/C₃ runs), septum inlets, regulated supply of nitrogen, ethylene and propylene, and equipped with disposable PEEK mechanical stirrers (800 RPM). The autoclaves were prepared by purging with dry nitrogen at 110°C or 115°C for 5 hours and then at 25°C for 5 hours.

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

[00308] The reactor was prepared as described above, and then purged with ethylene. For MAO activated runs, toluene, 1-octene (100 μ L when used), and activator (MAO) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (80°C) and charged with ethylene to process pressure (75 psig=618.5 kPa or 200 psig=1480.3 kPa) while stirring at 800 RPM. The pre-catalyst solution was then added via syringe to the reactor at process conditions. For dimethylanilinium tetrakis(perfluorophenyl)borate activated runs, toluene, 1-octene (100 μ L or 200 μ L when used) and scavenger (TnOAl, 0.5 μ mol) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (80°C) and charged with ethylene to process pressure (75 psig=618.5 kPa or 200 psig=1480.3 kPa) while stirring at 800 RPM. The activator solution, followed by the pre-catalyst solution, was injected via syringe to the reactor at process conditions. Ethylene was allowed to enter (through the use of computer controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure (+/-2 psig). Reactor temperature was monitored and typically maintained within +/-1°C. Polymerizations were halted by addition of approximately 50 psi O₂/Ar (5 mole % O₂) gas mixture to the autoclave for approximately 30 seconds. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been added (maximum quench value in psi) or for a maximum of 30 minutes polymerization time (maximum quench time). Afterwards, the reactors were cooled and vented. Polymers were isolated after the solvent was removed in-vacuo. Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol transition metal compound per hour of reaction time (g/mmol•hr). Ethylene homopolymerization runs are summarized in Table 1, and ethylene/1-octene copolymerization runs are summarized in Tables 2a and 2b.

25 Ethylene/1-decene Copolymerization (ED):

[00309] The reactor was prepared as described above, and then purged with ethylene. Toluene (4.0 ml), 1-decene (1.0 ml) and scavenger (TnOAl, 1.0 μ mol) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature (T = 80, 100 or 120°C) and charged with ethylene to process pressure (50 psig=446.1 kPa) while stirring at 800 RPM. The activator solution, followed by the pre-catalyst solution, was injected via syringe to the reactor at process conditions. Ethylene was allowed to enter (through the use of computer controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure (+/-2 psig). Reactor temperature was monitored and typically maintained within +/-1°C. Polymerizations were halted by addition of approximately 50 psi O₂/Ar (5 mole % O₂) gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been added (a max quench value of 20 psi) or for a maximum of 30 minutes polymerization time. The reactors were cooled and vented. The

polymers were isolated after the solvent was removed in-vacuo. The actual polymerization time (quench time) and yields are reported in Table 3. Reported yields include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol transition metal compound per hour of reaction time (g/mmol•hr).

5 Propylene Polymerization (PP):

[00310] The reactor was prepared as described above, then heated to 40°C, and then purged with propylene gas at atmospheric pressure. For MAO activated runs, toluene or isohexane, MAO, and liquid propylene (1.0 mL) were added via syringe. The reactor was then heated to process temperature (70°C or 100°C) while stirring at 800 RPM. The pre-catalyst solution was added via syringe with the reactor at process conditions. For dimethylanilinium tetrakis(perfluorophenyl)borate or dimethylanilinium tetrakis(perfluoronaphthyl)borate activated runs, isohexanes, liquid propylene (1.0 mL) and scavenger (TnOAl, 0.5 μmol) were added via syringe. The reactor was then brought to process temperature (70°C or 100°C) while stirring at 800 RPM. The activator solution, followed by the pre-catalyst solution, were injected via syringe to the reactor at process conditions. Reactor temperature was monitored and typically maintained within $\pm 1^\circ\text{C}$. Polymerizations were halted by addition of approximately 50 psi O₂/Ar (5 mole % O₂) gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched based on a predetermined pressure loss of approximately 8-20 psi (max quench value in psi) or for a maximum of 30 minutes polymerization time for experiments listed in Table 5a, or for a maximum of 45 minutes polymerization time for experiments listed in Table 4a. The reactors were cooled and vented. The polymers were isolated after the solvent was removed in-vacuo. The actual quench time (s) and max quench value (psi) are reported. Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol transition metal compound per hour of reaction time (g/mmol•hr). Propylene homopolymerization examples are reported in Tables 4a and 4b (Ex# starting with PP or CPP only) and in Tables 5a and 5b.

25 Ethylene-Propylene Copolymerization (EP):

[00311] The reactor was prepared as described above, then heated to 40°C, and then purged with ethylene gas at atmospheric pressure. The listed ethylene pressure (10, 20, 40, 60 or 80 psid) was then added to the reactor. Isohexanes and scavenger (TnOAl, 0.5 μmol) were added via syringe. The stirrers were then started and maintained at 800 RPM. Liquid propylene (1.0 ml) was then injected into the reactor. The reactor was then brought to process temperature (70°C). The activator solution, followed by the pre-catalyst solution, was injected via syringe to the reactor at process conditions. 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) gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched based on a predetermined pressure loss of approximately 10-20 psi or for a maximum of 45 minutes polymerization time. The reactors were cooled and

vented. The polymer was isolated after the solvent was removed in-vacuo. The quench time (s) and max quench value (psi) are reported in Tables 4a for each run. Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol transition metal compound per hour of reaction time (g/mmol•hr).
5 Ethylene/propylene copolymerization examples are collected in Tables 4a and 4b.

1-Decene (PD) and 1-Octene (PO) Homopolymerizations:

[00312] The reactor was prepared as described above. Toluene (4.0 ml), 1-decene or 1-octene (1.0 ml) and scavenger (TnOAl, 2.0 μ mol) were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to process temperature ($T = 80, 100$
10 or 120°C) while stirring at 800 RPM. The activator solution (0.044 μ mol), followed by the pre-catalyst solution (0.040 μ mol), was injected via syringe to the reactor at process conditions. The reactor temperature was monitored and typically maintained within $\pm 1^{\circ}\text{C}$. The polymerization was halted after 120 minutes of reaction time. The reactor was cooled and
15 vented. The polymer was isolated after the solvent was removed in-vacuo. Reported yields include total weight of polymer and residual catalyst. Catalyst activity is reported as grams of polymer per mmol transition metal compound per hour of reaction time (g/mmol•hr). Examples of 1-decene homopolymerizations and 1-octene homopolymerizations are collected in Table 7.

Polymer Characterization

[00313] For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity from Sigma-Aldrich) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99% from Aldrich) at 165°C in a shaker oven for approximately 3 hours. The typical concentration of polymer in solution was between 0.1 to 0.9 mg/mL with a BHT concentration of 1.25 mg BHT/mL of TCB. Samples were cooled to
25 135°C for testing.

[00314] High temperature size exclusion chromatography was performed using an automated "Rapid GPC" system as described in U.S. Patent Nos. 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
30 molecular weight (Mw) and number average molecular weight (Mn)) and molecular weight distribution ($\text{MWD} = \text{Mw}/\text{Mn}$), 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 and calibrated using polystyrene standards (Polymer Laboratories: Polystyrene Calibration Kit S-M-10: Mp (peak
35 Mw) between 5000 and 3,390,000). Samples (250 μ L of a polymer solution in TCB were injected into the system) were run at an eluent flow rate of 2.0 mL/minute (135°C sample temperatures, 165°C oven/columns) using three Polymer Laboratories: PLgel 10 μ m Mixed-B 300 x 7.5mm columns in series. No column spreading corrections were employed. Numerical

analyses were performed using Epoch® software available from Symyx Technologies. The molecular weights obtained are relative to linear polystyrene standards. Molecular weight data is reported in Tables 1, 2b, 3, 4b, 5b and 7 under the headings Mn, Mw and PDI as defined above.

5 [00315] Differential Scanning Calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220°C for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220°C at a rate of 100°C/minute and then cooled at a rate of 50°C/minute. Melting points were collected during the heating period. The results are reported in the Tables
10 1, 2b, 4b and 5b under the heading, T_m (°C).

[00316] Samples for infrared analysis were prepared by depositing the stabilized polymer solution onto a silanized wafer (Part number S10860, Symyx). By this method, approximately between 0.12 and 0.24 mg of polymer is deposited on the wafer cell. The samples were subsequently analyzed on a Bruker Equinox 55 FTIR spectrometer equipped with Pikes' MappIR specular reflectance sample accessory. Spectra, covering a spectral range of 5000 cm^{-1}
15 to 500 cm^{-1} , were collected at a 2 cm^{-1} resolution with 32 scans.

[00317] For ethylene-1-octene copolymers, the wt% octene in the copolymer was determined via measurement of the methyl deformation band at $\sim 1375 \text{ cm}^{-1}$. The peak height of this band was normalized by the combination and overtone band at $\sim 4321 \text{ cm}^{-1}$, which
20 corrects for path length differences. The normalized peak height was correlated to individual calibration curves from ^1H NMR data to predict the wt% octene content within a concentration range of ~ 2 to 35 wt% for octene. Typically, R^2 correlations of 0.98 or greater are achieved. These numbers are reported in Table 2b under the heading C8 wt%.

[00318] For ethylene-propylene copolymers, the wt.% ethylene is determined via
25 measurement of the methylene rocking band ($\sim 770 \text{ cm}^{-1}$ to 700 cm^{-1}). The peak area of this band is normalized by sum of the band areas of the combination and overtone bands in the 4500 cm^{-1} to 4000 cm^{-1} range. The normalized band area is then correlated to a calibration curve from ^{13}C NMR data to predict the wt.% ethylene within a concentration range of ~ 5 to 40 wt.%. Typically, R^2 correlations of 0.98 or greater are achieved. These numbers are
30 reported in Table 4b under the heading C2 wt.%.

[00319] ^{13}C NMR spectroscopy was used to characterize some polypropylene polymer samples produced in experiments collected in Tables 5a and 5b. Unless otherwise indicated the polymer samples for ^{13}C NMR spectroscopy were dissolved in d_2 -1,1,2,2-tetrachloroethane and the samples were recorded at 125°C using a NMR spectrometer with a
35 ^{13}C NMR frequency of 150 MHz. Polymer resonance peaks are referenced to $\text{mmmm}=21.8$ ppm. Calculations involved in the characterization of polymers by NMR follow the work of F. A. Bovey in "Polymer Conformation and Configuration" Academic Press, New York 1969 and J. Randall in "Polymer Sequence Determination, Carbon-13 NMR Method", Academic Press,

New York, 1977.

[00320] The stereodefects measured as “stereo defects/10,000 monomer units” are calculated from the sum of the intensities of mmrr, mmrm+rrmr, and rmmr resonance peaks times 5000. The intensities used in the calculations are normalized to the total number of monomers in the sample. Methods for measuring 2,1 regio defects/10,000 monomers and 1,3 regio defects/10,000 monomers follow standard methods. Additional references include Grassi, A. et.al. *Macromolecules*, **1988**, 21, 617-622 and Busico et.al. *Macromolecules*, **1994**, 27, 7538-7543. The average meso run length = $10000/[(\text{stereo defects}/10000 \text{ C}) + (2,1\text{-regio defects}/10000 \text{ C}) + (1,3\text{-regio-defects}/10000 \text{ C})]$.

[00321] For some samples, polymer end-group analysis was determined by ^1H NMR using a Varian Unity+400 MHz instrument run with a single 30° flip angle, RF pulse. 120 pulses with a delay of 8 seconds between pulses were signal averaged. The polymer sample was dissolved in heated d_2 -1,1,2,2-tetrachloroethane and signal collection took place at 120°C . Vinylenes were measured as the number of vinylenes per 1000 carbon atoms using the resonances between 5.55-5.31 ppm. Trisubstituted end-groups (“trisubs”) were measured as the number of trisubstituted groups per 1000 carbon atoms using the resonances between 5.30-5.11 ppm. Vinyl end-groups were measured as the number of vinyls per 1000 carbon atoms using the resonances between 5.13-4.98 ppm. Vinylidene end-groups were measured as the number of vinylidenes per 1000 carbon atoms using the resonances between 4.88-4.69 ppm. The values reported in Table 4b are % vinylene, % trisubstituted (% trisub), % vinyl and % vinylidene where the percentage is relative to the total olefinic unsaturation per 1000 carbon atoms.

[00322] Polymerization results are collected in Tables 1, 2a, 2b, 3, 4a, 4b, 5a, 5b, 6 and 7 below. “Ex#” stands for example number. Under the Ex# column heading, the following abbreviations are defined: PE = polyethylene, EO = ethylene-1-octene, ED = ethylene-1-decene, PP = polypropylene, EP = ethylene-propylene; CPP = comparative polypropylene, CEP = comparative ethylene-propylene, PD = polydecene, and PO = polyoctene. Examples starting with a “C” as in CPP and CEP are comparative examples. “Cat ID” identifies the pre-catalyst used in the experiment. Corresponding numbers identifying the pre-catalyst are located in the synthetic experimental section. Comparative pre-catalysts are named with a “C” followed by a dash and a letter, such as C-A. An asterisk next to the Cat ID number indicates that the pre-catalyst was pre-alkylated with 20 equivalents of TiBAI. “Act ID” identifies the activator used. “A” corresponds to MAO, “B” corresponds to dimethylanilinium tetrakis(perfluorophenyl)borate, and “C” corresponds to dimethylanilinium tetrakis(perfluoronaphthyl)borate. “Cat (μmol)” is the amount of pre-catalyst added to the reactor. For all experiments using MAO as the activator, the molar ratio of activator/pre-catalyst was 500. For all experiments using borate activators B or C, the molar ratio of activator/pre-catalyst was 1.1. $T(^{\circ}\text{C})$ is the polymerization temperature which was typically maintained within $\pm 1^{\circ}\text{C}$. “Yield” is polymer yield, and is not corrected for catalyst residue.

“Quench time (s)” is the actual duration of the polymerization run in seconds. “Quench Value (psi)” for ethylene based polymerization runs is the set maximum amount of ethylene uptake (conversion) for the experiment. If a polymerization quench time is less than the maximum time set, then the polymerization ran until the set maximum value of ethylene uptake was reached. For propylene, 1-octene or 1-decene homopolymerization runs, quench value indicates the maximum set pressure loss (conversion) of propylene, 1-octene, or 1-decene during the polymerization.

