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- (71) **Applicants:** **EXXONMOBIL CHEMICAL PATENTS INC.** [US/US]; 5200 Bayway Dr., Baytown, Texas 77200 (US). **RAMOT AT TEL-AVIV UNIVERSITY LTD.** [IL/IL]; P.O. Box 39296, 61392 Tel Aviv (IL).
- (72) **Inventors:** **GIESBRECHT, Garth R.**; 66 North Emory Bend Place, The Woodlands, Texas 77381 (US). **HOLT-CAMP, Matthew, W.**; 26935 Carol Dr., Huffman, Texas 77336 (US). **KOL, Moshe**; 12 HaAluf Nechemia Tamari St., 52377 Ramat Gan (IL). **PRESS, Konstantin**; 2 Ha Nofar St., 75429 Rishon LeZion (IL).
- (74) **Agent:** **LUNDEEN, Daniel, N.**; 2710 Louisiana St., Houston, Texas 77006 (US).

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(54) **Title:** POLYALPHAOLEFINS PREPARED USING MODIFIED SALAN CATALYST COMPOUNDS

(57) **Abstract:** Disclosed herein are polyalphaolefins and Salan catalysts, catalyst systems, and processes to produce the polyalphaolefins. The salan catalysts of the invention are applied as unitary compounds with the activators built in the conjugate ring structure, wrapping around a Group IV metal. The method allows production of highly stereoregular products with narrow distribution of molecular masses of the growing polymer chains.



TITLE: Polyalphaolefins Prepared Using Modified Salan Catalyst Compounds

RELATED APPLICATIONS:

This application claims priority to and the benefit of provisional application
5 US 61/679,640, filed August 3, 2012.

FIELD OF THE INVENTION

This invention relates to polyalphaolefin polymers made with novel catalyst
compounds comprising Salan ligands.

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BACKGROUND OF THE INVENTION

Polyalpha-olefins (PAOs) comprise a class of hydrocarbons typically
manufactured by the catalytic oligomerization (polymerization to low-molecular-
weight products) of linear alpha-olefin (LAO) monomers. These typically range from
15 1-octene to 1-dodecene, with 1-decene being a suitable material, although oligomeric
copolymers of lower olefins such as ethylene and propylene may also be used,
including copolymers of ethylene with higher olefins. PAO products have achieved
importance in the lubricating oil market. Typically there are two classes of synthetic
hydrocarbon fluids (SHF) produced from linear alpha-olefins, the two classes of SHF
20 being denoted as PAO and HVI-PAO (high viscosity index PAOs). PAOs and HVI-
PAOs of different viscosity grades are typically produced using promoted BF_3 or
 AlCl_3 catalysts. Subsequent to polymerization, the PAO lubricant range products are
typically hydrogenated in order to reduce the residual unsaturation, generally to a level
of greater than 90%.

25 Synthetic PAOs have found wide acceptability and commercial success in the
lubricant field for their superiority to mineral based lubricants. In terms of lubricant
property improvement, industrial research efforts on synthetic lubricants have led to
PAO fluids exhibiting useful viscosities over a wide range of temperature, i.e.,
improved viscosity index, while also showing lubricity, thermal and oxidative stability
30 and pour point equal to or better than mineral oil. These relatively new synthetic
lubricants lower mechanical friction, enhancing mechanical efficiency over the full
spectrum of mechanical loads and do so over a wider range of operating conditions
than mineral oil lubricants.

Efforts have been made to prepare various PAOs using metallocene catalyst systems where PAOs are produced from meso-forms of certain metallocene catalysts under high hydrogen pressure. The use of rac-ethyl-bis(indenyl) zirconium dichloride or rac-dimethylsilyl-bis(2-methyl-indenyl) zirconium dichloride in combination with
5 MAO at 40 °C (at 200 psi hydrogen or 1 mole of hydrogen) to produce isotactic polydecene have also been reported. Others have made various PAOs, such as polydecene, using various metallocene catalysts not typically known to produce polymers or oligomers with any specific tacticity.

To date however, PAOs made with metallocenes have not found wide
10 applicability in the marketplace, particularly the lubricant marketplace, due to inefficient process, cost and property deficits. Accordingly, there exists a need in the art for providing PAOs and or HVI-PAOs and an improved process to produce them. There is a need in the art for new and improved catalysts and catalyst systems to obtain new and improved PAOs, polymerization processes, and the like. Accordingly,
15 there is a need in the art for new and improved catalyst systems for the polymerization of olefins, in order to achieve specific properties.

SUMMARY OF THE INVENTION

The instant disclosure is directed to catalyst compounds, catalyst systems
20 comprising such compounds, processes for the preparation of the catalyst compounds and systems, and processes for the polymerization of olefins using such catalyst compounds and systems, and the polymers produced thereby.

In an embodiment, a process comprises contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to
25 produce a polyalphaolefin comprising at least 50 mol% C₅ to C₂₄ olefin, wherein the catalyst system comprises Group 3, 4, 5 and/or 6 disubstituted compounds supported by a tetradentate di-anionic Salan ligand.

In an embodiment, a process comprises contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to
30 produce a polyalphaolefin comprising at least 50 mol% C₅ to C₂₄ olefin, wherein the catalyst system comprises Group 3, 4, 5 and/or 6 disubstituted compounds supported by a heteroaryl-substituted tetradentate di-anionic Salan ligand.

In an embodiment, a process comprises contacting one or more olefins with a

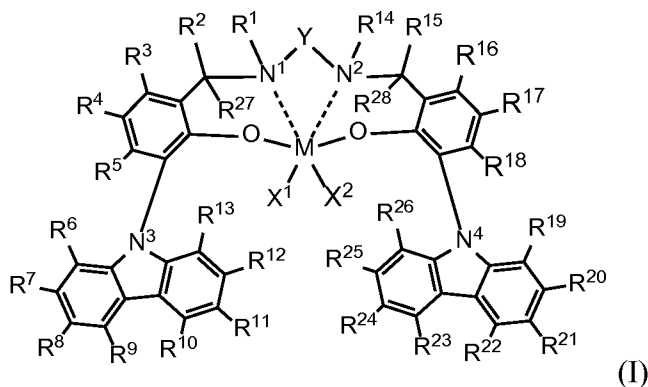
catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin comprising at least 50 mol% C₅ to C₂₄ olefin, wherein the catalyst system comprises Group 3, 4, 5 and/or 6 disubstituted compounds supported by a non-symmetrical heteroaryl-substituted tetradentate di-anionic Salan ligand.

5 In an embodiment, a process comprises contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin comprising at least 50 mol% C₅ to C₂₄ olefin, wherein the catalyst system comprises Group 3, 4, 5 and/or 6 disubstituted compounds supported by a carbazole-substituted tetradentate di-anionic Salan ligand.

10 In an embodiment, a process comprises contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin comprising at least 50 mol% C₅ to C₂₄ olefin, wherein the catalyst system comprises Group 3, 4, 5 and/or 6 disubstituted compounds supported by a halogenated tetradentate di-anionic Salan ligand.

15 In an embodiment, a process comprises contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin comprising at least 50 mol% C₅ to C₂₄ olefin; the catalyst system comprising an activator and a catalyst compound according to Formula I, Formula II, Formula III, or a combination thereof:

20 Formula I being represented by:



wherein M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements,

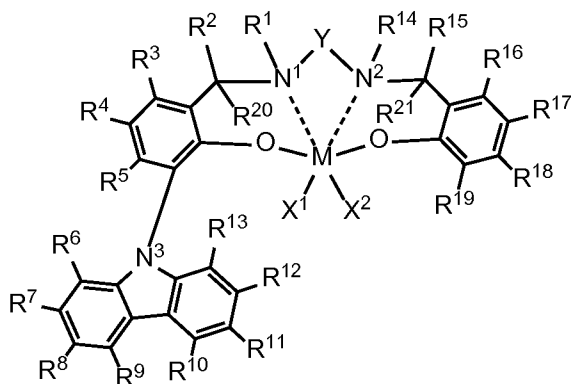
25 or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹,

R^{20} , R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} , and R^{28} is, independently, a hydrogen, a C_1 - C_{40} hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or two or more of R^1 to R^{28} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, or a combination thereof, or a combination thereof; and

Y is a divalent C_1 to C_{20} hydrocarbyl;

Formula II being represented by:



(II)

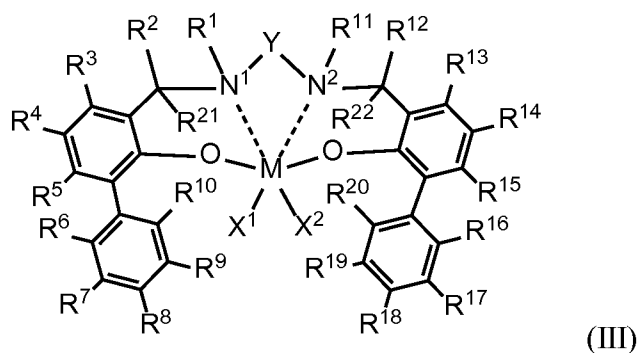
wherein M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C_1 to C_{20} hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X^1 and X^2 join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, provided, however, where M is trivalent then X^2 is not present;

each R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , and R^{21} is, independently, a hydrogen, a C_1 - C_{40} hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R^1 to R^{21} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, or a combination thereof; subject to the proviso that R^{19} is not a carbazole or a substituted carbazole radical, and

Y is a divalent C_1 to C_{20} hydrocarbyl radical;

Formula III being represented by:



wherein M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²¹ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof;

at least one of R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁶, R¹⁷, R¹⁸, R¹⁹, or R²⁰ comprise fluorine; and Y is a divalent C₁ to C₂₀ hydrocarbyl radical.

In an embodiment, a polyalphaolefin comprises the polymer produced by any one of the foregoing processes. In an embodiment, a polyalphaolefin comprises at least 50 mol% C₅ to C₂₄ olefin, the polymer produced by a process comprising contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin, the catalyst system comprising an activator and a catalyst as described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a ¹³C NMR image for poly-(1-hexene) made with Compound B/MAO according to an embodiment of the invention.

Figure 2 is a ¹³C NMR image for poly-(1-hexene) made with Compound B/B(C₆F₅)₃ according to an embodiment of the invention.

DETAILED DESCRIPTION

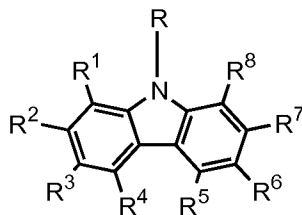
For the purposes of this invention and the claims thereto, the new numbering scheme for the Periodic Table Groups is used as in Chem. Eng. News, 1985, 63, 27. Therefore, a "Group 4 metal" is an element from Group 4 of the Periodic Table.

5 In the structures depicted throughout this specification and the claims, a solid line indicates a bond, an arrow indicates that the bond may be dative, and each dashed line represents a bond having varying degrees of covalency and a varying degree of coordination.

For the purposes herein the term "polyalphaolefin" or "PAO" includes
10 homopolymers and copolymers of alpha-olefin monomers.

The terms "hydrocarbyl radical," "hydrocarbyl" and "hydrocarbyl group" are used interchangeably throughout this document unless otherwise specified. For purposes of this disclosure, a hydrocarbyl radical is defined to be C₁ to C₇₀ radicals, or C₁ to C₂₀ radicals, or C₁ to C₁₀ radicals, or C₆ to C₇₀ radicals, or C₆ to C₂₀
15 radicals, or C₇ to C₂₀ radicals that may be linear, branched, or cyclic where appropriate (aromatic or non-aromatic); and includes hydrocarbyl radicals substituted with other hydrocarbyl radicals and/or one or more functional groups comprising elements from Groups 13 – 17 of the periodic table of the elements. In addition two or more such hydrocarbyl radicals may together form a fused ring system, including
20 partially or fully hydrogenated fused ring systems, which may include heterocyclic radicals.

For purposes herein, a carbazole or substituted carbazole radical is represented by the formula:



25 wherein each R¹ through R⁸ is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R¹ to R⁸ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof.

The term "substituted" means that a hydrogen atom and/or a carbon atom in
30 the base structure has been replaced with a hydrocarbyl radical, and/or a functional

group, and/or a heteroatom or a heteroatom containing group. Accordingly, the term hydrocarbyl radical includes heteroatom containing groups. For purposes herein, a heteroatom is defined as any atom other than carbon and hydrogen. For example, methyl cyclopentadiene (Cp) is a Cp group, which is the base structure, substituted
 5 with a methyl radical, which may also be referred to as a methyl functional group, ethyl alcohol is an ethyl group, which is the base structure, substituted with an -OH functional group, and pyridine is a phenyl group having a carbon in the base structure of the benzene ring substituted with a nitrogen atom.

For purposes herein, a hydrocarbyl radical may be independently selected from
 10 substituted or unsubstituted methyl, ethyl, ethenyl and isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl,
 15 dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, hexacosenyl, heptacosenyl, octacosenyl, nonacosenyl, triacontenyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, tridecynyl, tetradecynyl, pentadecynyl, hexadecynyl,
 20 heptadecynyl, octadecynyl, nonadecynyl, eicosynyl, heneicosynyl, docosynyl, tricosynyl, tetracosynyl, pentacosynyl, hexacosynyl, heptacosynyl, octacosynyl, nonacosynyl, and triacontynyl.

For purposes herein, hydrocarbyl radicals may also include isomers of saturated, partially unsaturated and aromatic cyclic structures wherein the radical may
 25 additionally be subjected to the types of substitutions described above. The term “aryl”, “aryl radical”, and/or “aryl group” refers to aromatic cyclic structures, which may be substituted with hydrocarbyl radicals and/or functional groups as defined herein. Examples of aryl radicals include: acenaphthenyl, acenaphthylenyl, acridinyl, anthracenyl, benzanthracenyls, benzimidazolyl, benzisoxazolyl, benzofluoranthenyls,
 30 benzofuranyl, benzoperylenyls, benzopyrenyls, benzothiazolyl, benzothiophenyls, benzoxazolyl, benzyl, carbazolyl, carbolinyl, chrysenyl, cinnolinyl, coronenyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, dibenzoanthracenyls, fluoranthenyl, fluorenyl, furanyl, imidazolyl, indazolyl, indenopyrenyls, indolyl, indolinyl,

isobenzofuranyl, isoindolyl, isoquinolinyl, isoxazolyl, methyl benzyl, methylphenyl, naphthyl, oxazolyl, phenanthrenyl, phenyl, purinyl, pyrazinyl, pyrazolyl, pyrenyl, pyridazinyl, pyridinyl, pyrimidinyl, pyrrolyl, quinazolinyl, quinolonyl, quinoxalanyl, thiazolyl, thiophenyl, and the like.

5 It is to be understood that for purposes herein, when a radical is listed, it indicates that the base structure of the radical (the radical type) and all other radicals formed when that radical is subjected to the substitutions defined above. Alkyl, alkenyl, and alkynyl radicals listed include all isomers including where appropriate cyclic isomers, for example, butyl includes *n*-butyl, 2-methylpropyl, 1-methylpropyl, 10 *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 15 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.

20 Likewise the terms “functional group”, “group” and “substituent” are also used interchangeably throughout this document unless otherwise specified. For purposes herein, a functional group includes both organic and inorganic radicals or moieties comprising elements from Groups 13, 14, 15, 16, 17 of the periodic table of elements. Suitable functional groups may include hydrocarbyl radicals, e.g., alkyl radicals, 25 alkene radicals, aryl radicals, and/or halogen (Cl, Br, I, F), O, S, Se, Te, NR^{*}_x, OR^{*}, SeR^{*}, TeR^{*}, PR^{*}_x, AsR^{*}_x, SbR^{*}_x, SR^{*}, BR^{*}_x, SiR^{*}_x, GeR^{*}_x, SnR^{*}_x, PbR^{*}_x, and/or the like, wherein R is a C₁ to C₂₀ hydrocarbyl as defined above and wherein x is the appropriate integer to provide an electron neutral moiety. Other examples of functional groups include those typically referred to as amines, imides, amides, ethers, 30 alcohols (hydroxides), sulfides, sulfates, phosphides, halides, phosphonates, alkoxides, esters, carboxylates, aldehydes, and the like.

For purposes herein an “olefin,” alternatively referred to as “alkene,” is a linear, branched, or cyclic compound comprising 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.

For purposes herein 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" in reference 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 as Mn of less than 25,000 g/mol, or in an embodiment 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.

For the purposes of this disclosure, the term " α -olefin" includes C₂-C₂₂ olefins. Non-limiting examples of α -olefins include ethylene, 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. Non-limiting examples of cyclic olefins and diolefins include cyclopropene, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclononene, cyclodecene, norbornene, 4-methylnorbornene, 2-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.

The terms "catalyst", "catalyst compound", and "transition metal compound" are defined to mean a compound capable of initiating polymerization catalysis under the appropriate conditions. In the description herein, the catalyst may be described as a catalyst precursor, a pre-catalyst compound, or a transition metal compound, and these terms are used interchangeably. A catalyst compound may be used by itself to initiate catalysis or may be used in combination with an activator to initiate catalysis.

When the catalyst compound is combined with an activator to initiate catalysis, the catalyst compound is often referred to as a pre-catalyst or catalyst precursor. A "catalyst system" is combination of at least one catalyst compound, at least one activator, which may include a co-activator, and/or a support material, where the system can polymerize monomers to polymer. 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.

For purposes herein the term "catalyst productivity" is a measure of how many grams of polymer (P) are produced using a polymerization catalyst comprising W g of catalyst (cat), over a period of time of T hours; and may be expressed by the following formula: $P/(T \times W)$ and expressed in units of $\text{gP/gcat}^{-1}\text{hr}^{-1}$. Conversion is the amount of monomer that is converted to polymer product, and is reported as mol% and is calculated based on the polymer yield and the amount of monomer fed into the reactor. Catalyst activity is a measure of how active the catalyst is and is reported as the mass of product polymer (P) produced per mole of catalyst (cat) used (kg P/mol cat).

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.

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 an embodiment a co-activator can be pre-mixed with the catalyst compound to form an alkylated catalyst compound.

A propylene polymer is a polymer having at least 50 mol% of propylene. As used herein, Mn is number average molecular weight as determined by proton nuclear magnetic resonance spectroscopy (^1H NMR) unless stated otherwise, Mw is weight average molecular weight determined by gel permeation chromatography (GPC), and Mz is z average molecular weight determined by GPC, wt% is weight percent, and mol% is mole percent. Molecular weight distribution (MWD) 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 through this specification: Me is methyl, Ph is phenyl, Et is ethyl, Pr is propyl, iPr is isopropyl, n-Pr is normal propyl, Bu is butyl, iso-butyl is isobutyl, sec-butyl refers to secondary butyl, tert-butyl, refers to tertiary butyl, n-butyl is normal butyl, pMe is para-methyl, Bz is benzyl, THF is tetrahydrofuran, Mes is mesityl, also known as 1,3,5-trimethylbenzene, Tol is toluene, TMS is trimethylsilyl, TIBAL is triisobutylaluminum, TNOAL is triisobutyl n-octylaluminum, MAO is methylalumoxane, and MOMO is methoxymethoxy (also referred to as methoxymethyl ether).

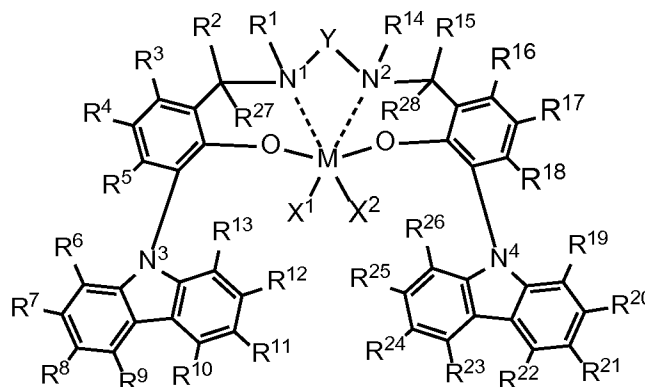
For purposes herein, RT is room temperature, which is defined as 25 °C unless otherwise specified. All percentages are weight percent (wt%) unless otherwise specified.

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

CATALYST COMPOUNDS

In an embodiment, the catalyst comprises Group 3, 4, 5 and/or 6 disubstituted compounds supported by a tetradentate di-anionic Salan ligand, useful to polymerize olefins and/or α -olefins to produce polyolefins and/or poly(α -olefins). In an embodiment the ligand is heteroaryl-substituted. In an embodiment the heteroaryl substituent comprises nitrogen, or comprises carbazole. In an embodiment, the heteroaryl-substituted ligand is non-symmetrical. In an additional or alternative embodiment, the ligand is halogenated.