Table 1: Ethylene polymerization examples

Ex#	Cat ID	Cat (μmol)	Act ID	quench time (s)	yield (g)	Activity (g/ mmol·hr)	Mn	Mw	PDI	T _m (°C)
PE-1	2	0.025	B	101	0.0868	123,632	1,070,846	1,518,449	1.42	136.2
PE-2	2	0.025	B	158	0.0821	74,778	1,057,208	1,512,708	1.43	133.6
PE-3	2	0.025	B	101	0.0873	125,087	1,019,201	1,629,328	1.60	135.9
PE-4	2	0.025	A	255	0.0830	46,834	970,754	1,474,822	1.52	136.1
PE-5	2	0.025	A	304	0.0824	38,993	1,030,988	1,535,122	1.49	133.9
PE-6	2	0.025	A	263	0.0821	44,918	1,019,870	1,540,932	1.51	na
PE-7	3	0.025	A	230	0.1233	77,321	882,914	1,845,483	2.09	135.6
PE-8	3	0.025	A	240	0.0811	48,719	824,911	1,620,163	1.96	135.4
PE-9	3	0.025	A	228	0.0813	51,345	753,991	1,591,038	2.11	135.0
PE-10	4	0.025	A	263	0.0859	47,068	651,576	1,196,234	1.84	135.7
PE-11	4	0.025	A	1538	0.1927	18,047	662,420	1,315,190	1.99	135.2
PE-12	4	0.025	A	256	0.0854	48,034	599,564	1,112,115	1.85	135.7
PE-13	5	0.025	A	266	0.0909	49,154	845,060	1,521,045	1.80	135.0
PE-14	5	0.025	A	204	0.0841	59,286	805,419	1,571,219	1.95	135.7
PE-15	5	0.025	A	283	0.0924	46,990	965,331	1,772,930	1.84	135.6
PE-16	7	0.025	A	196	0.0843	61,903	537,979	1,041,401	1.94	135.0
PE-17	7	0.025	A	245	0.0852	49,995	537,403	952,229	1.77	134.4
PE-18	7	0.025	A	216	0.0808	53,842	537,558	982,698	1.83	134.8
PE-19	7*	0.025	B	267	0.0841	45,425	643,285	1,376,345	2.14	136.9
PE-20	7*	0.025	B	288	0.0808	40,470	794,629	1,478,512	1.86	135.6
PE-21	7*	0.025	B	252	0.0770	44,035	578,035	1,208,193	2.09	137.1
PE-22	8	0.025	A	194	0.0926	68,699	674,417	948,245	1.41	134.4
PE-23	8	0.025	A	109	0.0884	117,000	655,584	929,683	1.42	136.2
PE-24	8	0.025	A	226	0.0930	59,204	710,923	1,013,839	1.43	134.0
PE-25	8*	0.025	B	191	0.0846	63,883	538,250	1,025,989	1.91	136.6
PE-26	8*	0.025	B	262	0.0826	45,347	547,733	1,012,506	1.85	136.2
PE-27	8*	0.025	B	230	0.0801	50,215	505,738	937,411	1.85	99.6
PE-28	9	0.025	A	217	0.0839	55,727	509,860	847,920	1.66	136.3
PE-29	9	0.025	A	112	0.0812	104,774	470,640	790,946	1.68	136.5
PE-30	9	0.025	A	190	0.0845	64,143	510,010	855,630	1.68	136.0
PE-31	9*	0.030	B	204	0.0834	49,035	669,138	1,379,705	2.06	136.7
PE-32	9*	0.030	B	234	0.0806	41,298	605,305	1,174,472	1.94	136.2
PE-33	9*	0.030	B	210	0.0802	45,785	552,745	1,116,826	2.02	137.3
PE-34	10	0.025	A	246	0.0537	31,485	775,046	1,172,312	1.51	137.6
PE-35	10	0.025	A	273	0.0505	26,657	749,725	1,123,596	1.50	138.3
PE-36	10	0.025	A	187	0.0497	38,251	779,237	1,162,187	1.49	137.8

PE-37	10*	0.025	B	210	0.0638	43,665	648,726	1,255,447	1.94	138.2
PE-38	10*	0.025	B	279	0.0568	29,274	697,568	1,261,564	1.81	137.9
PE-39	10*	0.025	B	201	0.0620	44,529	665,459	1,380,895	2.08	138.6
PE-40	11	0.025	A	170	0.0915	77,324	818,758	1,173,011	1.43	136.7
PE-41	11	0.025	A	190	0.0943	71,545	774,419	1,101,164	1.42	137.7
PE-42	12	0.025	A	327	0.0730	32,166	1,120,389	1,536,754	1.37	134.4
PE-43	12	0.025	A	303	0.0780	37,057	1,125,740	1,574,548	1.40	136.1
PE-44	12	0.025	A	326	0.0760	33,601	1,177,671	1,623,550	1.38	134.6
PE-45	12	0.020	B	113	0.0856	135,873	1,387,654	2,076,448	1.50	134.3
PE-46	12	0.020	B	26	0.0952	649,091	1,238,196	2,148,569	1.74	136.2
PE-47	12	0.020	B	34	0.0878	471,761	na	na	na	134.5
PE-48	13	0.025	A	207	0.0923	64,364	896,000	1,241,195	1.39	135.7
PE-49	13	0.025	A	283	0.0901	45,911	852,740	1,202,268	1.41	136.7
PE-50	13	0.025	A	103	0.0690	96,372	879,596	1,191,288	1.35	136.0
PE-51	14	0.025	A	354	0.0809	32,871	981,851	1,384,790	1.41	136.1
PE-52	14	0.025	A	390	0.0789	29,140	998,760	1,382,159	1.38	134.8
PE-53	14	0.025	A	380	0.0818	30,990	928,635	1,450,055	1.56	77.1
PE-54	14	0.020	B	30	0.0994	592,450	1,381,118	2,383,408	1.73	136.3
PE-55	14	0.020	B	28	0.0885	573,022	1,183,449	2,187,415	1.85	134.8
PE-56	14	0.020	B	18	0.1016	1,045,029	1,209,575	2,235,566	1.85	135.9
PE-57	15	0.025	A	90	0.0980	157,676	867,492	1,857,310	2.14	134.1
PE-58	15	0.025	A	72	0.1057	212,285	828,469	1,876,473	2.26	135.8
PE-59	15	0.025	A	123	0.0995	116,583	900,258	1,923,671	2.14	133.9
PE-60	15*	0.025	B	91	0.1063	167,842	1,084,267	1,888,013	1.74	135.7
PE-61	15*	0.025	B	119	0.0871	105,576	1,824,818	2,923,672	1.60	134.3
PE-62	15*	0.025	B	80	0.0892	159,960	1,022,462	1,705,534	1.67	135.8
PE-63	16	0.020	A	87	0.0908	188,078	995,450	1,551,403	1.56	135.4
PE-64	16	0.020	A	118	0.0891	136,031	1,064,337	1,614,983	1.52	134.6
PE-65	16	0.020	A	80	0.0926	209,397	1,513,302	1,932,804	1.28	135.6
PE-66	16	0.025	B	48	0.0944	282,025	1,407,310	1,983,886	1.41	136.0
PE-67	16	0.025	B	99	0.0828	120,925	1,217,069	1,894,685	1.56	134.5
PE-68	16	0.025	B	57	0.0871	219,657	1,277,577	2,015,795	1.58	136.2
PE-69	17	0.025	A	313	0.0798	36,725	806,301	1,767,029	2.19	135.2
PE-70	17	0.025	A	293	0.0788	38,781	844,621	1,729,780	2.05	133.6
PE-71	17	0.025	A	318	0.0761	34,471	784,682	1,680,269	2.14	134.9
PE-72	17*	0.025	B	167	0.0841	72,735	1,171,148	1,879,924	1.61	135.4
PE-73	17*	0.025	B	113	0.0857	109,404	1,194,673	1,886,194	1.58	136.5
PE-74	17*	0.025	B	142	0.0849	86,217	1,036,655	1,622,213	1.56	135.6
PE-75	18	0.025	A	306	0.0881	41,418	695,123	1,437,092	2.07	133.4
PE-76	18	0.025	A	296	0.0839	40,871	679,857	1,459,137	2.15	134.7
PE-77	18	0.025	A	277	0.0855	44,512	668,907	1,322,131	1.98	133.9
PE-78	18*	0.025	B	375	0.0812	31,189	811,715	1,462,489	1.80	135.5
PE-79	18*	0.025	B	235	0.0740	45,306	609,737	1,189,969	1.95	136.7
PE-80	18*	0.025	B	232	0.0825	51,295	947,685	1,734,465	1.83	135.0

[00323] For all runs, the total amount of toluene added to the reactor was 5 ml, the ethylene pressure was maintained at 75 psig of ethylene, and the maximum quench value was set to 20 psi. All polymerization examples quenched with ethylene uptake (maximum or max quench value) vs. maximum polymerization time. “na” indicates that the data was not available.

Table 2a: Ethylene-Octene copolymerization examples - Part 1

Ex#	Cat ID	Act ID	Cat (μmol)	C2 (psig)	1-octene (μL)	Max Quench value (psi)	quench time (s)	yield (g)	Activity (g/ $\text{mmol}\cdot\text{hr}$)
EO-1	2	A	0.025	75	100	20	505	0.0847	24,133
EO-2	2	A	0.025	75	100	20	464	0.0890	27,633
EO-3	2	A	0.025	75	100	20	467	0.0874	26,961
EO-4	2	A	0.025	200	100	15	139	0.1802	187,356
EO-5	2	A	0.025	200	100	15	140	0.1735	178,712
EO-6	2	B	0.025	75	100	20	108	0.1171	156,714
EO-7	2	B	0.025	75	100	20	157	0.1180	108,023
EO-8	2	B	0.025	75	100	20	166	0.1158	100,212
EO-9	2	B	0.025	200	100	15	55	0.1983	519,185
EO-10	2	B	0.025	200	100	15	43	0.1673	558,961
EO-11	2	B	0.025	200	100	15	45	0.1858	594,560
EO-12	3	A	0.025	75	100	20	358	0.0705	28,368
EO-13	3	A	0.025	75	100	20	313	0.0626	28,826
EO-14	3	A	0.025	75	100	20	500	0.0830	23,894
EO-15	3	A	0.025	200	100	15	207	0.1261	87,696
EO-16	3	A	0.025	200	100	15	212	0.1463	99,168
EO-17	3	A	0.025	200	100	15	201	0.1525	109,521
EO-18	4	A	0.025	75	100	20	137	0.0606	63,543
EO-19	4	A	0.025	75	100	20	161	0.0574	51,377
EO-20	4	A	0.025	75	100	20	140	0.0553	56,811
EO-21	4	A	0.025	200	100	15	169	0.1705	145,364
EO-22	4	A	0.025	200	100	15	150	0.1697	162,652
EO-23	4	A	0.025	200	100	15	164	0.1697	148,778
EO-24	5	A	0.025	75	100	20	280	0.0937	48,258
EO-25	5	A	0.025	75	100	20	173	0.0770	64,156
EO-26	5	A	0.025	75	100	20	345	0.0992	41,367
EO-27	5	A	0.025	200	100	15	136	0.1632	172,293
EO-28	5	A	0.025	200	100	15	131	0.1713	188,270
EO-29	5	A	0.025	200	100	15	139	0.1625	168,116
EO-30	7	A	0.025	75	100	20	115	0.0647	81,086
EO-31	7	A	0.025	75	100	20	100	0.0695	99,781
EO-32	7	A	0.025	75	100	20	101	0.0666	95,049
EO-33	7	A	0.025	200	100	15	125	0.1744	200,268
EO-34	7	A	0.025	200	100	15	130	0.1696	188,444
EO-35	7	A	0.025	200	100	15	68	0.0818	174,507
EO-36	7*	B	0.025	75	100	20	301	0.1022	48,893
EO-37	7*	B	0.025	75	100	20	331	0.1005	43,788
EO-38	7*	B	0.025	200	100	15	107	0.1698	227,877
EO-39	7*	B	0.025	200	100	15	121	0.1675	200,166
EO-40	7*	B	0.025	200	100	15	99	0.1607	234,456
EO-41	8	A	0.025	75	100	20	138	0.0621	64,613
EO-42	8	A	0.025	75	100	20	136	0.0583	61,684
EO-43	8	A	0.025	75	100	20	129	0.0572	64,050
EO-44	8	A	0.025	200	100	15	141	0.1471	150,017
EO-45	8	A	0.025	200	100	15	143	0.1675	169,144

EO-46	8	A	0.025	200	100	15	147	0.1690	165,890
EO-47	8*	B	0.025	75	100	20	210	0.1010	69,422
EO-48	8*	B	0.025	75	100	20	134	0.0636	68,551
EO-49	8*	B	0.025	75	100	20	142	0.0861	87,067
EO-50	8*	B	0.025	200	100	15	139	0.1817	188,643
EO-51	8*	B	0.025	200	100	15	133	0.1779	192,180
EO-52	8*	B	0.025	200	100	15	142	0.1802	182,609
EO-53	9	A	0.025	75	100	20	94	0.0580	88,946
EO-54	9	A	0.025	75	100	20	101	0.0583	83,203
EO-55	9	A	0.025	75	100	20	99	0.0572	83,538
EO-56	9	A	0.025	200	100	15	135	0.1683	179,122
EO-57	9	A	0.025	200	100	15	118	0.1670	203,452
EO-58	9	A	0.025	200	100	15	98	0.1465	215,046
EO-59	9*	B	0.030	75	100	20	580	0.0315	6,523
EO-60	9*	B	0.030	75	100	20	234	0.1027	52,689
EO-61	9*	B	0.030	75	100	20	101	0.0655	77,976
EO-62	9*	B	0.030	200	100	15	234	0.1586	81,229
EO-63	9*	B	0.030	200	100	15	164	0.1611	118,239
EO-64	9*	B	0.030	200	100	15	143	0.1447	121,597
EO-65	10	A	0.025	75	100	20	288	0.0334	16,694
EO-66	10	A	0.025	75	100	20	341	0.0327	13,805
EO-67	10	A	0.025	75	100	20	315	0.0318	14,546
EO-68	10	A	0.025	200	100	15	174	0.0777	64,340
EO-69	10	A	0.025	200	100	15	118	0.0487	59,481
EO-70	10	A	0.025	200	100	15	127	0.0601	68,145
EO-71	10*	B	0.025	75	100	20	366	0.0351	13,825
EO-72	10*	B	0.025	75	100	20	396	0.0368	13,392
EO-73	10*	B	0.025	75	100	20	351	0.0349	14,310
EO-74	10*	B	0.025	200	100	15	213	0.0815	54,995
EO-75	10*	B	0.025	200	100	15	215	0.0384	25,695
EO-76	10*	B	0.025	200	100	15	160	0.0789	71,010
EO-77	11	A	0.025	75	100	20	197	0.0723	52,902
EO-78	11	A	0.025	75	100	20	179	0.0633	51,037
EO-79	11	A	0.025	75	100	20	215	0.0696	46,724
EO-80	11	A	0.025	200	100	15	197	0.1561	113,930
EO-81	11	A	0.025	200	100	15	189	0.1474	112,603
EO-82	11	A	0.025	200	100	15	176	0.1601	131,140
EO-83	12	A	0.025	75	100	20	260	0.0483	26,740
EO-84	12	A	0.025	75	100	20	272	0.0456	24,132
EO-85	12	A	0.025	75	100	20	239	0.0478	28,788
EO-86	12	A	0.025	200	100	15	252	0.1181	67,620
EO-87	12	A	0.025	200	100	15	204	0.1182	83,354
EO-88	12	A	0.025	200	100	15	233	0.1162	71,722
EO-89	12	B	0.020	75	100	20	44	0.1280	520,090
EO-90	12	B	0.020	75	100	20	45	0.1325	527,655
EO-91	12	B	0.020	75	100	20	46	0.1288	502,907
EO-92	12	B	0.020	200	200	15	50	0.2390	855,268
EO-93	12	B	0.020	200	200	15	57	0.2245	708,947
EO-94	12	B	0.020	200	200	15	51	0.2316	820,630