In an embodiment, the catalyst compounds are represented by the following structure:



where each solid line represents a covalent bond and each dashed line represents a bond having varying degrees of covalency and a varying degree of coordination;

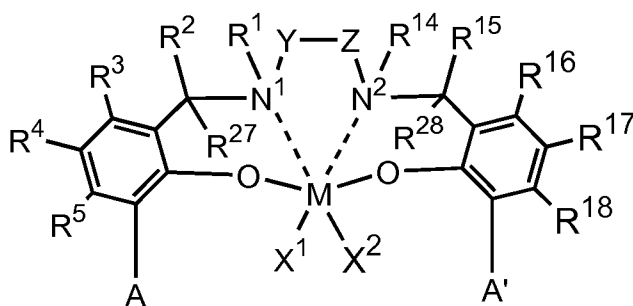
M is a Group 3, 4, 5 or 6 transition metal covalently bonded to each oxygen atom, and bonded with varying degrees of covalency and coordination to each of nitrogen atoms N¹ and N²;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

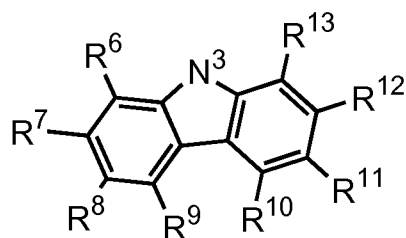
each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷ and R²⁸ is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²⁸ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof; and

Y is a divalent hydrocarbyl radical covalently bonded to and bridging between both of the nitrogen atoms N¹ and N². In an embodiment, two or more of R¹ to R²⁸ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure.

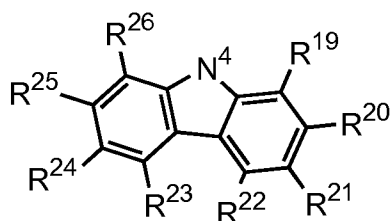
In an embodiment, the catalyst compound is represented by the formula:



wherein: A is represented by the formula, attached to the nitrogen atom, labeled N³ of the carbazole ring:



- 5 wherein A' is represented by the formula, attached to the nitrogen atom labeled N⁴ of the carbazole ring:



Wherein M is a Group 3, 4, 5 or 6 transition metal;

- each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

- each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷, and R²⁸ is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²⁸ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof; and

- Y and Z form a divalent C₁ to C₂₀ hydrocarbyl radical. In an embodiment, Y and Z are identical. In an embodiment, Y and Z are different.

In an embodiment, M is a Group 4 metal, or M is Hf, Ti and/or Zr, or M is

Hf or Zr. In an embodiment, each of X^1 and X^2 is independently selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides having from 1 to 20 carbon atoms, sulfides, phosphides, halides, amines, phosphines, ethers, and combinations thereof.

5 In an embodiment, X^1 and X^2 together form a part of a fused ring or a ring system having from 4 to 62 carbon atoms.

In an embodiment, each of X^1 and X^2 is independently selected from the group consisting of halides, alkyl radicals having from 1 to 7 carbon atoms, benzyl radicals, or a combination thereof.

10 In an embodiment, Y is a divalent C_1 - C_{40} hydrocarbyl radical comprising a portion that comprises a linker backbone comprising from 1 to 18 carbon atoms linking or bridging between nitrogen atoms N^1 and N^2 . In an embodiment, Y is a C_1 - C_{40} hydrocarbyl radical comprising a portion that comprises a linker backbone comprising from 1 to 18 carbon atoms linking the nitrogen atoms N^1 and N^2 wherein
 15 the hydrocarbyl comprises O, S, S(O), S(O)₂, Si(R^{*})₂, P(R^{*}), N or N(R^{*}), wherein each R^{*} is independently a C_1 - C_{18} hydrocarbyl. In an embodiment, Y is selected from the group consisting of ethylene (-CH₂CH₂-) and 1,2-cyclohexylene, and/or -CH₂CH₂CH₂- derived from propylene. In an embodiment, Y is -CH₂CH₂CH₂- derived from propylene.

20 In an embodiment, each X is, independently, a halogen or a C_1 to C_7 hydrocarbyl radical.

In an embodiment, each X is a benzyl radical. In an embodiment, each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}$, and R^{28} is, independently, hydrogen, a halogen, or a
 25 C_1 to C_{30} hydrocarbyl radical, or a C_1 to C_{10} hydrocarbyl radical. In an embodiment, one or more of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}$, and R^{28} is a methyl radical, a fluoride, or a combination thereof.

30 In an embodiment, M is Zr; X^1 and X^2 are benzyl radicals; R^1 and R^{14} are methyl radicals; R^2 through R^{13} and R^{15} through R^{28} are hydrogen; and Y is ethylene (-CH₂CH₂-).

In an embodiment, M is Zr; X^1 and X^2 are benzyl radicals; R^1, R^4, R^{14} and R^{17} are methyl radicals; R^2, R^3, R^5 through R^{13}, R^{15}, R^{16} and R^{18} through R^{28} are

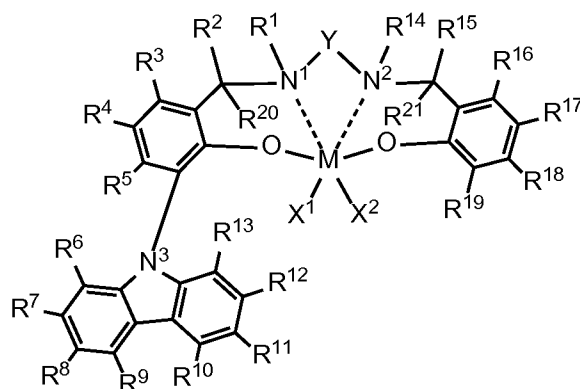
hydrogen; and Y is ethylene ($-\text{CH}_2\text{CH}_2-$).

In an embodiment, M is Zr; X^1 and X^2 are benzyl radicals; R^1 and R^{14} are methyl radicals; R^4 and R^{17} are fluoro (F) functional groups; R^2 , R^3 , R^5 through R^{13} , R^{15} , R^{16} and R^{18} through R^{28} are hydrogen; and Y is ethylene ($-\text{CH}_2\text{CH}_2-$).

5 In an embodiment, M is Zr; X^1 and X^2 are benzyl radicals; R^1 , R^4 , R^{14} and R^{17} are methyl radicals; R^8 , R^{11} , R^{21} and R^{24} are tert-butyl radicals; R^2 , R^3 , R^5 , R^6 , R^7 , R^9 , R^{10} , R^{12} , R^{13} , R^{15} , R^{16} , R^{18} , R^{19} , R^{20} , R^{22} , R^{23} , R^{25} , R^{26} , R^{27} , and R^{28} are hydrogen; and Y is ethylene ($-\text{CH}_2\text{CH}_2-$).

10 In an embodiment, M is Zr; X^1 and X^2 are benzyl radicals; R^1 , R^4 , R^{14} and R^{17} are methyl radicals; R^8 , R^{11} , R^{21} and R^{24} are mesityl radicals; R^2 , R^3 , R^5 , R^6 , R^7 , R^9 , R^{10} , R^{12} , R^{13} , R^{15} , R^{16} , R^{18} , R^{19} , R^{20} , R^{22} , R^{23} , R^{25} , R^{26} , R^{27} , and R^{28} are hydrogen; and Y is ethylene ($-\text{CH}_2\text{CH}_2-$).

In an embodiment, the catalyst comprises Group 3, 4, 5 and/or 6 disubstituted compounds supported by a tetradentate di-anionic Salan ligand, useful to polymerize
15 olefins and/or α -olefins to produce polyolefins and/or poly(α -olefins). In an embodiment, the catalyst compounds are represented by the following structure:



where each solid line represents a covalent bond and each dashed line represents a bond having varying degrees of covalency and a varying degree of coordination;

20 M is a Group 3, 4, 5 or 6 transition metal covalently bonded to each oxygen atom, and bonded with varying degrees of covalency and coordination to each of nitrogen atoms N^1 and N^2 ;

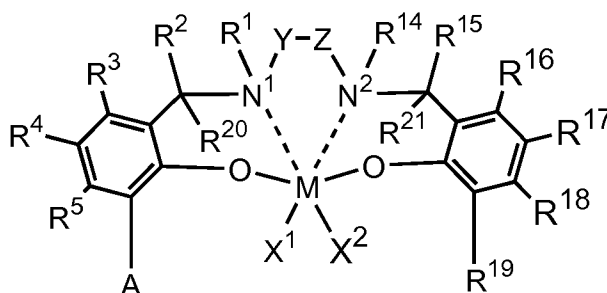
each X is, independently, a univalent C_1 to C_{20} hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements,
25 or X^1 and X^2 join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, provided, however, where M is trivalent then X^2 is not present;

each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}$, and R^{21} is independently, a hydrogen, a C_1 - C_{40} hydrocarbyl, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R^1 to R^{21} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, or a combination thereof, subject to the proviso that R^{19} is not a carbazole or a substituted carbazole radical; and

Y is a divalent hydrocarbyl radical covalently bonded to and bridging between both of the nitrogen atoms N^1 and N^2 . In an embodiment, two or more of R^1 to R^{21} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure.

Accordingly, an embodiment of the instant disclosure is directed to non-symmetrical Salan catalysts. The Salan catalysts disclosed in an embodiment herein are devoid of a symmetry element, having a non-symmetric or non-palindromic structure. By non-symmetric, it is meant that the two phenol moieties of the Salan compound are substituted differently when comparing the substitutions of one phenol, which comprises a carbazole or substituted carbazole radical, and the other phenol which does not comprise a carbazole or a substituted carbazole radical at position R^{19} (i.e., subject to the proviso that R^{19} is not a carbazole or a substituted carbazole radical), as is shown in the above structure.

In an embodiment, the catalyst compounds are represented by the formula:



wherein A is a heteroaryl radical;

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

each X is, independently, a univalent C_1 to C_{20} hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X^1 and X^2 join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, provided, however, where M is trivalent then X^2 is not present;

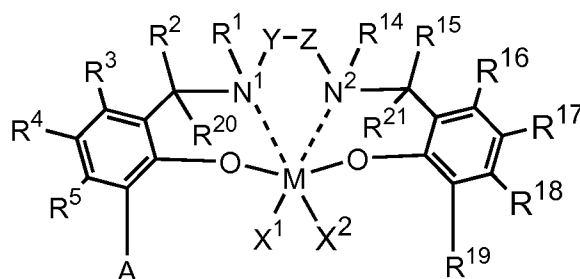
each $R^1, R^2, R^3, R^4, R^5, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}$, and R^{21} is independently, a hydrogen, a C_1 - C_{40} hydrocarbyl, a functional group comprising elements from Group

13 – 17 of the periodic table of the elements, or two or more of R^1 to R^5 and R^{14} to R^{21} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, or a combination thereof, subject to the proviso that R^{19} is not identical to A; and

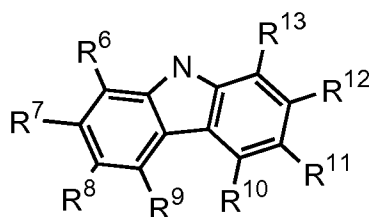
5 Y and Z together form a divalent C_1 to C_{20} hydrocarbyl radical.

In an embodiment, A comprises a heteroaryl radical comprising nitrogen. In an embodiment A comprises a carbazolyl radical. In an embodiment, R^{19} is a carbazole that is substituted differently than R^6 - R^{13} of the carbazolyl radical A. E.g., if all of R^6 through R^{13} of the carbazolyl radical A are hydrogen (unsubstituted), then
 10 in an embodiment, R^{19} comprises a carbazole ring wherein one or more of the substituents of the R^{19} carbazole ring are substituted. In an embodiment, if one or more of R^6 through R^{13} of the carbazolyl radical A are substituted, then the corresponding substituents of an R^{19} carbazole ring are unsubstituted, each have different substituents, or the substituents are located at different positions relative to
 15 the ring structure. In an embodiment, R^{19} is not a nitrogen containing heteroaryl. In an embodiment, R^{19} is a nitrogen containing heteroaryl other than carbazole. In an embodiment, R^{19} comprises hydrogen or a C_1 - C_{40} hydrocarbyl.

In an embodiment, a catalyst compound is represented by the structure



20 wherein A is represented by the structure attached at the carbazole nitrogen atom:



where each solid line represents a covalent bond and each dashed line represents a bond having varying degrees of covalency and a varying degree of coordination;

M is a Group 3, 4, 5 or 6 transition metal covalently bonded to each oxygen atom, and

25 bonded with varying degrees of covalency and coordination to each of nitrogen atoms

N^1 and N^2 ;

each X is, independently, a univalent C_1 to C_{20} hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X^1 and X^2 join together to form a C_4 to C_{62} cyclic or polycyclic ring structure,

5 provided, however, where M is trivalent then X^2 is not present;

each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}$, and R^{21} is independently, a hydrogen, a C_1 - C_{40} hydrocarbyl, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or a combination thereof, subject to the proviso that R^{19} is not identical to A; and

10 Y and Z form a divalent hydrocarbyl radical covalently bonded to and bridging between both of the nitrogen atoms N^1 and N^2 . In an embodiment, Y is identical to Z. In an embodiment, Y is different to Z. In an embodiment, two or more of R^1 to R^{21} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure.

15 In an embodiment, M is a Group 4 metal, or M is Hf, Ti and/or Zr, or M is Hf or Zr. In an embodiment, each of X^1 and X^2 is independently selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides having from 1 to 20 carbon atoms, sulfides, phosphides, halides, amines, phosphines, ethers, and combinations thereof.

20 In an embodiment, X^1 and X^2 together form a part of a fused ring or a ring system having from 4 to 62 carbon atoms.

In an embodiment, each of X^1 and X^2 is independently selected from the group consisting of halides, alkyl radicals having from 1 to 7 carbon atoms, benzyl radicals, or a combination thereof.

25 In an embodiment, Y is a divalent C_1 - C_{40} hydrocarbyl radical comprising a portion that comprises a linker backbone comprising from 1 to 18 carbon atoms linking or bridging between nitrogen atoms N^1 and N^2 . In an embodiment, Y is a C_1 - C_{40} hydrocarbyl radical comprising a portion that comprises a linker backbone comprising from 1 to 18 carbon atoms linking the nitrogen atoms N^1 and N^2 wherein
30 the hydrocarbyl comprises O, S, S(O), S(O)₂, Si(R^{*})₂, P(R^{*}), N or N(R^{*}), wherein each R^{*} is independently a C_1 - C_{18} hydrocarbyl. In an embodiment, Y is selected from the group consisting of ethylene (-CH₂CH₂-) and 1,2-cyclohexylene, and/or -CH₂CH₂CH₂- derived from propylene. In an embodiment, Y is -CH₂CH₂CH₂-

derived from propylene.

In an embodiment, each X is, independently, a halogen or a C₁ to C₇ hydrocarbyl radical.

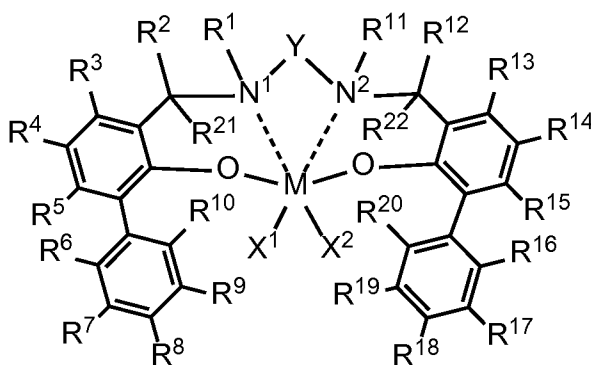
In an embodiment, each X is a benzyl radical. In an embodiment, each
 5 R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰,
 and R²¹ is, independently, hydrogen, a halogen, or a C₁ to C₃₀ hydrocarbyl radical, or
 a C₁ to C₁₀ hydrocarbyl radical, subject to the proviso that R¹⁹ is not a carbazole or a
 substituted carbazole radical. In an embodiment, one or more of R¹, R², R³, R⁴, R⁵,
 R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, and R²¹ is a methyl
 10 radical, a bromine, an adamantyl radical, or a combination thereof.

In an embodiment, M is Zr; X¹ and X² are benzyl; R¹ and R¹⁴ are methyl; R²
 through R¹³, R¹⁵, R¹⁶, R¹⁸, R²⁰ and R²¹ are hydrogen; R¹⁷ and R¹⁹ are bromine; and Y
 is -CH₂CH₂-.

In an embodiment, M is Zr; X¹ and X² are benzyl; R¹, R¹⁴ and R¹⁷ are methyl;
 15 R² through R¹³, R¹⁵, R¹⁶, R¹⁸, R²⁰ and R²¹ are hydrogen; R¹⁹ is 1-adamantyl; and Y is -
 CH₂CH₂-.

In an embodiment, M is Hf; X¹ and X² are benzyl; R¹ and R¹⁴ are methyl; R²
 through R¹³, R¹⁵, R¹⁶, R¹⁸, R²⁰ and R²¹ are hydrogen; R¹⁷ is methyl; R¹⁹ is 1-
 adamantyl; and Y is -CH₂CH₂-.

20 In an embodiment, the catalyst comprises a compound represented by the
 formula:



where each solid line represents a covalent bond and each dashed line represents a
 bond having varying degrees of covalency and a varying degree of coordination;

25 M is a Group 3, 4, 5 or 6 transition metal covalently bonded to each oxygen atom, and
 bonded with varying degrees of covalency and coordination to each of nitrogen atoms
 N¹ and N²;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

5 each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or a combination thereof;

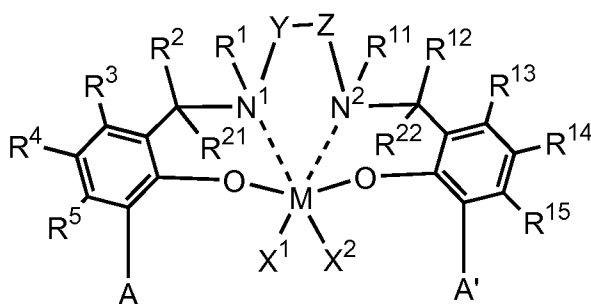
wherein at least one of R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁶, R¹⁷, R¹⁸, R¹⁹, or R²⁰ comprise fluorine;

10 and

Y is a divalent hydrocarbyl radical covalently bonded to and bridging between both of the nitrogen atoms N¹ and N².

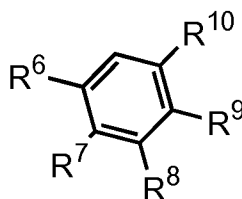
In an embodiment, two or more of R¹ to R²² may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure. Accordingly, the instant
15 disclosure is directed to non-symmetrical Salan catalysts. The Salan catalysts disclosed herein are at least partially fluorinated, and may include perfluorinated or partially perfluorinated aromatic ring systems as substituents.

In an embodiment, the catalyst compound is represented by the following formula:

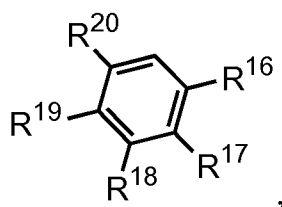


20

wherein substituent A is represented by the following formula, attached to the benzene ring:



wherein substituent A' is represented by the following formula attached to the
25 benzene ring:



where each solid line represents a covalent bond and each dashed line represents a bond having varying degrees of covalency and a varying degree of coordination;

M is a Group 3, 4, 5 or 6 transition metal covalently bonded to each oxygen atom, and
 5 bonded with varying degrees of covalency and coordination to each of nitrogen atoms N¹ and N²;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure,
 10 provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or a combination thereof;

15 at least one of R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁶, R¹⁷, R¹⁸, R¹⁹, or R²⁰ comprise fluorine; and

Y and Z form divalent hydrocarbyl radical covalently bonded to and bridging between both of the nitrogen atoms N¹ and N². In an embodiment, two or more of R¹ to R²² may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure. In an embodiment, Y is identical to Z. In an embodiment, Y is different
 20 than Z.

For purposes herein, a perfluorinated ring is defined as a ring system wherein each of the available hydrogen atoms are substituted with a fluorine atom, also referred to as a fluoride.