EO-95	13	A	0.025	75	100	20	290	0.0649	32,282
EO-96	13	A	0.025	75	100	20	233	0.0616	38,038
EO-97	13	A	0.025	75	100	20	366	0.0872	34,299
EO-98	13	A	0.025	200	100	15	179	0.1464	118,104
EO-99	13	A	0.025	200	100	15	167	0.1505	129,617
EO-100	13	A	0.025	200	100	15	191	0.1488	112,243
EO-101	14	A	0.025	75	100	20	226	0.0491	31,340
EO-102	14	A	0.025	75	100	20	199	0.0509	36,906
EO-103	14	A	0.025	75	100	20	208	0.0472	32,756
EO-104	14	A	0.025	200	100	15	175	0.1236	101,473
EO-105	14	A	0.025	200	100	15	232	0.1240	76,966
EO-106	14	A	0.025	200	100	15	214	0.1200	80,937
EO-107	14	B	0.020	75	100	20	57	0.1290	410,973
EO-108	14	B	0.020	75	100	20	57	0.1214	385,397
EO-109	14	B	0.020	75	100	20	55	0.1286	423,181
EO-110	14	B	0.020	200	200	15	53	0.2328	784,719
EO-111	14	B	0.020	200	200	15	58	0.2276	708,789
EO-112	14	B	0.020	200	200	15	54	0.2236	745,333
EO-113	15	A	0.025	75	100	20	214	0.1143	77,056
EO-114	15	A	0.025	75	100	20	279	0.1074	55,452
EO-115	15	A	0.025	75	100	20	220	0.1080	70,820
EO-116	15	A	0.025	200	100	15	24	0.2057	1,213,967
EO-117	15	A	0.025	200	100	15	26	0.2036	1,127,631
EO-118	15	A	0.025	200	100	15	20	0.2120	1,526,400
EO-119	15*	B	0.025	75	100	20	359	0.1281	51,340
EO-120	15*	B	0.025	75	100	20	275	0.1124	58,771
EO-121	15*	B	0.025	75	100	20	474	0.1076	32,675
EO-122	15*	B	0.025	200	100	15	39	0.1973	726,629
EO-123	15*	B	0.025	200	100	15	31	0.1926	891,781
EO-124	16	A	0.020	75	100	20	343	0.1041	54,694
EO-125	16	A	0.020	75	100	20	443	0.1052	42,716
EO-126	16	A	0.020	75	100	20	457	0.1102	43,414
EO-127	16	A	0.020	200	100	15	67	0.1921	519,189
EO-128	16	A	0.020	200	100	15	33	0.1811	1,003,015
EO-129	16	A	0.020	200	100	15	44	0.1957	798,776
EO-130	16	B	0.025	75	100	20	185	0.1161	90,468
EO-131	16	B	0.025	75	100	20	198	0.1205	87,858
EO-132	16	B	0.025	200	100	15	25	0.1955	1,144,390
EO-133	16	B	0.025	200	100	15	25	0.1903	1,100,530
EO-134	16	B	0.025	200	100	15	19	0.1773	1,316,041
EO-135	17	A	0.025	75	100	20	290	0.0418	20,777
EO-136	17	A	0.025	75	100	20	398	0.0409	14,783
EO-137	17	A	0.025	75	100	20	367	0.0392	15,394
EO-138	17	A	0.025	200	100	15	275	0.0599	31,320
EO-139	17	A	0.025	200	100	15	280	0.1103	56,787
EO-140	17	A	0.025	200	100	15	284	0.0471	23,890
EO-141	17*	B	0.025	75	100	20	132	0.1235	134,932
EO-142	17*	B	0.025	75	100	20	169	0.0906	77,381
EO-143	17*	B	0.025	75	100	20	193	0.1208	90,224

EO-144	17*	B	0.025	200	100	15	89	0.1924	310,949
EO-145	17*	B	0.025	200	100	15	74	0.1947	379,902
EO-146	17*	B	0.025	200	100	15	72	0.1913	383,132
EO-147	18	A	0.025	75	100	20	113	0.0687	87,780
EO-148	18	A	0.025	75	100	20	130	0.0651	72,166
EO-149	18	A	0.025	75	100	20	128	0.0668	75,033
EO-150	18	A	0.025	200	100	15	153	0.1667	156,485
EO-151	18	A	0.025	200	100	15	145	0.1728	171,727
EO-152	18	A	0.025	200	100	15	133	0.1662	179,946
EO-153	18*	B	0.025	75	100	20	172	0.1073	89,885
EO-154	18*	B	0.025	75	100	20	166	0.0995	86,209
EO-155	18*	B	0.025	75	100	20	118	0.1060	129,028
EO-156	18*	B	0.025	200	100	15	129	0.1695	188,770
EO-157	18*	B	0.025	200	100	15	99	0.1811	262,358
EO-158	18*	B	0.025	200	100	15	108	0.1800	240,669

[00324] For all runs, the total amount of toluene added to the reactor was 4.9 ml when 100 ul of 1-octene was added, or 4.8 ml when 200 ul of 1-octene was added; the ethylene pressure was maintained at 75 psig or 200 psig of ethylene as indicated by experiment. All polymerization examples quenched with ethylene uptake (max quench value) vs. maximum polymerization time.

Table 2b: Ethylene-Octene copolymerization examples - Part 2

Ex#	Cat ID	Act ID	Mn	Mw	PDI	C8 (wt%)	T _m (°C)
EO-1	2	A	774,669	1,179,487	1.52	15.0	101.0
EO-2	2	A	760,376	1,198,137	1.58	16.7	101.0
EO-3	2	A	734,049	1,145,675	1.56	18.4	99.6
EO-4	2	A	821,136	1,283,824	1.56	9.0	115.7
EO-5	2	A	843,059	1,358,059	1.61	9.1	114.2
EO-6	2	B	69,635	695,717	9.99	30.3	104.3
EO-7	2	B	45,771	572,632	12.51	33.6	98.1
EO-8	2	B	95,346	944,583	9.91	25.9	106.9
EO-9	2	B	416,366	931,111	2.24	17.5	112.5
EO-10	2	B	320,118	891,175	2.78	17.3	112.2
EO-11	2	B	417,684	958,432	2.29	16.5	112.7
EO-12	3	A	786,133	1,304,185	1.66	na	80.8
EO-13	3	A	794,126	1,322,829	1.67	na	80.5
EO-14	3	A	642,826	1,195,965	1.86	na	77.6
EO-15	3	A	978,483	1,780,270	1.82	na	112.5
EO-16	3	A	943,006	1,850,910	1.96	na	111.9
EO-17	3	A	870,295	1,681,592	1.93	na	110.5
EO-18	4	A	537,661	884,888	1.65	na	113.5
EO-19	4	A	521,904	837,411	1.60	na	113.0
EO-20	4	A	483,567	868,475	1.80	na	113.8
EO-21	4	A	519,949	922,283	1.77	na	118.7
EO-22	4	A	464,500	902,187	1.94	na	119.6
EO-23	4	A	503,852	909,090	1.80	na	118.8

EO-24	5	A	492,503	900,983	1.83	na	106.1
EO-25	5	A	555,613	940,507	1.69	na	107.6
EO-26	5	A	413,461	879,954	2.13	na	105.9
EO-27	5	A	619,264	1,192,055	1.92	na	115.3
EO-28	5	A	485,320	1,106,295	2.28	na	114.3
EO-29	5	A	600,703	1,155,536	1.92	na	115.5
EO-30	7	A	377,956	651,542	1.72	9.4	115.2
EO-31	7	A	411,652	748,357	1.82	11.6	114.1
EO-32	7	A	422,726	718,801	1.70	12.3	114.0
EO-33	7	A	397,266	749,161	1.89	7.2	120.3
EO-34	7	A	395,763	746,305	1.89	7.3	119.9
EO-35	7	A	401,601	656,020	1.63	3.2**	125.0
EO-36	7*	B	307,746	578,413	1.88	26.7	111.1
EO-37	7*	B	349,853	599,921	1.71	24.5	111.1
EO-38	7*	B	426,368	885,651	2.08	10.9	118.8
EO-39	7*	B	437,107	871,683	1.99	11.5	118.1
EO-40	7*	B	436,499	905,386	2.07	11.9	117.8
EO-41	8	A	599,869	818,132	1.36	9.6	115.0
EO-42	8	A	590,501	805,692	1.36	9.6	115.1
EO-43	8	A	606,220	836,493	1.38	9.4	115.6
EO-44	8	A	553,115	799,283	1.45	6.6	120.7
EO-45	8	A	546,822	776,511	1.42	7.2	120.0
EO-46	8	A	548,297	799,462	1.46	6.7	120.5
EO-47	8*	B	333,264	546,078	1.64	24.6	110.0
EO-48	8*	B	448,326	725,367	1.62	15.3	109.9
EO-49	8*	B	402,885	647,137	1.61	19.8	109.2
EO-50	8*	B	327,944	750,502	2.29	14.4	117.4
EO-51	8*	B	351,576	773,003	2.20	15.0	116.9
EO-52	8*	B	306,621	749,511	2.44	14.3	116.9
EO-53	9	A	393,609	605,586	1.54	10.3	115.4
EO-54	9	A	371,589	574,720	1.55	9.9	115.6
EO-55	9	A	372,352	569,505	1.53	9.6	115.7
EO-56	9	A	364,467	636,148	1.75	6.9	120.7
EO-57	9	A	368,151	634,398	1.72	7.4	120.7
EO-58	9	A	375,078	609,384	1.62	5.7	121.8
EO-59	9*	B	619,301	1,118,954	1.81	15.0	112.7
EO-60	9*	B	320,867	589,813	1.84	22.6	112.0
EO-61	9*	B	406,949	692,588	1.70	17.5	111.8
EO-62	9*	B	382,036	738,495	1.93	9.7	120.7
EO-63	9*	B	346,859	672,121	1.94	10.3	120.0
EO-64	9*	B	350,274	692,498	1.98	6.7	121.2
EO-65	10	A	662,778	990,217	1.49	2.3	126.7
EO-66	10	A	692,301	1,038,446	1.50	2.5	127.0
EO-67	10	A	630,888	967,353	1.53	2.3	126.7
EO-68	10	A	698,125	1,044,756	1.50	1.4**	130.9
EO-69	10	A	757,526	1,133,906	1.50	1.8**	130.6

EO-70	10	A	726,786	1,085,439	1.49	1.7**	130.7
EO-71	10*	B	465,149	660,101	1.42	4.6	124.9
EO-72	10*	B	550,698	792,437	1.44	4.8	124.5
EO-73	10*	B	484,607	662,502	1.37	5.1	124.9
EO-74	10*	B	570,786	887,280	1.55	2.4**	128.6
EO-75	10*	B	618,507	1,003,419	1.62	2.8**	128.7
EO-76	10*	B	525,168	891,146	1.70	2.6**	128.6
EO-77	11	A	612,759	854,137	1.39	8.7	121.0
EO-78	11	A	633,328	865,883	1.37	9.2	120.6
EO-79	11	A	593,985	824,900	1.39	7.6	121.0
EO-80	11	A	674,273	940,312	1.39	7.1	122.6
EO-81	11	A	654,021	926,013	1.42	5.2	123.7
EO-82	11	A	595,685	877,685	1.47	5.2	123.7
EO-83	12	A	520,078	1,301,764	2.50	13.8	95.0
EO-84	12	A	919,059	1,240,811	1.35	12.8	96.8
EO-85	12	A	723,661	1,652,182	2.28	13.4	95.9
EO-86	12	A	1,337,841	1,922,275	1.44	8.1	116.0
EO-87	12	A	1,212,198	1,789,881	1.48	7.6	116.6
EO-88	12	A	1,322,332	1,904,464	1.44	7.8	116.8
EO-89	12	B	38,521	192,778	5.00	31.7	87.2
EO-90	12	B	50,303	324,767	6.46	30.4	88.5
EO-91	12	B	49,260	303,629	6.16	31.7	87.8
EO-92	12	B	401,398	780,723	1.95	26.3	95.2
EO-93	12	B	393,193	783,665	1.99	24.5	95.7
EO-94	12	B	337,500	720,210	2.13	29.0	95.4
EO-95	13	A	677,260	946,895	1.40	10.5	120.4
EO-96	13	A	703,609	950,340	1.35	8.0	121.1
EO-97	13	A	716,327	984,275	1.37	10.2	119.9
EO-98	13	A	772,737	1,055,688	1.37	5.7	123.3
EO-99	13	A	759,262	1,035,760	1.36	6.0	122.8
EO-100	13	A	788,629	1,064,367	1.35	6.4	122.9
EO-101	14	A	844,368	1,125,957	1.33	10.6	116.7
EO-102	14	A	822,381	1,133,174	1.38	10.9	115.6
EO-103	14	A	817,768	1,158,703	1.42	11.1	116.7
EO-104	14	A	1,329,952	1,794,806	1.35	8.4	116.4
EO-105	14	A	1,108,643	1,691,492	1.53	7.6	119.5
EO-106	14	A	922,317	1,556,351	1.69	6.9	119.8
EO-107	14	B	55,699	337,896	6.07	30.0	87.5
EO-108	14	B	280,889	566,968	2.02	30.5	86.0
EO-109	14	B	50,460	338,592	6.71	30.4	129.5
EO-110	14	B	404,080	828,208	2.05	26.6	94.4
EO-111	14	B	401,613	871,048	2.17	25.1	93.9
EO-112	14	B	451,668	861,123	1.91	26.2	94.4
EO-113	15	A	130,794	954,589	7.30	24.9	100.7
EO-114	15	A	163,387	1,359,482	8.32	23.9	104.3
EO-115	15	A	146,496	1,186,574	8.10	26.8	102.8
EO-116	15	A	332,849	1,515,427	4.55	12.0	116.7
EO-117	15	A	247,068	1,423,993	5.76	11.5	116.7
EO-118	15	A	224,554	1,452,920	6.47	13.0	118.3
EO-119	15*	B	136,798	899,633	6.58	28.5	98.9

EO-120	15*	B	164,469	950,718	5.78	27.7	101.4
EO-121	15*	B	229,571	935,573	4.08	28.2	97.4
EO-122	15*	B	638,781	1,319,317	2.07	11.9	117.4
EO-123	15*	B	619,903	1,218,738	1.97	11.1	115.9
EO-124	16	A	298,034	965,910	3.24	27.2	98.3
EO-125	16	A	224,680	1,117,856	4.98	26.0	104.4
EO-126	16	A	309,544	1,248,852	4.03	25.2	103.9
EO-127	16	A	948,878	1,673,240	1.76	12.1	118.3
EO-128	16	A	818,397	1,495,586	1.83	8.7	117.3
EO-129	16	A	977,295	1,737,272	1.78	10.2	117.9
EO-130	16	B	na	na	na	23.4	108.4
EO-131	16	B	2,081,910	3,452,185	1.66	18.8	109.6
EO-132	16	B	532,105	1,344,631	2.53	14.0	116.9
EO-133	16	B	695,741	1,436,589	2.06	12.2	115.9
EO-134	16	B	534,242	1,293,709	2.42	11.4	116.2
EO-135	17	A	648,033	1,336,868	2.06	12.1	113.4
EO-136	17	A	617,052	1,308,548	2.12	10.6	114.1
EO-137	17	A	615,830	1,311,092	2.13	11.2	113.7
EO-138	17	A	508,453	1,427,296	2.81	5.1	121.9
EO-139	17	A	568,577	1,500,181	2.64	5.5	121.0
EO-140	17	A	446,060	1,326,247	2.97	4.0**	123.1
EO-141	17*	B	111,354	381,097	3.42	33.1	
EO-142	17*	B	249,949	628,698	2.52	27.2	
EO-143	17*	B	129,554	569,339	4.39	34.0	
EO-144	17*	B	359,252	900,026	2.51	15.8	112.2
EO-145	17*	B	426,610	916,364	2.15	13.6	112.6
EO-146	17*	B	338,914	868,113	2.56	14.8	112.4
EO-147	18	A	430,429	834,308	1.94	16.5	111.7
EO-148	18	A	518,100	897,380	1.73	16.0	110.9
EO-149	18	A	464,677	838,650	1.80	14.7	111.4
EO-150	18	A	420,200	850,821	2.02	9.6	116.8
EO-151	18	A	404,822	835,989	2.07	9.2	117.6
EO-152	18	A	450,789	910,358	2.02	10.5	117.3
EO-153	18*	B	294,144	538,357	1.83	28.9	105.5
EO-154	18*	B	330,361	560,766	1.70	26.5	104.7
EO-155	18*	B	249,553	461,756	1.85	29.2	104.7
EO-156	18*	B	446,334	882,748	1.98	14.9	114.5
EO-157	18*	B	389,621	818,467	2.10	15.6	114.9
EO-158	18*	B	439,269	896,318	2.04	14.9	115.4

“na” indicates that the data was not available.

**Values outside of the calibration range

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Table 3: Ethylene-1-decene copolymerization examples

Ex#	Cat ID	Act ID	Cat (μmol)	T(°C)	quench time (s)	yield (g)	Activity (g/mmol•hr)	Mn	Mw	PDI
ED-1	2	B	0.025	80	190	0.2759	209,323	184,273	274,235	1.49
ED-2	2	B	0.025	80	115	0.3861	483,464	119,724	191,039	1.60
ED-3	2	B	0.025	100	1801	0.2163	17,295	36,976	57,285	1.55

ED-4	2	B	0.025	100	1801	0.3247	25,957	39,604	66,204	1.67
ED-5	2	B	0.025	120	1800	0.1923	15,381	20,215	28,983	1.43
ED-6	2	B	0.025	120	1802	0.0491	3,923	26,138	39,770	1.52
ED-7	2	C	0.025	80	152	0.4158	393,140	148,553	232,882	1.57
ED-8	2	C	0.025	80	133	0.4576	494,332	137,274	227,241	1.66
ED-9	2	C	0.025	100	533	0.4892	132,241	30,494	52,274	1.71
ED-10	2	C	0.025	100	465	0.4316	133,686	37,284	63,945	1.72
ED-11	2	C	0.025	120	1800	0.0446	3,568	32,585	46,447	1.43
ED-12	2	C	0.025	120	1802	0.0375	2,997	33,062	49,171	1.49

Table 4a: Propylene polymerization & Ethylene-propylene copolymerization examples - Part 1.

Ex#	Cat ID	Act ID	Cat (μmol)	Iso-hex-ane (uL)	Tolu-ene (uL)	T ($^{\circ}\text{C}$)	C2 (psid)	Max quench value (psi)	quench time (s)	yield (g)	Activity (g/mmol $\cdot$ hr)
PP-1	2	B	0.025	3869	231	70	0	15	32	0.2408	1,070,222
PP-2	2	B	0.025	3869	231	70	0	15	29	0.2728	1,345,315
PP-3	2	B	0.025	3869	231	70	0	15	36	0.3330	1,317,363
EP-1	2	B	0.025	3849	231	70	10	15	25	0.3019	1,738,944
EP-2	2	B	0.025	3829	231	70	20	15	22	0.3053	1,971,444
EP-3	2	B	0.025	3829	231	70	20	15	24	0.3097	1,897,736
EP-4	2	B	0.025	3809	231	70	40	15	17	0.3197	2,740,286
EP-5	2	B	0.025	3809	231	70	40	15	18	0.3268	2,614,400
EP-6	2	B	0.025	3789	231	70	60	15	17	0.3218	2,758,286
EP-7	2	B	0.025	3789	231	70	60	15	14	0.3330	3,425,143
EP-8	2	B	0.025	3769	231	70	80	15	16	0.3254	2,928,600
EP-9	2	B	0.025	3769	231	70	80	15	14	0.3459	3,662,471
PP-4	2	B	0.012	3916	184	70	0	15	73	0.1714	700,545
PP-5	2	B	0.012	3916	184	70	0	15	79	0.2490	946,768
PP-6	2	B	0.012	3916	184	100	0	15	92	0.1555	504,870
PP-7	2	B	0.012	3916	184	100	0	15	68	0.1661	738,222
PP-8	2	B	0.015	3895	205	70	0	15	66	0.2865	1,041,818
PP-9	2	B	0.015	3895	205	70	0	15	64	0.2663	1,003,328
PP-10	2	B	0.015	3895	205	100	0	15	88	0.1681	457,415
PP-11	2	B	0.015	3895	205	100	0	15	79	0.1815	550,000
PP-12	2	C	0.012	3916	184	70	0	15	90	0.2335	779,199
PP-13	2	C	0.012	3916	184	70	0	15	113	0.2297	610,904
PP-14	2	C	0.012	3916	184	100	0	15	138	0.1663	360,999
PP-15	2	C	0.012	3916	184	100	0	15	73	0.1971	814,463
PP-16	2	C	0.015	3895	205	70	0	15	243	0.1566	154,986
PP-17	2	C	0.015	3895	205	70	0	15	142	0.1520	256,180
PP-18	2	C	0.015	3895	205	100	0	15	88	0.1644	446,840
PP-19	2	C	0.015	3895	205	100	0	15	66	0.1983	723,283
PP-20	12	B	0.020	3790	310	70	0	20	154	0.2265	264,054
PP-21	12	B	0.020	3790	310	70	0	20	159	0.1751	198,226
EP-10	12	B	0.020	3770	310	70	10	20	100	0.2047	368,460
EP-11	12	B	0.020	3770	310	70	10	20	112	0.1877	302,471
EP-12	12	B	0.020	3750	310	70	20	20	93	0.1998	385,054

EP-13	12	B	0.020	3750	310	70	20	20	91	0.2064	409,163
EP-14	12	B	0.020	3730	310	70	40	20	75	0.2028	486,072
EP-15	12	B	0.020	3730	310	70	40	20	74	0.2148	523,194
EP-16	12	B	0.020	3710	310	70	60	20	55	0.2453	810,165
EP-17	12	B	0.020	3710	310	70	60	20	58	0.2615	811,552
EP-18	12	B	0.020	3690	310	70	80	20	47	0.2873	1,112,129
EP-19	12	B	0.020	3690	310	70	80	20	43	0.2860	1,200,000
PP-22	14	B	0.020	3790	310	70	0	20	144	0.2353	293,310
PP-23	14	B	0.020	3790	310	70	0	20	156	0.2393	275,585
PP-24	14	B	0.040	3832	268	70	0	15	98	0.2318	212,228
PP-25	14	B	0.040	3832	268	70	0	15	96	0.2349	220,448
PP-26	14	B	0.040	3832	268	100	0	15	107	0.1530	129,296
PP-27	14	B	0.040	3832	268	100	0	15	64	0.1855	260,452
EP-20	14	B	0.020	3770	310	70	10	20	78	0.2129	492,571
EP-21	14	B	0.020	3770	310	70	10	20	68	0.2240	589,474
EP-22	14	B	0.020	3750	310	70	20	20	61	0.2170	644,554
EP-23	14	B	0.020	3750	310	70	20	20	66	0.2364	648,659
EP-24	14	B	0.020	3730	310	70	40	20	64	0.2327	653,448
EP-25	14	B	0.020	3730	310	70	40	20	52	0.2404	835,367
EP-26	14	B	0.025	3855	205	70	40	15	79	0.1662	301,421
EP-27	14	B	0.025	3855	205	70	40	15	46	0.1978	624,632
EP-28	14	B	0.025	3855	205	100	40	15	53	0.1552	422,473
EP-29	14	B	0.025	3855	205	100	40	15	45	0.1622	520,196
EP-30	14	B	0.020	3710	310	70	60	20	55	0.2484	812,945
EP-31	14	B	0.020	3710	310	70	60	20	50	0.2831	1,011,071
EP-32	14	B	0.025	3835	205	70	60	15	50	0.2182	630,940
EP-33	14	B	0.025	3835	205	70	60	15	37	0.2686	1,039,742
EP-34	14	B	0.025	3835	205	100	60	15	35	0.1695	695,385
EP-35	14	B	0.025	3835	205	100	60	15	31	0.1761	818,013
EP-36	14	B	0.020	3690	310	70	80	20	41	0.2630	1,163,145
EP-37	14	B	0.020	3690	310	70	80	20	36	0.2650	1,336,134
PP-28	14	C	0.040	3832	268	70	0	15	289	0.1597	49,820
PP-29	14	C	0.040	3832	268	70	0	15	202	0.1732	77,168
PP-30	14	C	0.040	3832	268	100	0	15	149	0.1509	91,455
PP-31	14	C	0.040	3832	268	100	0	15	182	0.1421	70,231
EP-38	14	C	0.025	3855	205	70	40	15	57	0.2299	576,753
EP-39	14	C	0.025	3855	205	70	40	15	71	0.2006	409,736
EP-40	14	C	0.025	3855	205	100	40	15	51	0.1450	413,465
EP-41	14	C	0.025	3855	205	100	40	15	44	0.1710	564,771
EP-42	14	C	0.025	3835	205	70	60	15	35	0.2880	1,171,525
EP-43	14	C	0.025	3835	205	100	60	15	48	0.1611	485,322
EP-44	14	C	0.025	3835	205	100	60	15	51	0.1472	414,810
PP-32	16	B	0.012	3899	201	70	0	10	111	0.1903	514,324
PP-33	16	B	0.012	3899	201	70	0	10	123	0.2105	513,415
EP-45	16	B	0.012	3879	201	70	10	10	33	0.2823	2,589,908
EP-46	16	B	0.012	3879	201	70	10	10	31	0.2501	2,436,039
EP-47	16	B	0.012	3859	201	70	20	10	28	0.2713	2,927,698
EP-48	16	B	0.012	3859	201	70	20	10	28	0.2819	3,042,086
EP-49	16	B	0.012	3839	201	70	40	10	22	0.2818	3,808,108
EP-50	16	B	0.012	3839	201	70	40	10	24	0.3049	3,827,197

EP-51	16	B	0.012	3819	201	70	60	10	18	0.2868	4,861,017
EP-52	16	B	0.012	3819	201	70	60	10	18	0.3357	5,657,865
EP-53	16	B	0.012	3799	201	70	80	10	15	0.3107	6,052,597
EP-54	16	B	0.012	3799	201	70	80	10	13	0.3002	6,874,809
CPP-1	C-A	B	0.020	3790	310	70	0	20	119	0.2449	372,000
CPP-2	C-A	B	0.020	3790	310	70	0	20	133	0.2616	354,578
CEP-1	C-A	B	0.020	3770	310	70	10	20	92	0.1996	390,098
CEP-2	C-A	B	0.020	3770	310	70	10	20	106	0.2013	341,830
CEP-3	C-A	B	0.020	3750	310	70	20	20	99	0.1781	323,491
CEP-4	C-A	B	0.020	3750	310	70	20	20	101	0.1954	348,583
CEP-5	C-A	B	0.020	3730	310	70	40	20	77	0.1900	443,005
CEP-6	C-A	B	0.020	3730	310	70	40	20	74	0.2010	488,919
CEP-7	C-A	B	0.020	3710	310	70	60	20	62	0.1996	581,359
CEP-8	C-A	B	0.020	3710	310	70	60	20	67	0.2271	612,864
CEP-9	C-A	B	0.020	3690	310	70	80	20	44	0.1503	619,085
CEP-10	C-A	B	0.020	3690	310	70	80	20	45	0.1803	722,806
CPP-3	C-B	B	0.020	3790	310	70	0	20	158	0.2327	265,943
CPP-4	C-B	B	0.020	3790	310	70	0	20	159	0.2146	243,096
CEP-11	C-B	B	0.020	3770	310	70	10	20	107	0.1954	328,097
CEP-12	C-B	B	0.020	3770	310	70	10	20	97	0.2165	400,926
CEP-13	C-B	B	0.020	3750	310	70	20	20	85	0.2107	448,298
CEP-14	C-B	B	0.020	3750	310	70	20	20	75	0.2229	533,537
CEP-15	C-B	B	0.020	3730	310	70	40	20	76	0.2110	503,046
CEP-16	C-B	B	0.020	3730	310	70	40	20	67	0.2206	589,139
CEP-17	C-B	B	0.020	3710	310	70	60	20	57	0.2388	752,785
CEP-18	C-B	B	0.020	3710	310	70	60	20	59	0.2460	756,923
CEP-19	C-B	B	0.020	3690	310	70	80	20	43	0.2672	1,129,014
CEP-20	C-B	B	0.020	3690	310	70	80	20	41	0.2701	1,197,488
CPP-5	C-C	B	0.080	3664	436	70	0	12	2423	0.1071	1,989
CPP-6	C-C	B	0.080	3664	436	70	0	12	2215	0.1037	2,107
CEP-21	C-C	B	0.040	3812	268	70	10	12	1212	0.0795	5,905
CEP-22	C-C	B	0.040	3812	268	70	10	12	930	0.0778	7,531
CEP-23	C-C	B	0.040	3792	268	70	20	12	676	0.0807	10,741
CEP-24	C-C	B	0.040	3792	268	70	20	12	576	0.0812	12,688
CEP-25	C-C	B	0.040	3772	268	70	40	12	327	0.0761	20,932
CEP-26	C-C	B	0.040	3772	268	70	40	12	324	0.0779	21,619
CEP-27	C-C	B	0.040	3752	268	70	60	12	221	0.0769	31,317
CEP-28	C-C	B	0.040	3752	268	70	60	12	206	0.0777	33,897
CEP-29	C-C	B	0.040	3732	268	70	80	12	160	0.0825	46,319
CEP-30	C-C	B	0.040	3732	268	70	80	12	169	0.0840	44,813
CPP-7	C-D	B	0.025	3869	231	70	0	12	209	0.1795	123,438
CPP-8	C-D	B	0.025	3869	231	70	0	12	191	0.1721	130,023
CEP-31	C-D	B	0.025	3849	231	70	10	12	130	0.1845	205,000
CEP-32	C-D	B	0.025	3849	231	70	10	12	81	0.2568	457,098
CEP-33	C-D	B	0.025	3829	231	70	20	12	121	0.1647	195,683
CEP-34	C-D	B	0.025	3829	231	70	20	12	182	0.1248	98,580
CEP-35	C-D	B	0.025	3809	231	70	40	12	42	0.2829	969,943
CEP-36	C-D	B	0.025	3809	231	70	40	12	49	0.3139	926,262
CEP-37	C-D	B	0.025	3789	231	70	60	12	103	0.1457	203,302
CEP-38	C-D	B	0.025	3789	231	70	60	12	34	0.2770	1,183,620