In an embodiment, M is a Group 4 metal, or M is Hf, Ti and/or Zr, or M is Ti
 25 or Zr. In an embodiment, each of X¹ and X² is independently selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides having from 1 to 20 carbon atoms, sulfides, phosphides, halides, amines, phosphines, ethers, an combinations thereof.

In an embodiment, X¹ and X² together form a part of a fused ring or a ring
 30 system having from 4 to 62 carbon atoms.

In an embodiment, each of X^1 and X^2 is independently selected from the group consisting of halides, alkyl radicals having from 1 to 7 carbon atoms, benzyl radicals, or a combination thereof.

In an embodiment, Y is a divalent C_1 - C_{40} hydrocarbyl radical comprising a portion that comprises a linker backbone comprising from 1 to 18 carbon atoms linking or bridging between nitrogen atoms N^1 and N^2 . In an embodiment, Y is a C_1 - C_{40} hydrocarbyl radical comprising a portion that comprises a linker backbone comprising from 1 to 18 carbon atoms linking the nitrogen atoms N^1 and N^2 wherein the hydrocarbyl comprises O, S, S(O), S(O)₂, Si(R^{*})₂, P(R^{*}), N or N(R^{*}), wherein each R^{*} is independently a C_1 - C_{18} hydrocarbyl. In an embodiment, Y is selected from the group consisting of ethylene (-CH₂CH₂-) and 1,2-cyclohexylene, and/or -CH₂CH₂CH₂- derived from propylene. In an embodiment, Y is -CH₂CH₂CH₂- derived from propylene.

In an embodiment, each X is, independently, a halogen or a C_1 to C_7 hydrocarbyl radical. In an embodiment, each X is a benzyl radical.

In an embodiment, each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² is, independently, hydrogen, a halogen, or a C_1 to C_{30} hydrocarbyl radical, or a C_1 to C_{10} hydrocarbyl radical.

In an embodiment, one or more of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² is a methyl radical, or a fluoride, which may also be referred to as a fluorine or a fluorine functional group.

In an embodiment, M is Ti; X^1 and X^2 are benzyl radicals; R¹ and R¹¹ are methyl radicals; R², R³, R⁵, R¹², R¹³, R¹⁵, R²¹ and R²² are hydrogen; R⁴, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁴, R¹⁶, R¹⁷, R¹⁸, R¹⁹, and R²⁰ are fluorine; and Y is -CH₂CH₂-.

In an embodiment, M is Ti; X^1 and X^2 are benzyl radicals; R¹, R⁴, R¹¹, and R¹⁴ are methyl radicals; R², R³, R⁵, R¹², R¹³, R¹⁵, R²¹ and R²² are hydrogen; R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁶, R¹⁷, R¹⁸, R¹⁹, and R²⁰ are fluorine; and Y is -CH₂CH₂-.

In an embodiment, M is Zr; X^1 and X^2 are benzyl radicals; R¹ and R¹¹ are methyl radicals; R², R³, R⁵, R¹², R¹³, R¹⁵, R²¹ and R²² are hydrogen; R⁴, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁴, R¹⁶, R¹⁷, R¹⁸, R¹⁹, and R²⁰ are fluorine; and Y is -CH₂CH₂-.

In an embodiment, M is Zr; X^1 and X^2 are benzyl radicals; R¹, R⁴, R¹¹, and R¹⁴ are methyl radicals; R², R³, R⁵, R¹², R¹³, R¹⁵, R²¹ and R²² are hydrogen; R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁶, R¹⁷, R¹⁸, R¹⁹, and R²⁰ are fluorine; and Y is -CH₂CH₂-.

In an embodiment, two or more different catalyst compounds are present in the catalyst system used herein. In an embodiment, two or more different catalyst compounds are present in the reaction zone where the process(es) described herein occur. When two transition metal compound based catalysts are used in one reactor as
5 a mixed catalyst system, the two transition metal compounds are chosen such that the two are compatible. Compatible catalysts are those catalysts having similar kinetics of termination and insertion of monomer and comonomer(s) and/or do not detrimentally interact with each other. For purposes herein, the term "incompatible catalysts" refers to and means catalysts that satisfy one or more of the following:

- 10 1) those catalysts that when present together reduce the activity of at least one of the catalysts by greater than 50%;
- 2) those catalysts that under the same reactive conditions produce polymers such that one of the polymers has a molecular weight that is more than twice the molecular weight of the other polymer; and
- 15 3) those catalysts that differ in comonomer incorporation or reactivity ratio under the same conditions by more than about 30%. 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. In an embodiment, the catalyst systems use the same activator for the catalyst compounds. In an embodiment, two or
20 more different activators, such as a non-coordinating anion activator and an alumoxane, can be used in combination. If one or more catalyst compounds contain an X^1 or X^2 ligand which is not a hydride, or a hydrocarbyl, then in an embodiment the alumoxane is contacted with the catalyst compounds prior to addition of the non-coordinating anion activator.

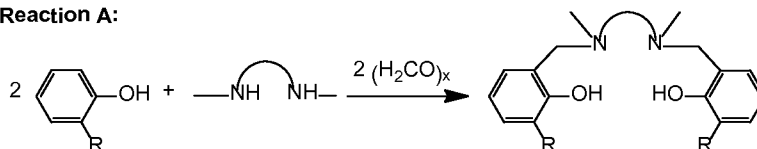
25 In an embodiment, when two transition metal compounds (pre-catalysts) are utilized, they may be used in any ratio. In an embodiment, a molar ratio of a first transition metal compound (A) to a second transition metal compound (B) will fall within the range of (A:B) 1:1000 to 1000:1, or 1:100 to 500:1, or 1:10 to 200:1, or 1:1 to 100:1, or 1:1 to 75:1, or 5:1 to 50:1. The particular ratio chosen will depend on
30 the exact pre-catalysts chosen, the method of activation, and the end product desired. In an embodiment, when using two pre-catalysts, where both are activated with the same activator, useful mole percents, based upon the total moles of the pre-catalysts, are 10:90 to 0.1:99, or 25:75 to 99:1, or 50:50 to 99.5:0.5, or 50:50 to 99:1, or 75:25

to 99:1, or 90:10 to 99:1.

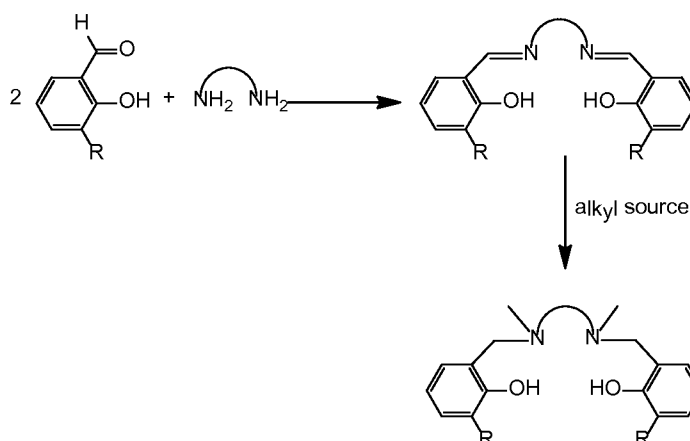
Methods to Prepare the Catalyst Compounds.

In embodiments the symmetric transition metal compounds may be prepared by two general synthetic routes. The parent salan ligands are prepared by a one-step Mannich reaction from the parent phenol (Reaction A) or by a two-step imine-condensation/alkylation procedure if the salicylaldehyde is used (Reaction B). The ligand is then converted into the metal dibenzyl catalyst precursor by reaction with the metal tetra-aryl starting material, e.g., tetrabenzyl, to yield the finished complex (Reaction C).

Reaction A:



Reaction B:



Reaction C:



ACTIVATORS

The terms “cocatalyst” and “activator” are used interchangeably to describe activators 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. Activators may 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.

In one embodiment, alumoxane activators are utilized as an activator in the catalyst composition. Alumoxanes are generally oligomeric compounds containing -Al(R¹)-O- sub-units, where R¹ is an alkyl radical. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the catalyst precursor compound comprises an abstractable ligand which is an alkyl, halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. In an embodiment, visually clear methylalumoxane may be used. 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) described in U.S. Patent No. 5,041,584 and/or commercially available from Akzo Chemicals, Inc. under the trade designation Modified Methylalumoxane type 3A. Solid alumoxanes may also be used.

When the activator is an alumoxane (modified or unmodified), in an embodiment, the maximum amount of activator at a 5000-fold molar excess Al/M over the catalyst compound (per metal catalytic site). In an embodiment, the minimum activator-to-catalyst-compound, which is determined according to molar concentration of the transition metal M, in an embodiment is 1 mole aluminum or less to mole of transition metal M. In an embodiment, the activator comprises alumoxane and the alumoxane is present at a ratio of 1 mole aluminum or more to mole of catalyst compound. In an embodiment, the minimum activator-to-catalyst-compound molar ratio is a 1:1 molar ratio. Other embodiments of Al:M ranges include from 1:1 to 500:1, or from 1:1 to 200:1, or from 1:1 to 100:1, or from 1:1 to 50:1.

In an embodiment, little or no alumoxane (i.e., less than 0.001wt%) is used in the polymerization processes described herein. In an embodiment, alumoxane is present at 0.00 mole %, or the alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal less than 500:1, or less than 300:1, or less than 100:1, or less than 1:1.

The term "non-coordinating anion" (NCA) refers to 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 with the polymerization or catalyst system, stabilize the transition metal cation in the sense of balancing its ionic charge at +1, and yet are sufficiently labile to permit displacement during polymerization.

In an embodiment, an ionizing or stoichiometric activator may be used, which may be neutral or ionic, such as tri (n-butyl) ammonium boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (U.S. Patent No. 5,942,459), or a combination thereof. In an embodiment, neutral or ionic activators alone or in combination with alumoxane or modified alumoxane activators may be used.