CEP-39	C-D	B	0.025	3769	231	70	80	12	39	0.2553	942,646
CEP-40	C-D	B	0.025	3769	231	70	80	12	32	0.3078	1,402,633
CPP-9	C-E	B	0.015	3843	257	70	0	20	66	0.3674	1,346,198
CPP-10	C-E	B	0.015	3843	257	70	0	20	71	0.3655	1,237,236
CPP-11	C-E	B	0.015	3843	257	70	0	20	72	0.3585	1,195,000
CPP-12	C-E	B	0.015	3843	257	70	0	20	71	0.3706	1,261,617
CEP-41	C-E	B	0.015	3803	257	70	40	20	22	0.3874	4,169,327
CEP-42	C-E	B	0.015	3803	257	70	40	20	22	0.3980	4,422,222
CEP-43	C-E	B	0.015	3803	257	70	40	20	23	0.3957	4,183,612
CEP-44	C-E	B	0.015	3803	257	70	40	20	22	0.3927	4,363,333
CEP-45	C-E	B	0.015	3763	257	70	80	20	17	0.4360	6,048,555
CEP-46	C-E	B	0.015	3763	257	70	80	20	17	0.4172	5,855,439
CEP-47	C-E	B	0.015	3763	257	70	80	20	19	0.4824	6,224,516
CEP-48	C-E	B	0.015	3763	257	70	80	20	21	0.3735	4,372,683

Table 4b: Propylene polymerization & Ethylene-Propylene copolymerization examples - Part 2.

Ex#	Cat ID	Act ID	Mn	Mw	PDI	C2 (wt%)	T _m (°C)	% vinylene	% trisub	% vinyl	% vinylidene
PP-1	2	B	9,638	28,402	2.95		141.3	0.0	7.2	79.3	13.5
PP-2	2	B	9,852	27,279	2.77		140.7	1.1	2.6	81.6	14.7
PP-3	2	B	8,027	26,634	3.32		140.6	0.0	1.5	83.8	14.7
EP-1	2	B	9,950	34,071	3.42	6.7	100.3	0.8	1.6	82.6	15.1
EP-2	2	B	10,701	38,543	3.60	11.2	90.1	0.0	1.5	83.1	15.4
EP-3	2	B	10,167	38,311	3.77	9.4	91.9	0.0	1.1	85.1	13.8
EP-4	2	B	9,576	41,253	4.31	14.6		0.0	0.9	84.5	14.5
EP-5	2	B	9,235	40,154	4.35	13.6		0.0	1.4	84.6	13.9
EP-6	2	B	9,301	44,887	4.83	15.3		0.6	2.3	82.7	14.3
EP-7	2	B	9,096	42,947	4.72	17.4		0.8	2.9	82.1	14.2
EP-8	2	B	10,427	51,822	4.97	19.2		1.2	4.3	80.9	13.7
EP-9	2	B	9,147	49,408	5.40	27.8		1.9	7.8	77.5	12.8
PP-4	2	B	23,592	45,180	1.92		146.7	0.0	8.5	74.4	17.1
PP-5	2	B	19,627	43,962	2.24		145.8	4.6	5.5	77.1	12.8
PP-6	2	B	5,823	10,579	1.82		138.7	0.7	2.6	88.8	7.9
PP-7	2	B	5,585	9,840	1.76		136.8	0.6	5.1	85.0	9.3
PP-8	2	B	15,798	39,708	2.51		144.8	2.5	14.4	66.9	16.3
PP-9	2	B	15,230	39,075	2.57		144.3	0.0	2.4	87.4	10.2
PP-10	2	B	5,606	10,137	1.81		138.0	1.0	3.2	89.0	6.8
PP-11	2	B	4,809	9,027	1.88		136.0	1.4	3.8	87.9	6.9
PP-12	2	C	31,704	66,032	2.08		147.9	0.0	10.6	80.3	9.1
PP-13	2	C	34,261	68,830	2.01		148.2	2.3	16.3	73.3	8.1
PP-14	2	C	8,493	15,276	1.80		140.9	0.0	0.9	93.6	5.6
PP-15	2	C	6,720	12,807	1.91		138.0	1.0	2.1	92.8	4.1
PP-16	2	C	69,487	119,005	1.71		152.0	3.7	16.7	59.3	20.4
PP-17	2	C	49,419	90,662	1.83		150.4	0.0	11.3	75.5	13.2
PP-18	2	C	6,371	11,709	1.84		137.6	0.9	2.2	93.2	3.7
PP-19	2	C	5,813	11,048	1.90		136.5	0.0	1.8	94.4	3.9
PP-20	12	B	34,622	49,928	1.44		139.4	0.0	0.0	54.5	45.5

PP-21	12	B	33,780	48,236	1.43		139.7	0.0	14.0	56.1	29.8
EP-10	12	B	26,816	42,824	1.60	8.5	96.2	1.2	0.0	51.2	47.6
EP-11	12	B	28,678	45,051	1.57	9.0	100.2	2.6	15.7	41.7	40.0
EP-12	12	B	28,359	45,205	1.59	11.1		0.0	0.0	51.9	48.1
EP-13	12	B	28,717	46,258	1.61	9.1		3.3	4.4	47.8	44.4
EP-14	12	B	33,914	55,114	1.63	15.4		0.0	1.4	48.6	50.0
EP-15	12	B	30,289	50,468	1.67	13.4		0.0	1.1	54.4	44.4
EP-16	12	B	28,818	51,643	1.79	17.6		1.0	10.3	45.4	43.3
EP-17	12	B	25,971	47,922	1.85	16.6		1.1	5.3	52.6	41.1
EP-18	12	B	21,946	48,382	2.20	20.6		0.9	3.5	44.2	51.3
EP-19	12	B	23,068	47,223	2.05	20.4		1.0	2.9	53.3	42.9
PP-22	14	B	23,015	34,305	1.49		137.5	1.8	4.4	67.3	26.5
PP-23	14	B	21,775	32,897	1.51		137.7	3.2	8.0	64.0	24.8
PP-24	14	B	12,960	26,637	2.06		136.1	0.0	6.7	64.0	29.3
PP-25	14	B	13,465	26,822	1.99		136.8	2.8	6.8	63.8	26.6
PP-26	14	B	4,143	6,698	1.62		123.3	1.1	11.7	70.0	17.2
PP-27	14	B	3,947	6,552	1.66		122.8	1.1	4.3	71.2	23.4
EP-20	14	B	20,710	32,957	1.59	3.0		1.4	5.8	65.5	27.3
EP-21	14	B	21,367	33,415	1.56	6.1	92.1	1.4	2.8	66.0	29.8
EP-22	14	B	18,690	30,217	1.62	8.7	84.5	2.5	1.2	66.0	30.2
EP-23	14	B	17,875	29,992	1.68	8.9	84.8	0.6	3.0	65.1	31.3
EP-24	14	B	24,261	40,211	1.66	13.7	84.2	1.4	3.6	63.8	31.2
EP-25	14	B	22,976	38,365	1.67	12.8		2.1	4.1	62.8	31.0
EP-26	14	B	26,727	51,710	1.93	12.9		4.9	13.0	50.4	31.7
EP-27	14	B	20,556	41,140	2.00	15.8		3.5	11.1	57.6	27.8
EP-28	14	B	6,548	12,395	1.89	19.3		0.5	2.2	69.5	27.7
EP-29	14	B	6,251	11,881	1.90	19.2		0.5	1.8	69.6	28.1
EP-30	14	B	21,929	39,968	1.82	21.0		0.9	4.6	62.0	32.4
EP-31	14	B	18,133	35,440	1.95	20.3	118.7	0.0	0.8	64.1	35.2
EP-32	14	B	22,011	49,009	2.23	18.9		3.0	9.8	57.1	30.1
EP-33	14	B	15,005	38,214	2.55	18.9		3.6	19.8	55.3	21.3
EP-34	14	B	6,499	13,213	2.03	25.0		1.5	6.1	67.6	24.7
EP-35	14	B	6,333	13,207	2.09	24.6		0.0	0.5	70.8	28.6
EP-36	14	B	16,660	48,598	2.92	25.7	137.9	0.0	1.7	65.0	33.3
EP-37	14	B	16,087	39,315	2.44	26.9		0.0	3.9	64.1	32.0
PP-28	14	C	31,451	54,060	1.72		139.5	1.4	5.6	80.6	12.5
PP-29	14	C	28,047	48,549	1.73		138.2	0.0	0.0	88.0	12.0
PP-30	14	C	5,681	9,837	1.73		124.7	0.7	2.7	89.6	7.0
PP-31	14	C	5,323	9,264	1.74		125.4	1.3	3.7	87.1	7.9
EP-38	14	C	28,030	62,608	2.23	17.2		3.6	7.1	75.0	14.3
EP-39	14	C	34,179	71,414	2.09	18.2		3.3	18.7	69.2	8.8
EP-40	14	C	11,078	21,485	1.94	22.1		1.8	3.1	85.1	10.1
EP-41	14	C	8,349	16,728	2.00	20.3		1.3	2.5	88.6	7.6
EP-42	14	C	22,419	59,214	2.64	19.0		3.0	11.2	71.6	14.2
EP-43	14	C	11,508	24,271	2.11	27.8		2.6	7.0	80.9	9.6
EP-44	14	C	12,324	24,099	1.96	27.8		1.7	6.7	82.1	9.6
PP-32	16	B	47,429	82,418	1.74		151.5	0.0	13.0	75.9	11.1
PP-33	16	B	42,074	78,314	1.86		150.7	7.6	21.5	62.0	8.9
EP-45	16	B	17,652	56,954	3.23	8.8	100.3	2.0	4.7	78.7	14.7
EP-46	16	B	16,256	54,287	3.34	8.3	104.5	0.0	0.0	86.9	13.1

EP-47	16	B	16,632	61,724	3.71	11.4	91.3	2.5	5.7	77.2	14.6
EP-48	16	B	16,261	63,177	3.89	12.8	90.0	2.5	5.5	79.1	12.9
EP-49	16	B	15,300	65,806	4.30	16.1		2.3	5.7	78.2	13.8
EP-50	16	B	14,261	70,657	4.95	15.3		2.6	7.2	76.3	13.9
EP-51	16	B	13,162	82,508	6.27	21.0		1.5	7.8	77.9	12.7
EP-52	16	B	13,629	87,474	6.42	19.8		1.9	6.1	77.8	14.2
EP-53	16	B	12,831	98,154	7.65	25.2		1.7	7.3	73.2	17.9
EP-54	16	B	13,417	97,515	7.27	24.4		1.4	4.5	79.1	15.0
CPP-1	C-A	B	25,220	53,948	2.14		138.7	3.3	4.4	37.8	54.4
CPP-2	C-A	B	28,677	44,260	1.54		138.4	5.3	7.4	38.9	48.4
CEP-1	C-A	B	32,880	52,880	1.61	3.6	105.8	2.4	1.2	40.0	56.5
CEP-2	C-A	B	28,858	47,365	1.64	8.0	100.2	1.0	3.1	39.8	56.1
CEP-3	C-A	B	34,383	54,039	1.57	9.5	88.9	0.0	4.7	38.8	56.5
CEP-4	C-A	B	30,928	52,200	1.69	9.7	89.5	2.1	3.2	37.9	56.8
CEP-5	C-A	B	36,261	60,943	1.68	13.4		3.3	4.4	36.7	55.6
CEP-6	C-A	B	35,037	58,905	1.68	13.6		4.3	3.3	35.9	56.5
CEP-7	C-A	B	30,348	53,280	1.76	20.7	112.7	3.2	11.7	35.1	50.0
CEP-8	C-A	B	30,461	236,939	7.78	28.7	111.2	1.9	4.8	39.0	54.3
CEP-9	C-A	B	29,857	55,730	1.87	27.4	115.7	1.2	4.9	35.4	58.5
CEP-10	C-A	B	23,616	116,202	4.92	23.1	115.7	1.1	4.4	37.8	56.7
CPP-3	C-B	B	27,587	40,180	1.46		138.9	3.6	5.5	52.7	38.2
CPP-4	C-B	B	34,671	48,766	1.41		140.9	2.7	19.5	31.9	46.0
CEP-11	C-B	B	29,431	45,421	1.54	6.8	97.3	1.3	2.5	38.8	57.5
CEP-12	C-B	B	25,567	41,455	1.62	9.5	93.7	0.0	2.3	40.2	57.5
CEP-13	C-B	B	26,490	42,679	1.61	10.3		2.2	2.2	38.7	57.0
CEP-14	C-B	B	23,326	38,249	1.64	8.4		0.9	0.0	44.0	55.0
CEP-15	C-B	B	32,878	53,423	1.62	14.1		0.0	0.0	39.7	60.3
CEP-16	C-B	B	27,356	47,093	1.72	15.2		1.1	2.3	40.9	55.7
CEP-17	C-B	B	29,236	52,558	1.80	18.0		0.0	2.4	40.5	57.1
CEP-18	C-B	B	27,041	49,550	1.83	15.3		1.1	3.2	41.1	54.7
CEP-19	C-B	B	21,704	48,769	2.25	20.5		0.8	4.2	45.0	50.0
CEP-20	C-B	B	22,483	47,343	2.11	22.0		0.0	1.8	55.8	42.5
CPP-5	C-C	B	3,643	5,514	1.51			0.5	1.7	41.5	56.3
CPP-6	C-C	B	3,571	5,343	1.50			0.5	1.8	41.8	56.0
CEP-21	C-C	B	5,418	9,627	1.78	23.6		0.6	4.6	32.5	62.3
CEP-22	C-C	B	5,502	9,939	1.81	20.4		1.0	5.0	34.3	59.8
CEP-23	C-C	B	7,184	13,035	1.81	25.6		0.0	2.5	36.0	61.5
CEP-24	C-C	B	6,673	12,081	1.81	24.2		0.0	3.7	37.3	59.0
CEP-25	C-C	B	13,406	22,369	1.67	41.9		0.0	3.9	39.0	57.1
CEP-26	C-C	B	13,109	21,678	1.65	45.0		0.4	6.1	38.2	55.3
CEP-27	C-C	B	21,359	32,888	1.54	53.5		0.0	8.9	37.0	54.1
CEP-28	C-C	B	20,742	34,206	1.65	46.6		0.0	9.5	38.1	52.4
CEP-29	C-C	B	25,915	41,693	1.61	55.2		0.9	8.5	36.8	53.8
CEP-30	C-C	B	26,539	41,978	1.58	54.9		0.0	7.6	38.1	54.3
CPP-7	C-D	B	89,641	147,267	1.64		141.8	6.7	20.0	20.0	53.3
CPP-8	C-D	B	90,190	147,358	1.63		142.0	5.6	24.1	24.1	46.3
CEP-31	C-D	B	109,130	182,358	1.67	8.1		0.0	5.0	10.0	85.0
CEP-32	C-D	B	59,009	113,096	1.92	6.3	95.7	2.1	0.0	10.6	87.2
CEP-33	C-D	B	117,536	197,873	1.68	13.2		4.4	0.0	8.9	86.7
CEP-34	C-D	B	143,952	238,408	1.66	14.9		4.1	14.3	12.2	69.4

CEP-35	C-D	B	60,933	122,443	2.01	17.4		0.0	8.0	20.0	72.0
CEP-36	C-D	B	48,758	110,165	2.26	15.8		5.6	4.2	16.7	73.6
CEP-37	C-D	B	129,035	218,743	1.70	19.6		4.2	4.2	10.4	81.3
CEP-38	C-D	B	31,549	98,597	3.13	16.8		1.1	0.0	22.0	76.9
CEP-39	C-D	B	67,240	153,942	2.29	27.5		3.3	8.3	16.7	71.7
CEP-40	C-D	B	35,389	115,893	3.27	24.5		2.2	6.7	23.3	67.8
CPP-9	C-E	B	47237	100374	2.12		148.4				
CPP-10	C-E	B	63174	137415	2.18		153.5	5.2	37.1	37.1	20.6
CPP-11	C-E	B	58584	129890	2.22		152.9				
CPP-12	C-E	B	48120	109203	2.27		150.7	5.4	29.8	35.1	29.8
CEP-41	C-E	B	24197	64519	2.67	14.72	67.1				
CEP-42	C-E	B	26709	67617	2.53	14.94	76.4	0.0	8.3	31.0	60.7
CEP-43	C-E	B	23274	66644	2.86	14.04	77.5				
CEP-44	C-E	B	21988	57691	2.62	12.47	106.0	3.9	18.2	35.4	42.5
CEP-45	C-E	B	20590	64503	3.13	23.61	96.3				
CEP-46	C-E	B	21840	62130	2.84	23.16	128.5	0.5	4.3	36.2	59.0
CEP-47	C-E	B	46028	79578	1.73	20.37	67.1				
CEP-48	C-E	B	33243	72847	2.19	27.47	72.7	2.0	4.6	28.9	64.5

Table 5a: Propylene polymerization examples - Part 1

Ex#	Cat ID	Act ID	Cat (μ mol)	Iso-hexane (μ L)	Toluene (μ L)	T ($^{\circ}$ C)	Max quench value (psi)	quench time (s)	yield (g)	Activity (g/ mmol•hr)
PP-34	2	B	0.040	3832	268	70	15	26	0.3011	1,050,349
PP-35	2	B	0.040	3832	268	70	15	31	0.3400	977,636
PP-36	2	B	0.040	3832	268	70	15	29	0.3622	1,135,819
PP-37	2	B	0.040	3832	268	70	15	21	0.2954	1,290,583
PP-38	2	B	0.040	3832	268	70	15	28	0.2871	913,039
PP-39	2	B	0.040	3832	268	70	15	28	0.2700	870,968
PP-40	2	B	0.040	3832	268	100	15	19	0.2644	1,245,864
PP-41	2	B	0.040	3832	268	100	15	19	0.2565	1,221,429
PP-42	2	B	0.040	3832	268	100	15	19	0.2544	1,224,385
PP-43	2	B	0.040	3832	268	100	15	23	0.2624	1,022,338
PP-44	2	B	0.040	3832	268	100	15	31	0.2190	642,020
PP-45	2	B	0.040	3832	268	100	15	25	0.2398	863,280
PP-46	7	A	0.050	0	4099	70	8	835	0.0617	5,321
PP-47	7	A	0.050	0	4099	70	8	892	0.0612	4,941
PP-48	7	A	0.050	0	4099	70	8	944	0.0650	4,959
PP-49	7	A	0.050	0	4099	100	8	574	0.0544	6,821
PP-50	7	A	0.050	0	4099	100	8	591	0.0525	6,400
PP-51	7	A	0.050	0	4099	100	8	692	0.0520	5,408
PP-52	8	A	0.025	0	4099	70	8	1801	0.0408	3,263
PP-53	8	A	0.025	0	4099	70	8	1801	0.0409	3,271
PP-54	8	A	0.025	0	4099	70	8	1801	0.0379	3,031
PP-55	8	A	0.025	0	4099	100	8	1800	0.0233	1,864
PP-56	8	A	0.025	0	4099	100	8	1801	0.0329	2,631
PP-57	8	A	0.025	0	4099	100	8	1801	0.0341	2,727
PP-58	8	A	0.040	0	4099	70	8	1121	0.0513	4,117
PP-59	8	A	0.040	0	4099	70	8	1396	0.0533	3,436

PP-60	8	A	0.040	0	4099	70	8	1366	0.0582	3,835
PP-61	8	A	0.040	0	4099	100	8	1067	0.0538	4,539
PP-62	8	A	0.040	0	4099	100	8	968	0.0532	4,947
PP-63	8	A	0.040	0	4099	100	8	1026	0.0548	4,808
PP-64	9	A	0.080	0	4098	70	8	552	0.0651	5,308
PP-65	9	A	0.080	0	4098	70	8	523	0.0586	5,038
PP-66	9	A	0.080	0	4098	70	8	664	0.0711	4,821
PP-67	9	A	0.080	0	4098	100	8	427	0.0620	6,537
PP-68	9	A	0.080	0	4098	100	8	393	0.0645	7,389
PP-69	9	A	0.080	0	4098	100	8	431	0.0592	6,181
PP-70	10	A	0.080	0	4098	70	8	1802	0.0242	604
PP-71	10	A	0.080	0	4098	70	8	1800	0.0219	547
PP-72	10	A	0.080	0	4098	70	8	1803	0.0232	579
PP-73	10	A	0.080	0	4098	100	8	1803	0.0238	594
PP-74	10	A	0.080	0	4098	100	8	1800	0.0216	540
PP-75	10	A	0.080	0	4098	100	8	1803	0.0232	579
PP-76	11	A	0.080	3609	489	70	20	1801	0.1411	3,526
PP-77	11	A	0.080	3609	489	70	20	1802	0.1241	3,099
PP-78	11	A	0.080	3609	489	70	20	1801	0.1581	3,950
PP-79	11	A	0.080	3609	489	100	20	1445	0.1336	4,161
PP-80	11	A	0.080	3609	489	100	20	1520	0.1338	3,960
PP-81	11	A	0.080	3609	489	100	20	1458	0.1342	4,142
PP-82	12	A	0.080	3609	489	70	20	1801	0.1590	3,973
PP-83	12	A	0.080	3609	489	70	20	1654	0.1747	4,754
PP-84	12	A	0.080	3609	489	70	20	1773	0.1720	4,366
PP-85	12	A	0.080	3609	489	100	20	1281	0.1321	4,642
PP-86	12	A	0.080	3609	489	100	20	1475	0.1335	4,072
PP-87	12	A	0.080	3609	489	100	20	1522	0.1299	3,842
PP-88	12	B	0.080	3720	380	70	20	41	0.3537	385,387
PP-89	12	B	0.080	3720	380	70	20	43	0.3610	377,791
PP-90	12	B	0.080	3720	380	70	20	39	0.3489	403,612
PP-91	12	B	0.080	3720	380	100	20	34	0.2827	376,376
PP-92	12	B	0.080	3720	380	100	20	33	0.2885	395,808
PP-93	12	B	0.080	3720	380	100	20	25	0.2913	516,083
PP-94	13	A	0.080	3609	489	70	20	1800	0.1312	3,279
PP-95	13	A	0.080	3609	489	70	20	1801	0.1291	3,225
PP-96	13	A	0.080	3609	489	70	20	1801	0.1336	3,338
PP-97	13	A	0.080	3609	489	100	20	1802	0.1295	3,234
PP-98	13	A	0.080	3609	489	100	20	1802	0.1341	3,348
PP-99	13	A	0.080	3609	489	100	20	1800	0.1272	3,180
PP-100	14	A	0.080	3609	489	70	20	1802	0.1510	3,771
PP-101	14	A	0.080	3609	489	70	20	1801	0.1410	3,523
PP-102	14	A	0.080	3609	489	70	20	1800	0.1457	3,642
PP-103	14	A	0.080	3609	489	100	20	1473	0.1306	3,991
PP-104	14	A	0.080	3609	489	100	20	1489	0.1344	4,062
PP-105	14	A	0.080	3609	489	100	20	1522	0.1299	3,840
PP-106	14	B	0.080	3720	380	70	20	49	0.3424	315,738
PP-107	14	B	0.080	3720	380	70	20	46	0.3445	334,106
PP-108	14	B	0.080	3720	380	70	20	45	0.3417	338,689
PP-109	14	B	0.080	3720	380	100	20	33	0.2777	382,156

PP-110	14	B	0.080	3720	380	100	20	38	0.2740	321,932
PP-111	14	B	0.080	3720	380	100	20	30	0.2807	418,262
PP-112	15	A	0.025	0	4099	70	8	406	0.0826	29,289
PP-113	15	A	0.025	0	4099	70	8	366	0.0953	37,485
PP-114	15	A	0.025	0	4099	70	8	389	0.0835	30,934
PP-115	15	A	0.025	0	4099	100	8	613	0.0560	13,165
PP-116	15	A	0.025	0	4099	100	8	261	0.0756	41,647
PP-117	15	A	0.025	0	4099	100	8	249	0.0782	45,206
PP-118	16	A	0.025	0	4099	70	8	610	0.0606	14,313
PP-119	16	A	0.025	0	4099	70	8	658	0.0641	14,026
PP-120	16	A	0.025	0	4099	70	8	559	0.0615	15,843
PP-120	16	A	0.025	0	4099	100	8	349	0.0612	25,259
PP-122	16	A	0.025	0	4099	100	8	264	0.0583	31,860
PP-123	16	A	0.025	0	4099	100	8	343	0.0616	25,899
PP-124	16	A	0.060	0	4099	70	8	115	0.1654	86,146
PP-125	16	A	0.060	0	4099	70	8	116	0.1599	82,707
PP-126	16	A	0.060	0	4099	70	8	107	0.1428	79,851
PP-127	16	A	0.060	0	4099	100	8	73	0.1311	108,198
PP-128	16	A	0.060	0	4099	100	8	73	0.1247	103,200
PP-129	16	A	0.060	0	4099	100	8	64	0.1258	117,387
PP-130	16	B	0.025	3881	218	70	8	57	0.2885	735,292
PP-131	16	B	0.025	3881	218	70	8	62	0.2963	691,527
PP-132	16	B	0.025	3881	218	70	8	63	0.2903	666,718
PP-133	16	B	0.025	3881	218	100	8	37	0.2203	869,129
PP-134	16	B	0.025	3881	218	100	8	35	0.2226	915,840
PP-135	16	B	0.025	3881	218	100	8	36	0.2239	903,126
PP-136	17	A	0.050	0	4099	70	8	844	0.0546	4,657
PP-137	17	A	0.050	0	4099	70	8	1012	0.0627	4,460
PP-138	17	A	0.050	0	4099	70	8	940	0.0547	4,192
PP-139	17	A	0.050	0	4099	100	8	935	0.0518	3,991
PP-140	17	A	0.050	0	4099	100	8	954	0.0523	3,948
PP-141	17	A	0.050	0	4099	100	8	991	0.0515	3,742
PP-142	18	A	0.040	0	4099	70	8	1177	0.0686	5,246
PP-143	18	A	0.040	0	4099	70	8	1013	0.0567	5,036
PP-144	18	A	0.040	0	4099	70	8	1232	0.0531	3,879
PP-145	18	A	0.040	0	4099	100	8	718	0.0560	7,015
PP-146	18	A	0.040	0	4099	100	8	701	0.0508	6,526
PP-147	18	A	0.040	0	4099	100	8	760	0.0521	6,169
PP-148	18	A	0.050	0	4099	70	8	604	0.0680	8,102
PP-149	18	A	0.050	0	4099	100	8	443	0.0652	10,592
PP-150	18	A	0.050	0	4099	100	8	475	0.0622	9,428
PP-151	18	A	0.050	0	4099	100	8	464	0.0644	10,000
PP-152	18*	B	0.030	3874	226	70	8	1800	0.0091	607
PP-153	18*	B	0.030	3874	226	70	8	1802	0.0246	1,638
PP-154	18*	B	0.030	3874	226	70	8	1800	0.0119	793