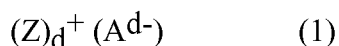
Examples of neutral stoichiometric activators include tri-substituted boron, tellurium, aluminum, gallium, and indium, or mixtures thereof. The three substituent groups or radicals can be the same or different and in an embodiment are each independently selected from substituted or unsubstituted alkyls, alkenyls, alkyns, aryls, alkoxy, and halogens. In an embodiment, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds, and mixtures thereof; or independently selected from alkenyl radicals having 1 to 20 carbon atoms, alkyl radicals having 1 to 20 carbon atoms, alkoxy radicals having 1 to 20 carbon atoms and aryl or substituted aryl radicals having 3 to 20 carbon atoms. In an embodiment, the three substituent groups are alkyl radicals having 1 to 20 carbon atoms, phenyl, naphthyl, or mixtures thereof. In an embodiment, the three groups are halogenated aryl groups, e.g., fluorinated aryl groups. In an embodiment the neutral stoichiometric activator is tris perfluorophenyl boron or tris perfluoronaphthyl boron.

In an embodiment, ionic stoichiometric activator compounds may include 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. Suitable examples include compounds and the like 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 WO 1996/04319; all of which are herein fully incorporated by reference.

In an embodiment compounds useful as an activator comprise a cation, which is, for example, 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, e.g.) which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic, diolefinic or acetylenically unsaturated substrates or other neutral Lewis bases, such as ethers, amines, and the like. Two classes of useful compatible non-coordinating anions are disclosed in EP 0 277,003 A1, and EP 0 277,004 A1, which include anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core; and anions comprising a plurality of boron atoms such as carboranes, metallacarboranes, and boranes.

In an embodiment, the stoichiometric activators include a cation and an anion component, and may be 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.

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 catalyst precursor, resulting in a cationic transition metal species, or the activating cation (L-H)_d⁺ is a Bronsted acid, capable of donating a proton to the catalyst precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, or 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, tetrahydrofuran, and dioxane, sulfoniums from thioethers, such as diethyl thioethers and tetrahydrothiophene, and mixtures thereof.

5 When Z is a reducible Lewis acid it may be represented by the formula: (Ar_3C^+) , where Ar is aryl or aryl substituted with a heteroatom, or a C_1 to C_{40} hydrocarbyl, the reducible Lewis acid may be represented by the formula: (Ph_3C^+) , where Ph is phenyl or phenyl substituted with a heteroatom, and/or a C_1 to C_{40} hydrocarbyl. In an embodiment, the reducible Lewis acid is triphenyl carbenium.

10 Embodiments of 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, or 3, 4, 5 or 6; $n - k = d$; M is an element selected from Group 13 of the Periodic Table of the Elements, or boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl radicals, said Q having up to 20 carbon atoms
15 with the proviso that in not more than one occurrence is Q a halide, and two Q groups may form a ring structure. Each Q may be a fluorinated hydrocarbyl radical having 1 to 20 carbon atoms, or each Q is a fluorinated aryl radical, or each Q is a pentafluoryl aryl radical. 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
20 reference.

In an embodiment, this invention relates to a method to polymerize olefins comprising contacting olefins (e.g., ethylene) with a Salan catalyst compound, a chain transfer agent (CTA) and a boron containing NCA activator represented by the formula (1) where: Z is (L-H) or a reducible Lewis acid; L is a neutral Lewis base
25 (as further described 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.

In an embodiment in any of the NCA's represented by Formula 1 described above, the anion component A^{d-} is represented by the formula $[M^{k*+}Q_{n*}]^{d*-}$
30 wherein k^* is 1, 2, or 3; n^* is 1, 2, 3, 4, 5, or 6 (or 1, 2, 3, or 4); $n^* - k^* = d^*$; M^* is boron; and Q^* is independently selected from hydride, bridged or unbridged dialkylamido, halogen, alkoxide, aryloxy, hydrocarbyl radicals, said Q^* having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q^* a halogen.

This invention also relates to a method to polymerize olefins comprising contacting olefins (such as ethylene) with a Salan catalyst compound as described above, which may include a CTA and an NCA activator represented by the Formula (2):



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 2 also comprises a suitable cation that is essentially non-interfering with the ionic catalyst complexes formed with the transition metal compounds, or the cation is Z_d⁺ as described above.

In an embodiment in any of the NCA's comprising an anion represented by Formula 2 described above, R is selected from the group consisting of C₁ to C₃₀ hydrocarbyl radicals. In an embodiment, C₁ to C₃₀ hydrocarbyl radicals may be substituted with one or more C₁ to C₂₀ hydrocarbyl radicals, halide, hydrocarbyl substituted organometalloid, dialkylamido, alkoxy, aryloxy, alkysulfido, arylsulfido, alkylphosphido, arylphosphide, or other anionic substituent; fluoride; bulky alkoxides, where bulky means C₄ to C₂₀ hydrocarbyl radicals; --SR¹, --NR²₂, and --PR³₂, where each R¹, R², or R³ is independently a C₁ to C₃₀ hydrocarbyl as defined above; or a C₁ to C₃₀ hydrocarbyl substituted organometalloid.

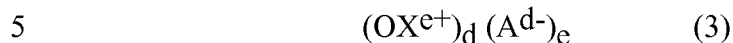
In an embodiment in any of the NCA's comprising an anion represented by Formula 2 described above, the NCA also comprises cation comprising a reducible Lewis acid represented by the formula: (Ar₃C⁺), where Ar is aryl or aryl substituted with a heteroatom, and/or a C₁ to C₄₀ hydrocarbyl, or the reducible Lewis acid represented by the formula: (Ph₃C⁺), where Ph is phenyl or phenyl substituted with one or more heteroatoms, and/or C₁ to C₄₀ hydrocarbyls.

In an embodiment in any of the NCA's comprising an anion represented by Formula 2 described above, the NCA may also comprise 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, or (L-H)_d⁺ is a Bronsted acid selected from ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof.

Further examples of useful activators include those disclosed in U.S. Patent

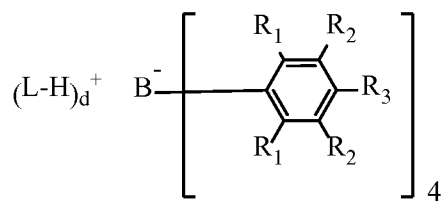
Nos. 7,297,653 and 7,799,879, which are fully incorporated by reference herein.

In an embodiment, an activator useful herein comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the Formula (3):



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} . Suitable embodiments of A^{d-} include tetrakis(pentafluorophenyl)borate.

In an embodiment, the Salan catalyst compounds, CTA's, and/or NCA's 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, or a fluoride;
 each R_2 is, independently, a halide, a C_6 to C_{20} substituted aromatic hydrocarbyl radical or a siloxy group of the formula $-O-Si-R_a$, where R_a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl radical (or R_2 is a fluoride or a perfluorinated phenyl radical);
 each R_3 is a halide, C_6 to C_{20} substituted aromatic hydrocarbyl radical or a siloxy group of the formula $-O-Si-R_a$, where R_a is a C_1 to C_{20} hydrocarbyl radical or hydrocarbylsilyl group (or R_3 is a fluoride or a C_6 perfluorinated aromatic hydrocarbyl radical); wherein R_2 and R_3 can form one or more saturated or unsaturated, substituted or unsubstituted rings (or R_2 and R_3 form a perfluorinated phenyl ring);
 L is an 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, or greater than 300 cubic Å, or greater than 500 cubic Å.

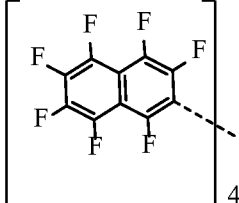
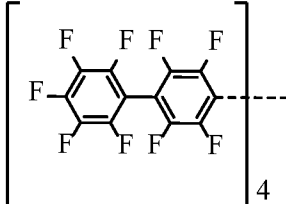
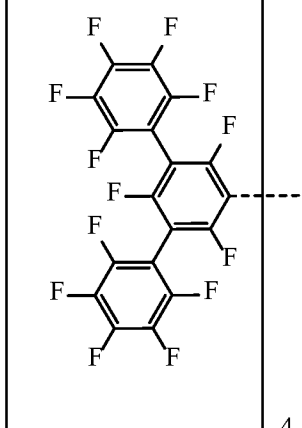
"Molecular volume" is used herein as an approximation of spatial steric bulk of an activator molecule in solution. Comparison of substituents with differing

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.

- 5 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
- 10 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

- Exemplary bulky substituents of activators suitable herein and their respective
- 15 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

Exemplary bulky activators useful in catalyst systems herein include:

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

Illustrative, but not limiting, examples of boron compounds which may be used as an activator in the processes according to the instant disclosure include:

- trimethylammonium tetraphenylborate,
 20 triethylammonium tetraphenylborate,
 tripropylammonium tetraphenylborate,
 tri(n-butyl)ammonium tetraphenylborate,
 tri(tert-butyl)ammonium tetraphenylborate,
 N,N-dimethylanilinium tetraphenylborate,
 25 N,N-diethylanilinium tetraphenylborate,
 N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate,
 tropillium tetraphenylborate,
 triphenylcarbenium tetraphenylborate,
 triphenylphosphonium tetraphenylborate,
 30 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,
5 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,
10 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,
15 tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate,
dimethyl(tert-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,
20 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,
25 trimethylammonium tetrakis(perfluoronaphthyl)borate,
triethylammonium tetrakis(perfluoronaphthyl)borate,
tripropylammonium tetrakis(perfluoronaphthyl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
tri(tert-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
30 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,
5 trimethylammonium tetrakis(perfluorobiphenyl)borate,
triethylammonium tetrakis(perfluorobiphenyl)borate,
tripropylammonium tetrakis(perfluorobiphenyl)borate,
tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
tri(tert-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
10 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,
15 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-bis(trifluoromethyl)phenyl)borate,
20 tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(tert-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,
25 N,N-dimethyl-(2,4,6-trimethylanilinium)tetrakis(3,5-bis(trifluoromethyl)
phenyl)borate,
tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
30 triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, 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.

5 Suitable 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,
 10 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,
 15 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine.

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

In an embodiment, the activator comprises one or more of trialkylammonium tetrakis(pentafluorophenyl)borate,

25 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,
 30 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 tert-butyl).

5 In an embodiment, any of the activators described herein may be mixed together before or after combination with the catalyst compound and/or CTA and/or NCA, or before being mixed with the catalyst compound and/or CTA, and/or NCA.

In an embodiment 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
10 ratio. In an embodiment, the molar ratio of the first NCA activator to the second NCA activator is 0.01:1 to 10,000:1, or 0.1:1 to 1000:1, or 1:1 to 100:1.

In an embodiment, the NCA activator-to-catalyst ratio is a 1:1 molar ratio, or 0.1:1 to 100:1, or 0.5:1 to 200:1, or 1:1 to 500:1 or 1:1 to 1000:1. In an embodiment, the NCA activator-to-catalyst ratio is 0.5:1 to 10:1, or 1:1 to 5:1.

15 In an embodiment, 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, all of which are incorporated by reference herein).

20

SCAVENGERS OR CO-ACTIVATORS

In an embodiment the catalyst system may further include scavengers and/or co-activators. Suitable 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
25 and the like. Other oxophilic species such as diethyl zinc may be used. In an embodiment, the scavengers and/or co-activators are present at less than 14 wt%, or from 0.1 to 10 wt%, or from 0.5 to 7 wt%, by weight of the catalyst system.

CATALYST SUPPORTS

30 In an embodiment, the catalyst system may comprise an inert support material. In an embodiment, the support material comprises a porous support material, for example, talc, and/or inorganic oxides. Other suitable support materials include

zeolites, clays, organoclays, or any other organic or inorganic support material and the like, or mixtures thereof.

In an embodiment, the support material is an inorganic oxide in a finely divided form. Suitable inorganic oxide materials for use in 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, and/or alumina include magnesia, titania, zirconia, montmorillonite, phyllosilicate, and/or the like. Other suitable support materials include finely divided functionalized polyolefins, such as finely divided polyethylene.

In an embodiment, the support material may have a surface area in the range of from about 10 to about 700 m²/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, or the surface area of the support material is in the range of from about 50 to about 500 m²/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. In an embodiment, a majority portion of the surface area of the support material is in the range is from about 100 to about 400 m²/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. In an embodiment, the average pore size of the support material is in the range of from 10 to 1000 Å, or 50 to about 500 Å, or 75 to about 350 Å. In an embodiment, the support material is a high surface area, amorphous silica having a surface area greater than or equal to about 300 m²/gm, and/or a pore volume of 1.65 cm³/gm. Suitable silicas are marketed under the tradenames of Davison 952 or Davison 955 by the Davison Chemical Division of W.R. Grace and Company. In an embodiment the support may comprise Davison 948.

In an embodiment, the support material should be essentially dry, that is, essentially free of absorbed water. Drying of the support material can be effected by heating or calcining at about 100 °C to about 1000 °C, or at a temperature of at least about 400 °C, or 500 °C, or 600 °C. When the support material is silica, it is heated to at least 200 °C, or about 200 °C to about 850 °C, or at least 600 °C for a time of about 1 minute to about 100 hours, or from about 12 hours to about 72 hours, or from about 24 hours to about 60 hours. In an embodiment, the calcined support material must have at least some reactive hydroxyl (OH) groups to produce supported catalyst systems according to the instant disclosure.

In an embodiment, the calcined support material is contacted with at least one polymerization catalyst comprising at least one catalyst compound and an activator. In an embodiment, the support material, having reactive surface groups, typically hydroxyl groups, is slurried in a non-polar solvent and the resulting slurry is contacted
5 with a solution of a catalyst compound and an activator. In an embodiment, 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, or from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours. The solution of the catalyst compound is then contacted with the isolated support/activator. In an embodiment, the supported
10 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, or from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours. The slurry of the supported catalyst compound is then contacted with the activator solution.

15 In an embodiment, the mixture of the catalyst, activator and support is heated to about 0 °C to about 70 °C, or to about 23 °C to about 60 °C, or to room temperature. Contact times typically range from about 0.5 hours to about 24 hours, or from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours.

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

POLYMERIZATION PROCESSES

Monomers useful herein include substituted or unsubstituted C₂ to C₄₀ alpha olefins, or C₂ to C₂₀ alpha olefins, or C₂ to C₁₂ alpha olefins, or ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and
30 isomers thereof. In an embodiment of the invention, the polyalphaolefin prepared herein comprises more than 50 mole % of one or more C₅ to C₂₄ alpha-olefin monomers.

In an embodiment, C₂ to C₄₀ olefin monomers and 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, or hexene, 5 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, or norbornene, norbornadiene, and dicyclopentadiene.

10 In an embodiment, 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.

15 In an embodiment, the monomers include C₅ to C₂₄ olefins, or C₆ to C₁₄ olefins, or C₈ to C₁₂ olefins. In an embodiment, monomers include linear, branched or cyclic alpha-olefins, or C₆ to C₂₀ alpha-olefins, or C₆ to C₁₄ alpha-olefins, and or C₈ to C₁₂ alpha-olefins.

20 In an embodiment olefin monomers include one or more of hexene, heptene, octene, nonene, decene, dodecene, 3-methyl-1-butene, and tetradecene.

In an embodiment, the process described herein may be used to produce PAO homopolymers or copolymers (for the purposes of this invention and the claims thereto, a co-polymer may comprise two, three, four, or more different monomer units). PAOs produced herein include homopolymers or copolymers of any of the 25 above monomers. In an embodiment the PAO is a homopolymer of any C₈ to C₁₂ alpha-olefin. Or the PAO is a homopolymer of 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, or 1-dodecene. Or the PAO a homopolymer of decene. In another embodiment the PAO is a copolymer comprising decene and one or more of any of the monomers listed above.

30 The alpha-olefins used to make PAOs include, but are not limited to, C₅ to C₂₄ alpha-olefins, with the C₆ to C₁₄ alpha-olefins, such as 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene and 1-tetradecene. In an embodiment, polyalpha-olefins include poly-1-hexene, poly-1-heptene, poly-1-

octene, poly-1-nonene, poly-1-decene, poly-1-undecene, poly-1-dodecene, poly-1-tridecene, and poly-1-tetradecene, although dimers of higher olefins in the range of C₁₂ to C₁₈ can be present in the final products. Useful PAOs are dimers, trimers, tetramers, pentamers, and higher polymers with carbon numbers starting from C₂₀ and higher made from C₄ to C₁₈ alpha-olefins in one embodiment, and polymers with carbon number starting from C₂₀ and higher made from C₆ to C₁₄ alpha-olefins in another embodiment. Suitable olefins include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene and 1-dodecene, 1-tridecene, 1-tetradecene. In one embodiment, the olefin is 1-decene, and the PAO is a mixture of dimers, trimers, tetramers and pentamers (and higher) of 1-decene. In another embodiment, the olefin is 1-dodecene, and the PAO is a mixture of trimers, tetramers and pentamers (and higher) of 1-dodecene. In another embodiment, the olefin is 1-octene, and the PAO is a mixture of trimers, tetramers and pentamers (and higher) of 1-octene. In another embodiment, the olefin is 1-hexene, and the PAO is a mixture of tetramers and pentamers (and higher) of 1-hexene.

In an embodiment, the PAO comprises two or more monomers, or three or more monomers, or four or more monomers, or five or more monomers. For example, a C₈, C₁₀, C₁₂-linear alpha-olefin mixture, or a C₆, C₇, C₈, C₉, C₁₀, C₁₁, C₁₂, C₁₃, C₁₄-linear alpha-olefin mixture, or a C₄, C₆, C₈, C₁₀, C₁₂, C₁₄, C₁₆, C₁₈-linear alpha-olefin mixture can be used as a feed.

In an alternate embodiment, the PAO comprises less than 50 mole% of C₂, C₃ and C₄ monomers, or less than 40 mole%, or less than 30 mole %, or less than 20 mole%, or less than 10 mole%, or less than 5 mole%, or less than 3 mole %, or 0%. Specifically, in an alternate embodiment, the PAO comprises less than 50 mole% of ethylene, propylene and butene, or less than 40 mole%, or less than 30 mole %, or less than 20 mole%, or less than 10 mole%, or less than 5 mole%, or less than 3 mole %, or 0%. In another embodiment, the PAO comprises less than 40 mole% of ethylene. In another embodiment, the PAO comprises less than 40 mole% of propylene. In another embodiment, the PAO comprises less than 40 mole% of butene. In another embodiment, the PAO comprises less than 10 mole% of ethylene. In another embodiment, the PAO comprises less than 10 mole% of propylene. In another embodiment, the PAO comprises less than 10 mole% of butene. In another embodiment, the PAO comprises less than 1 mole% of ethylene. In another

embodiment, the PAO comprises less than 1 mole% of propylene. In another embodiment, the PAO comprises less than 1 mole% of butene.

The alpha-olefins used herein can be produced directly from ethylene growth process as practiced by several commercial production processes, or they can be produced from Fischer-Tropsch hydrocarbon synthesis from CO/H₂ syngas, or from metathesis of internal olefins with ethylene, or from cracking of petroleum or Fischer-Tropsch synthetic wax at high temperature, or any other alpha-olefin synthesis routes. In an embodiment, a feed for this invention is at least 80 weight % alpha-olefin (or linear alpha-olefin), or at least 90 weight % alpha-olefin (or linear alpha-olefin), or 100% alpha-olefin (or linear alpha-olefin). However, alpha-olefin mixtures can also be used as feeds in this invention, especially if the other components are internal-olefins, branched olefins, paraffins, cyclic paraffins, aromatics (such as toluene and xylenes). These components have diluent effects and are believed to not have a substantial detrimental effect on the polymerization of alpha-olefins.

In an embodiment, a polymerization process includes contacting monomers (such as ethylene and propylene), which may include comonomers, with a catalyst system comprising an activator and at least one catalyst compound, as described above. In an embodiment, the catalyst compound and activator may be combined in any order, and may be combined prior to contacting with the monomer. In an embodiment, the catalyst compound and/or the activator are combined after contacting with the monomer.

Monomers useful herein include substituted or unsubstituted C₂ to C₄₀ alpha olefins, or C₂ to C₂₀ alpha olefins, or C₂ to C₁₂ alpha olefins, or ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In an embodiment of the invention, the monomer comprises propylene and comonomers comprising one or more ethylene or C₄ to C₄₀ olefins, or C₄ to C₂₀ olefins, or 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 include heteroatoms and/or one or more functional groups. In an embodiment, the monomer comprises ethylene or ethylene and a comonomer comprising one or more C₃ to C₄₀ olefins, or C₄ to C₂₀ olefins, or 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 include heteroatoms and/or one or more functional groups.

Exemplary C₂ to C₄₀ olefin monomers and 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, or 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, or norbornene, norbornadiene, and dicyclopentadiene.