Table 5b: Propylene polymerization examples - Part 2

Ex#	Cat ID	Act ID	Mn	Mw	PDI	T _m (°C)
PP-34	2	B	5,856	20,187	3.45	138.5
PP-35	2	B	5,239	17,503	3.34	136.9
PP-36	2	B	4,819	14,888	3.09	135.4
PP-37	2	B	6,856	23,457	3.42	138.9
PP-38	2	B	7,313	26,069	3.56	140.4
PP-39	2	B	6,707	27,166	4.05	139.0
PP-40	2	B	3,563	6,500	1.82	130.1
PP-41	2	B	3,821	7,304	1.91	132.6
PP-42	2	B	3,317	5,839	1.76	130.8
PP-43	2	B	3,509	6,987	1.99	132.6
PP-44	2	B	3,654	6,859	1.88	133.8
PP-45	2	B	3,781	7,333	1.94	134.2
PP-46	7	A	50,959	76,581	1.50	149.5
PP-47	7	A	52,441	79,829	1.52	149.9
PP-48	7	A	56,232	84,346	1.50	150.0
PP-49	7	A	13,376	20,509	1.53	141.6
PP-50	7	A	12,253	19,016	1.55	141.2
PP-51	7	A	11,035	17,207	1.56	140.3
PP-52	8	A	71,643	106,093	1.48	149.7
PP-53	8	A	83,262	124,778	1.50	150.5
PP-54	8	A	77,423	120,414	1.56	150.0
PP-55	8	A	22,912	33,633	1.47	143.9
PP-56	8	A	23,497	34,715	1.48	143.4
PP-57	8	A	24,694	36,270	1.47	143.4
PP-58	8	A	55,638	87,066	1.56	150.7
PP-59	8	A	42,485	67,921	1.60	150.0
PP-60	8	A	56,639	90,914	1.61	150.5
PP-61	8	A	16,990	25,991	1.53	143.8
PP-62	8	A	17,327	26,356	1.52	144.0
PP-63	8	A	16,488	25,228	1.53	144.4
PP-64	9	A	51,514	81,114	1.57	148.9
PP-65	9	A	59,629	94,591	1.59	149.4
PP-66	9	A	58,135	91,911	1.58	149.5
PP-67	9	A	14,137	21,965	1.55	140.1
PP-68	9	A	13,714	21,792	1.59	140.6
PP-69	9	A	13,623	21,521	1.58	141.5
PP-70	10	A	24,604	36,518	1.48	
PP-71	10	A	24,181	35,607	1.47	
PP-72	10	A	24,870	36,781	1.48	
PP-73	10	A	7,222	11,004	1.52	
PP-74	10	A	6,821	10,182	1.49	
PP-75	10	A	7,145	10,737	1.50	
PP-76	11	A	50,585	76,740	1.52	139.6
PP-77	11	A	52,762	80,621	1.53	140.4
PP-78	11	A	56,598	85,261	1.51	140.4
PP-79	11	A	7,328	12,324	1.68	124.9
PP-80	11	A	9,000	14,460	1.61	128.4

PP-81	11	A	8,976	14,426	1.61	128.5
PP-82	12	A	55,140	83,420	1.51	140.9
PP-83	12	A	54,728	102,854	1.88	140.8
PP-84	12	A	57,908	89,070	1.54	141.1
PP-85	12	A	10,115	17,366	1.72	129.5
PP-86	12	A	10,701	15,303	1.43	128.3
PP-87	12	A	11,272	15,855	1.41	129.9
PP-88	12	B	6,887	19,001	2.76	129.9
PP-89	12	B	5,993	16,559	2.76	130.2
PP-90	12	B	6,689	17,935	2.68	130.4
PP-91	12	B	3,461	5,361	1.55	119.0
PP-92	12	B	3,411	5,254	1.54	117.6
PP-93	12	B	3,776	6,124	1.62	119.3
PP-94	13	A	36,426	54,657	1.50	138.9
PP-95	13	A	41,306	62,787	1.52	139.7
PP-96	13	A	39,208	58,188	1.48	139.3
PP-97	13	A	6,917	10,918	1.58	126.0
PP-98	13	A	7,006	11,116	1.59	126.2
PP-99	13	A	5,808	9,189	1.58	121.9
PP-100	14	A	39,412	56,896	1.44	139.7
PP-101	14	A	33,934	66,447	1.96	139.8
PP-102	14	A	38,471	58,638	1.52	140.5
PP-103	14	A	8,266	11,895	1.44	128.5
PP-104	14	A	8,521	11,812	1.39	127.8
PP-105	14	A	7,257	11,284	1.55	127.0
PP-106	14	B	6,577	15,820	2.41	130.4
PP-107	14	B	7,045	17,506	2.48	130.1
PP-108	14	B	7,452	18,124	2.43	130.8
PP-109	14	B	3,416	5,071	1.48	120.4
PP-110	14	B	3,104	4,424	1.43	117.5
PP-111	14	B	3,351	4,867	1.45	118.0
PP-112	15	A	105,329	144,351	1.37	151.7
PP-113	15	A	95,651	135,662	1.42	151.7
PP-114	15	A	104,351	143,392	1.37	151.7
PP-115	15	A	18,362	25,732	1.40	145.9
PP-116	15	A	18,791	25,940	1.38	143.6
PP-117	15	A	17,827	25,938	1.45	144.7
PP-118	16	A	105,751	158,433	1.50	151.4
PP-119	16	A	122,794	174,176	1.42	152.3
PP-120	16	A	123,532	173,849	1.41	152.3
PP-120	16	A	21,182	30,514	1.44	144.8
PP-122	16	A	20,286	29,401	1.45	144.3
PP-123	16	A	18,540	29,074	1.57	144.5
PP-124	16	A	60,601	98,968	1.63	149.5
PP-125	16	A	61,400	99,289	1.62	149.7
PP-126	16	A	58,934	95,808	1.63	150.5
PP-127	16	A	10,899	18,738	1.72	141.2
PP-128	16	A	10,859	18,741	1.73	142.2
PP-129	16	A	10,612	18,319	1.73	141.7
PP-130	16	B	20,485	47,051	2.30	146.4

PP-131	16	B	23,036	51,949	2.26	147.1
PP-132	16	B	22,124	50,697	2.29	146.7
PP-133	16	B	5,074	10,086	1.99	137.4
PP-134	16	B	4,576	9,635	2.11	136.2
PP-135	16	B	4,742	9,410	1.98	137.1
PP-136	17	A	52,659	76,413	1.45	151.1
PP-137	17	A	60,653	86,614	1.43	150.1
PP-138	17	A	65,487	92,107	1.41	151.9
PP-139	17	A	10,812	15,855	1.47	141.0
PP-140	17	A	10,294	15,546	1.51	140.5
PP-141	17	A	10,167	15,047	1.48	140.5
PP-142	18	A	63,766	93,574	1.47	151.0
PP-143	18	A	58,765	86,242	1.47	151.3
PP-144	18	A	61,768	90,088	1.46	151.3
PP-145	18	A	13,883	21,142	1.52	141.5
PP-146	18	A	13,814	20,698	1.50	142.2
PP-147	18	A	13,427	20,250	1.51	142.6
PP-148	18	A	57,334	84,281	1.47	151.4
PP-149	18	A	14,456	21,744	1.50	141.3
PP-150	18	A	13,889	20,847	1.50	142.2
PP-151	18	A	13,614	20,798	1.53	141.7
PP-152	18*	B	na	na	na	na
PP-153	18*	B	98,962	174,084	1.76	151.8
PP-154	18*	B	89,066	156,410	1.76	152.2

“na” indicates that the data was not available.

Table 6: ^{13}C NMR data for select polypropylene examples

Ex#	Cat ID	Act ID	m	r	mmmm	mmmr	rmmr	mmrr	mmrm +rmrr	rmrm	rrrr	mr rr	mrrm	stereo defects/ 10000 monomer	total 2,1-regio defects/ 10000 monomer	1,3 regio defects/ 10000 monomer	ave. meso run length
PP-34	2	B	0.974	0.026	0.9371	0.0240	0.0000	0.0221	0.0035	0.0000	0.0005	0.0005	0.0123	127.7	8.3	50.5	53.6
PP-39	2	B	0.960	0.040	0.8430	0.0636	0.0317	0.0271	0.0009	0.0150	0.0047	0.0019	0.0122	215.0	0.0	105.4	31.2
PP-40	2	B	0.965	0.035	0.9172	0.0327	0.0007	0.0295	0.0000	0.0000	0.0010	0.0024	0.0166	147.6	0.0	94.0	41.4
PP-44	2	B	0.922	0.078	0.7799	0.0724	0.0311	0.0315	0.0139	0.0309	0.0202	0.0031	0.0170	381.5	0.0	74.4	21.9
**PP-46,47,48	7	A	0.930	0.070	0.8320	0.0312	0.0363	0.0153	0.0341	0.0125	0.0086	0.0155	0.0146	306.4	10.3	12.3	30.4
**PP-49,50,51	7	A	0.923	0.077	0.7939	0.0632	0.0303	0.0216	0.0289	0.0205	0.0092	0.0159	0.0164	352.7	0.0	14.4	27.2
PP-58,59,60	8	A	0.969	0.031	0.9037	0.0461	0.0107	0.0020	0.0069	0.0085	0.0056	0.0048	0.0118	85.4	23.6	18.0	78.7
**PP-64,65,66	9	A	0.950	0.050	0.8320	0.0738	0.0166	0.0247	0.0181	0.0121	0.0067	0.0067	0.0094	271.9	18.7	12.0	33.0
**PP-67,68,69	9	A	0.904	0.096	0.7479	0.0935	0.0255	0.0425	0.0227	0.0085	0.0170	0.0085	0.0340	359.1	0.0	55.2	24.1
PP-78	11	A	0.926	0.074	0.8090	0.0666	0.0104	0.0521	0.0158	0.0112	0.0027	0.0053	0.0269	395.5	8.0	90.0	20.3
PP-79	11	A	0.942	0.057	0.8420	0.0584	0.0096	0.0418	0.0134	0.0096	0.0014	0.0035	0.0201	324.0	13.0	116.0	22.1
PP-83	12	A	0.975	0.035	0.9203	0.0254	0.0110	0.0271	0.0068	0.0030	0.0015	0.0018	0.0131	184.5	15.0	67.0	37.5
PP-86	12	A	0.933	0.067	0.8631	0.0292	0.0020	0.0436	0.0239	0.0100	0.0019	0.0036	0.0227	387.5	1.0	57.0	22.4
PP-89	12	B	0.929	0.072	0.8413	0.0453	0.0034	0.0478	0.0159	0.0134	0.0035	0.0042	0.0253	385.5	8.0	92.0	20.6
PP-92	12	B	0.864	0.137	0.7165	0.0653	0.0068	0.0706	0.0409	0.0383	0.0102	0.0113	0.0401	749.0	1.0	94.0	11.8
PP-94	13	A	0.958	0.042	0.8874	0.0420	0.0077	0.0293	0.0075	0.0059	0.0019	0.0033	0.0151	213.5	12.0	80.0	32.7
PP-97	13	A	0.929	0.071	0.8144	0.0638	0.0126	0.0452	0.0171	0.0146	0.0034	0.0054	0.0237	384.5	4.0	117.0	19.8
PP-102	14	A	0.961	0.039	0.9169	0.0209	0.0013	0.0267	0.0122	0.0048	0.0012	0.0016	0.0144	218.5	9.0	50.0	36.0
PP-105	14	A	0.937	0.063	0.8587	0.0421	0.0020	0.0438	0.0121	0.0126	0.0024	0.0033	0.0230	342.5	4.0	117.0	21.6

Table 6: ^{13}C NMR data for select polypropylene examples

Ex#	Cat ID	Act ID	m	r	mmmm	mmmr	rmmr	mmrr	mmrm +rmrr	rmmr	rrrr	mrrr	mrrm	stereo defects/ 10000 monomer	total 2,1-regio defects/ 10000 monomer	1,3 regio defects/ 10000 monomer	ave. meso run length
PP-106	14	B	0.930	0.070	0.8460	0.0441	0.0021	0.0465	0.0162	0.0135	0.0026	0.0042	0.0248	381.0	4.0	91.0	21.0
PP-110	14	B	0.870	0.130	0.7281	0.0661	0.0045	0.0688	0.0368	0.0366	0.0090	0.0099	0.0403	711.0	1.0	99.0	12.3
**PP-112,113,114	15	A	0.851	0.149	0.8081	0.0076	0.0118	0.0017	0.0076	0.0387	0.0665	0.0025	0.0556	239.9	0.0	0.0	41.7
**PP-115,116,117	15	A	0.963	0.037	0.9020	0.0351	0.0127	0.0127	0.0040	0.0096	0.0127	0.0016	0.0096	125.8	0.0	102.9	43.7
PP-124	16	A	0.982	0.018	0.9222	0.0371	0.0153	0.0056	0.0006	0.0088	0.0040	0.0008	0.0057	72.9	17.3	60.8	66.2
**PP-127,128	16	A	0.982	0.018	0.9159	0.0452	0.0127	0.0105	0.0001	0.0068	0.0032	0.0013	0.0044	83.4	4.4	106.0	51.6
PP-131	16	B	0.981	0.019	0.9214	0.0415	0.0100	0.0072	0.0025	0.0058	0.0032	0.0023	0.0061	74.8	11.7	67.6	64.9
PP-134	16	B	0.963	0.037	0.8502	0.0618	0.0281	0.0219	0.0070	0.0166	0.0044	0.0009	0.0091	213.5	0.0	93.0	32.6
**PP-136,137,138	17	A	0.966	0.034	0.8648	0.0717	0.0167	0.0138	0.0060	0.0054	0.0088	0.0029	0.0100	125.2	0.0	21.7	68.1
**PP-142,143,144	18	A	0.977	0.023	0.8865	0.0684	0.0094	0.0178	0.0041	0.0026	0.0029	0.0007	0.0075	121.7	16.9	13.4	65.8
**PP-145,146,147	18	A	0.942	0.058	0.7602	0.1229	0.0267	0.0428	0.0127	0.0087	0.0067	0.0013	0.0180	312.9	0.0	35.9	28.7
PP-148	18	A	0.972	0.028	0.9280	0.0261	0.0074	0.0049	0.0099	0.0059	0.0069	0.0015	0.0094	103.6	0.0	0.0	96.5
**PP-149,150,151	18	A	0.940	0.060	0.8399	0.0353	0.0367	0.0268	0.0160	0.0127	0.0088	0.0110	0.0127	275.3	0.0	17.8	34.1

**The following polymer samples were mixed for ^{13}C NMR analysis:

PP-46,47,48; PP-49,50,51; PP-58,59,60; PP-64,65,66; PP-67,68,69; PP-112,113,114;

PP-115,116,117; PP-127,128; PP-136,137,138; PP-142,143,144; PP-145,146,147; PP-149,150,151

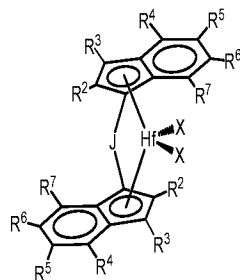
Table 7: 1-decene and 1-octene homopolymerization examples

Ex#*	Cat ID	Act ID	T (°C)	yield (g)	Activity (g/ mmol•hr)	Mn	Mw	PDI
PD-1	2	B	80	0.1544	1,929	23,808	34,299	1.44
PD-2	2	B	80	0.1125	1,406	24,480	34,693	1.42
PD-3	2	C	80	0.1323	1,654	25,346	37,500	1.48
PD-4	2	C	80	0.1270	1,587	28,256	39,134	1.38
PD-5	2	B	100	0.1313	1,641	12,385	18,168	1.47
PD-6	2	B	100	0.1775	2,219	13,388	19,069	1.42
PD-7	2	C	100	0.3404	4,254	14,558	20,553	1.41
PD-8	2	C	100	0.3368	4,210	15,010	20,922	1.39
PD-9	2	B	120	0.1015	1,269	7,121	10,335	1.45
PD-10	2	B	120	0.0745	931	6,862	9,807	1.43
PD-11	2	C	120	0.0833	1,041	8,371	11,926	1.42
PD-12	2	C	120	0.0515	644	8,224	11,690	1.42
PO-1	2	B	80	0.2549	3,185	26,013	36,658	1.41
PO-2	2	B	80	0.2650	3,311	26,235	37,029	1.41
PO-3	2	C	80	0.2101	2,626	28,984	41,115	1.42
PO-4	2	C	80	0.2308	2,885	29,406	41,521	1.41
PO-5	2	B	100	0.3340	4,174	13,738	19,422	1.41
PO-6	2	B	100	0.2863	3,578	14,144	20,197	1.43
PO-7	2	C	100	0.4072	5,089	15,365	22,084	1.44
PO-8	2	C	100	0.3905	4,881	16,415	23,379	1.42
PO-9	2	B	120	0.0994	1,242	7,131	10,152	1.42
PO-10	2	B	120	0.0711	889	7,462	10,548	1.41
PO-11	2	C	120	0.0656	820	8,433	12,233	1.45
PO-12	2	C	120	0.0829	1,036	8,859	12,669	1.43

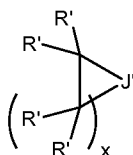
[00325] All documents described herein are incorporated by reference herein, including any
 priority documents and/or testing procedures to the extent they are not inconsistent with this
 text, provided however that any priority document not named in the initially filed application
 or filing documents is not incorporated by reference herein. 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 synonymous with the term "including"
 for purposes of Australian law. Likewise whenever a composition, an element or a group of
 elements is preceded with the transitional phrase "comprising", it is understood that we also
 contemplate the same composition or group of elements with transitional phrases "consisting
 essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the
 recitation of the composition, element, or elements and vice versa.

CLAIMS:

1. A metallocene catalyst compound represented by the formula:



- where each R^3 is hydrogen; each R^4 is independently a C_1 - C_{10} alkyl; each R^2 and R^7 is independently hydrogen, or C_1 - C_{10} alkyl, each R^5 and R^6 is independently hydrogen, C_1 - C_{50} substituted or unsubstituted hydrocarbyl, or C_1 - C_{50} substituted or unsubstituted halocarbyl; and R^4 and R^5 , R^5 and R^6 and/or R^6 and R^7 may optionally be bonded together to form a ring structure; J is a bridging group represented by the formula R^a_2J , where J is C or Si, and each R^a is, independently, C_1 to C_{20} substituted or unsubstituted hydrocarbyl, and the two R^a form a cyclic structure incorporating J and the cyclic structure may be a saturated or partially saturated cyclic or fused ring system; and each X is a univalent anionic ligand, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.
2. The metallocene catalyst compound of claim 1 wherein R^2 , R^4 and R^7 are, independently, a C_1 to C_{10} alkyl, and R^3 , R^5 and R^6 are hydrogen.
3. The metallocene catalyst compound of claim 1 wherein R^2 , R^4 and R^7 are, independently, selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl and an isomers thereof.
4. The metallocene catalyst compound of claim 1 wherein R^2 and R^4 are, independently, a C_1 to C_{10} alkyl.
5. The metallocene catalyst compound of claim 1 wherein R^4 and R^7 are, independently, a C_1 to C_{10} alkyl.
6. The metallocene catalyst compound of claim 1 wherein each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system).
7. The metallocene catalyst compound of claim 1 wherein J is represented by the formula:



- wherein J' is a carbon or silicon atom, x is 1, 2, 3, or 4, and each R' is, independently, hydrogen or C_1 - C_{10} hydrocarbyl.

8. The metallocene catalyst compound of claim 1 wherein J is cyclopentamethylenesilylene, cyclotetramethylenesilylene, cyclotrimethylenesilylene.

9. A metallocene catalyst compound selected from the group consisting of:
cyclotetramethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dimethyl,
5 cyclopentamethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2,4,7-trimethylinden-1-yl)hafnium dichloride,
10 cyclotetramethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride,
15 cyclotrimethylenesilylene-bis(2,4-dimethylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dichloride,
20 cyclopentamethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(4,7-dimethylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
25 cyclotetramethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2-methyl-4-cyclopropylindenyl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2-methyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclopentamethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
30 cyclotrimethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclotrimethylenesilylene-bis(2-ethyl-4-cyclopropylinden-1-yl)hafnium dichloride,
cyclotetramethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dimethyl,
35 cyclopentamethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dimethyl,
cyclotrimethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dimethyl,
cyclotetramethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dichloride,
cyclopentamethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dichloride,

cyclotrimethylenesilylene-bis(2-methyl-4-t-butylinden-1-yl)hafnium dichloride,
 cyclotetramethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dimethyl,
 cyclopentamethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dimethyl,
 cyclotrimethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dimethyl,
 5 cyclotetramethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dichloride,
 cyclopentamethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dichloride,
 cyclotrimethylenesilylene-bis(4,7-diethylinden-1-yl)hafnium dichloride,
 cyclotetramethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dimethyl,
 cyclopentamethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dimethyl,
 10 cyclotrimethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dimethyl,
 cyclotetramethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dichloride,
 cyclopentamethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dichloride,
 cyclotrimethylenesilylene-bis(2,4-diethylinden-1-yl)hafnium dichloride,
 cyclotetramethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dimethyl,
 15 cyclopentamethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dimethyl,
 cyclotrimethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dimethyl,
 cyclotetramethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dichloride,
 cyclopentamethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dichloride,
 cyclotrimethylenesilylene-bis(2-methyl-4,7-diethylinden-1-yl)hafnium dichloride,
 20 cyclotetramethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dimethyl,
 cyclopentamethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dimethyl,
 cyclotrimethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dimethyl,
 cyclotetramethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride,
 cyclopentamethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride,
 25 cyclotrimethylenesilylene-bis(2-ethyl-4-methylinden-1-yl)hafnium dichloride,
 cyclotetramethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dimethyl,
 cyclopentamethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dimethyl,
 cyclotrimethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dimethyl,
 cyclotetramethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dichloride,
 30 cyclopentamethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dichloride,
 cyclotrimethylenesilylene-bis(2-methyl-4-isopropylinden-1-yl)hafnium dichloride,
 cyclotetramethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium
 dimethyl,
 cyclopentamethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium
 35 dimethyl,
 cyclotrimethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium dimethyl,
 cyclotetramethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-*s*-indacen-5-yl)hafnium
 dichloride,

cyclopentamethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-s-indacen-5-yl)hafnium dichloride,

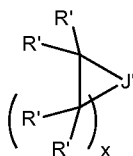
cyclotrimethylenesilylene-bis(4,6,8-trimethyl-1,2,3-trihydro-s-indacen-5-yl)hafnium dichloride; and any compound where the dimethyl in any of the compounds listed above is replaced with diethyl, dipropyl, diphenyl, dibenzyl, difluoride, dibromide, or diiodide.

10. A catalyst system comprising activator and the metallocene catalyst compound of claim 1.

11. A catalyst system comprising activator and the metallocene catalyst compound of claim 6, wherein R^2 , R^4 and R^7 are, independently, a C_1 to C_{10} alkyl, and R^3 , R^5 and R^6 are hydrogen.

12. The catalyst system of claim 10 wherein R^2 , R^4 and R^7 are, independently, selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl and an isomers thereof.

13. The catalyst system of claim 10 wherein J is represented by the formula:



wherein J' is a carbon or silicon atom, x is 1, 2, 3, or 4, and each R' is, independently, hydrogen or C_1 - C_{10} hydrocarbyl.

14. The catalyst system of claim 10 wherein J is cyclopentamethylenesilylene, cyclotetramethylenesilylene, cyclotrimethylenesilylene.

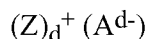
15. A catalyst system comprising activator and the metallocene catalyst compound of claim 9.

16. The catalyst system of claim 10 wherein the activator comprises alumoxane.

17. The catalyst system of claim 10 wherein alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal of 100:1 or more.

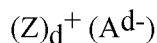
18. The catalyst system of claim 10 wherein the activator comprises a non-coordinating anion activator.

19. The catalyst system of claim 10 wherein activator is represented by the formula:



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 integer from 1 to 3.

20. The catalyst system of claim 10 wherein activator is represented by the formula:



wherein A^{d-} is a non-coordinating anion having the charge d-; d is an integer from 1 to 3, and Z is a reducible Lewis acid represented by the formula: (Ar_3C^+) , where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl.

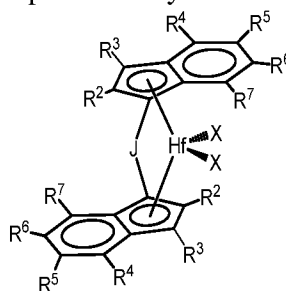
21. The catalyst system of claim 10 wherein the activator is one or more of:
- N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbenium
 tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate,
 triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium
 5 tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
 tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium
 tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
 N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium
 tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
 10 triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium
 tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
 trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium
 tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate, tri(n-
 butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(t-butyl)ammonium
 15 tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
 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, triethylsilylium
 20 tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, [4-t-
 butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B], trimethylammonium tetraphenylborate,
 triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-
 butyl)ammonium tetraphenylborate, tri(t-butyl)ammonium tetraphenylborate,
 N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate,
 25 N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate, tropillium tetraphenylborate,
 triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate,
 triethylsilylium tetraphenylborate, benzene(diazonium)tetraphenylborate, trimethylammonium
 tetrakis(pentafluorophenyl)borate, triethylammonium tetrakis(pentafluorophenyl)borate,
 tripropylammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium
 30 tetrakis(pentafluorophenyl)borate, 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
 35 tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate,
 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-tetrafluoro-phenyl)borate, 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, 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, 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, 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, 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, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine, and triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

22. The catalyst system of claim 10 wherein the catalyst system is supported.

23. The catalyst system of claim 10 wherein the catalyst system is supported on silica.

24. The catalyst system of claim 10 wherein the catalyst system comprises two catalyst compounds at least one of which is represented by the formula:



where each R^3 is hydrogen; each R^4 is independently a C_1 - C_{10} alkyl; each R^2 and R^7 is independently hydrogen, or C_1 - C_{10} alkyl, each R^5 and R^6 is independently hydrogen, C_1 - C_{50} substituted or unsubstituted hydrocarbyl, or C_1 - C_{50} substituted or unsubstituted halocarbyl; and

R^4 and R^5 , R^5 and R^6 and/or R^6 and R^7 may optionally be bonded together to form a ring structure; J is a bridging group represented by the formula R^a_2J , where J is C or Si, and each R^a is, independently, C_1 to C_{20} substituted or unsubstituted hydrocarbyl, and the two R^a form a cyclic structure incorporating J and the cyclic structure may be a saturated or partially saturated cyclic or fused ring system; and each X is a univalent anionic ligand, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.

25. A process to polymerize olefins comprising contacting one or more olefins with the catalyst system of claim 10.

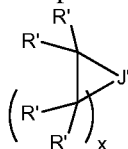
26. The process of claim 25 wherein each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system).

27. The process of claim 25 wherein R^4 and at least one of R^2 and R^7 are, independently, a C_1 to C_{10} alkyl.

28. The process of claim 25 wherein R^2 , R^4 and R^7 are, independently, a C_1 to C_{10} alkyl, and R^3 , R^5 and R^6 are hydrogen.

29. The process of claim 25 wherein R^2 , R^4 and R^7 are, independently, selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, heptyl, hexyl, octyl, nonyl, decyl and an isomers thereof.

30. The process of claim 25 wherein J is represented by the formula:



wherein J' is a carbon or silicon atom, x is 1, 2, 3, or 4, and each R' is, independently, hydrogen or C_1 - C_{10} hydrocarbyl.

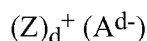
31. A process to polymerize olefins comprising contacting one or more olefins with the catalyst system of claim 15.

32. The process of claim 25 wherein the activator comprises alumoxane.

33. The process of claim 25 wherein alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal of 100:1 or more.

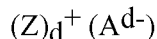
34. The process of claim 25 wherein the activator comprises a non-coordinating anion activator.

35. The process of claim 25 wherein activator is represented by the formula:



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 integer from 1 to 3.

36. The process of claim 25 wherein activator is represented by the formula:



wherein A^{d-} is a non-coordinating anion having the charge $d-$; d is an integer from 1 to 3, and Z is a reducible Lewis acid represented by the formula: (Ar_3C^+) , where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl.

37. The process of claim 25 wherein the activator is one or more of:

N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbenium
tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate,
triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium
tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium
tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium
tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium
tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)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,
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, triethylsilylium
tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, [4-t-
butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B], trimethylammonium tetraphenylborate,
triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-
butyl)ammonium tetraphenylborate, tri(t-butyl)ammonium tetraphenylborate,
N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate, tropillium tetraphenylborate,
triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate,
triethylsilylium tetraphenylborate, benzene(diazonium)tetraphenylborate, trimethylammonium
tetrakis(pentafluorophenyl)borate, triethylammonium tetrakis(pentafluorophenyl)borate,
tripropylammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium
tetrakis(pentafluorophenyl)borate, 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,
 benzene(diazonium) tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis-(2,3,4,6-
 tetrafluorophenyl) borate, triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 5 tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-
 (2,3,4,6-tetrafluoro-phenyl)borate, 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-
 10 tetrafluorophenyl)borate, 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,
 triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tripropylammonium
 15 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, N,N-diethylanilinium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-
 20 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, triethylsilylium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, benzene(diazonium) tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
 25 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, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-
 30 tetrafluoropyridine, and triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

38. The process of claim 25 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 MPa, and at a time up to 300 minutes.

39. The process of claim 25 further comprising obtaining polymer having at least 50% allyl
 35 chain ends.

40. The process of claim 25 wherein the olefins comprise ethylene and or propylene.