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

Diolefin monomers useful in this invention include any hydrocarbon structure, or 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). In an embodiment, the diolefin monomers may be selected from alpha, omega-diene monomers (i.e. di-vinyl monomers). Or, the diolefin monomers are linear di-vinyl monomers, most or those containing from 4 to 30 carbon atoms. Examples of 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, 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). Cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, ethylidene norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without

substituents at various ring positions.

In an embodiment, 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.

- 5 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.

- 10 Polymerization processes according to the instant disclosure may 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 suitable for use herein, wherein 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
- 15 suitable for use herein, wherein a bulk process is defined to be a process where monomer concentration in all feeds to the reactor is 70 volume % or more. In an embodiment, 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 such as propane in propylene). In an
- 20 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).

- 25 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
- 30 thereof, such as can be found commercially (Isopar™); perhalogenated hydrocarbons, such as perfluorinated C₄₋₁₀ alkanes, chlorobenzene, and aromatic and alkyl substituted aromatic compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or

comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In an 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 an embodiment, the solvent is not aromatic, or aromatics are present in the solvent at less than 1 wt%, or less than 0.5 wt%, or less than 0.0 wt% based upon the weight of the solvents.

10 In an embodiment, the feed concentration of the monomers and comonomers for the polymerization is 60 vol% solvent or less, or 40 vol% or less, or 20 vol% or less, based on the total volume of the feedstream. Or the polymerization is run in a bulk process.

Polymerizations can be run at any temperature and/or pressure suitable to obtain the desired ethylene polymers. Suitable temperatures and/or pressures include a temperature in the range of from about 0 °C to about 300 °C, or about 20 °C to about 200 °C, or about 35 °C to about 150 °C, or about 50 °C to about 150 °C, or from about 40 °C to about 120 °C, or from about 45 °C to about 80 °C; and at a pressure in the range of from about 0.35 MPa to about 10 MPa, or from about 0.45 MPa to about 6 MPa, or from about 0.5 MPa to about 4 MPa.

In an embodiment, the run time of the reaction is from about 0.1 minutes to about 24 hours, or up to 16 hours, or in the range of from about 5 to 250 minutes, or from about 10 to 120 minutes.

25 In an embodiment, hydrogen is present in the polymerization reactor at a partial pressure of 0.001 to 50 psig (0.007 to 345 kPa), or from 0.01 to 25 psig (0.07 to 172 kPa), or 0.1 to 10 psig (0.7 to 70 kPa).

In an embodiment, the activity of the catalyst is at least 50 g/mmol/hour, or 500 or more g/mmol/hour, or 5000 or more g/mmol/hr, or 50,000 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, or 20% or more, or 30% or more, or 50% or more, or 80% or more.

30 In an embodiment, the polymerization conditions include one or more of the following: 1) temperatures of 0 to 300 °C (or 25 to 150 °C, or 40 to 120 °C, or 45 to 80

°C); 2) a pressure of atmospheric pressure to 10 MPa (or 0.35 to 10 MPa, or from 0.45 to 6 MPa, or from 0.5 to 4 MPa); 3) the presence of 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; or where aromatics are or present in the solvent at less than 1 wt%, or less than 0.5 wt%, or at 0 wt% based upon the weight of the solvents); 4) wherein the catalyst system used in the polymerization comprises less than 0.5 mol%, or 0 mol% alumoxane, or the alumoxane is present at a molar ratio of aluminum to transition metal less than 500:1, or less than 300:1, or less than 100:1, or less than 1:1; 5) the polymerization or occurs in one reaction zone; 6) the productivity of the catalyst compound is at least 80,000 g/mmol/hr (or at least 150,000 g/mmol/hr, or at least 200,000 g/mmol/hr, or at least 250,000 g/mmol/hr, or at least 300,000 g/mmol/hr); 7) scavengers (such as trialkyl aluminum compounds) are absent (present at zero mol%) or the scavenger is present at a molar ratio of scavenger to transition metal of less than 100:1, or less than 50:1, or less than 15:1, or less than 10:1; and/or 8). In an embodiment, hydrogen is present in the polymerization reactor at a partial pressure of 0.007 to 345 kPa (0.001 to 50 psig) (or from 0.07 to 172 kPa (0.01 to 25 psig), or 0.7 to 70 kPa (0.1 to 10 psig)).

In an 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 an embodiment, the polymerization occurs in one reaction zone.

PAO PRODUCTS

In an embodiment, polyalphaolefins are produced by the methods described herein.

The polyalphaolefins produced herein, in an embodiment, are homopolymers of C₄ to C₄₀ alpha-olefins or copolymers of C₂ to C₄₀ alpha-olefins, where at least 50

mol% of the copolymer comprises C₄ or higher alpha-olefin, or a C₅ or higher alpha-olefin, or a C₆ or higher alpha-olefin.

In an embodiment, the process described herein produces PAOs comprising more than 50 mole % of one or more C₅ to C₂₄ alpha-olefin monomers (or C₆ to C₂₄ alpha-olefin monomers, or C₈ to C₂₄ alpha-olefin monomers), or 55 mole % or more, or 60 mole % or more, or 65 mole % or more, or 70 mole % or more, or 75 mole % or more, or 80 mole % or more, or 85 mole % or more, or 90 mole % or more, or 95 mole % or more, or 100 mole % based on the total moles of monomers present in the polyalpha-olefin, as measured by Carbon-13 NMR.

10 In an embodiment, any of the PAOs produced herein are hydrogenated and have a Bromine number of 1.8 or less as measured by ASTM D 1159, or 1.7 or less, or 1.6 or less, or 1.5 or less, or 1.4 or less, or 1.3 or less, or 1.2 or less, or 1.1 or less, or 1.0 or less, or 0.5 or less, or 0.1 or less.

15 In an embodiment, the PAOs produced herein may have less than 300 ppm of a Group 3, 4, 5, and/or 6 metal, or Ti, Hf or Zr, or less than 200 ppm, or less than 100 ppm, or less than 10 ppm, as measured by ASTM 5185.

In an embodiment, the polyalpha-olefins described herein have less than 300 ppm of Ti, or less than 200 ppm, or less than 100 ppm, or less than 50 ppm, or less than 10 ppm, as measured by ASTM 5185.

20 In an embodiment, any of the polyalpha-olefins described herein have less than 300 ppm of Hf, or less than 200 ppm, or less than 100 ppm, or less than 50 ppm, or less than 10 ppm, as measured by ASTM 5185.

In an embodiment, any of the polyalpha-olefins described herein have less than 300 ppm of Zr, or less than 200 ppm, or less than 100 ppm, or less than 50 ppm, or less than 10 ppm, as measured by ASTM 5185.

25 In an embodiment, any of the polyalpha-olefins described herein may have less than 100 ppm of Group 13 metals (or B or Al), or less than 50 ppm, or less than 10 ppm, as measured by ASTM 5185.

30 In an embodiment, any of the polyalpha-olefins described herein may have less than 100 ppm of boron, or less than 50 ppm, or less than 10 ppm, as measured by ASTM 5185.

In an embodiment, any of the polyalpha-olefins described herein may have less than 600 ppm of aluminum, or less than 500 ppm, or less than 400 ppm, or less than

300 ppm, or less than 200 ppm, or less than 100 ppm, or less than 50 ppm, or less than 10 ppm, as measured by ASTM 5185.

In an embodiment, any of the polyalpha-olefins described herein may have an Mw (weight average molecular weight) of 100,000 g/mol or less, or between 100
5 g/mol and 80,000 g/mol, or between 250 g/mol and 60,000 g/mol, or between 280 g/mol and 50,000 g/mol, or between 336 g/mol and 40,000 g/mol. In embodiments, Mw's include those from 224 g/mol to 55,100 g/mol, or from 392 g/mol to 30,000 g/mol, or 800 g/mol to 24,000 g/mol, or 2,000 g/mol to 17,000 g/mol. In further
10 g/mol to about 2720g/mol.

In an embodiment, any of the polyalpha-olefins described herein may have an Mn (number average molecular weight) of 50,000 g/mol or less, or between 200 g/mol and 40,000 g/mol, or between 250 g/mol and 30,000 g/mol, or between 500 g/mol and 20,000 g/mol., or from 280 g/mol to 10,000 g/mol, or from 280 g/mol to 4000 g/mol,
15 or from 200 g/mol to 20,900 g/mol, or 280 g/mol, to 10,000 g/mol, or 200 g/mol to 7000 g/mol, or 200 g/mol to 2000 g/mol, or 280 g/mol to 2900 g/mol, or 500 g/mol to 1700 g/mol.

In an embodiment, any of the polyalpha-olefins described herein may have an Mw/Mn of greater than 1 and less than 5, or less than 4, or less than 3, or less than
20 2.5, or less than 2, or between 1 and 2.5, or between 1 and 3.5.

In an embodiment, any PAO described herein may have a pour point of less than 0°C (as measured by ASTM D 97), or less than -10 °C, or less than -20 °C, or less than -25°C, or less than -30°C, or less than -35°C, or less than -50 °C, or between -10 and -80 °C, or between -15°C and -70°C.

25 In an embodiment, any PAO described herein may have a kinematic viscosity (at 40°C as measured by ASTM D 445) from about 4 to about 50,000 cSt, or from about 5 to about 30, 000 cSt at 40 °C, or from about 4 to about 100,000 cSt, or from about 6 to about 50,000 cSt, or from about 10 to about 30, 000 cSt at 40 °C.

30 In an embodiment any polyalpha olefin described herein may have a kinematic viscosity at 100°C (KV100) from about 1.5 to about 5,000 cSt, or from about 2 to about 3,000 cSt, or from about 3 to about 1,000 cSt, or from about 4 to about 1,000 cSt, or from about 8 to about 500 cSt as measured by ASTM D445.

In an embodiment any polyalpha-olefin described herein may have a flash

point of 150 °C or more, or 200 °C or more, or 210 °C or more, or 220 °C or more (as measured by ASTM D 56).

In an embodiment any polyalphaolefin described herein may have a dielectric constant of 2.5 or less (1 kHz at 23 as determined by ASTM D 924).

5 In an embodiment any polyalphaolefin described herein may have a specific gravity of 0.75 to 0.96 g/cm³, or 0.80 to 0.94 g/cm³, or 0.855 to 0.92 g/cm³, as determined according to ASTM D4052.

In an embodiment, the PAOs according to the instant disclosure may comprise dimers, trimers, tetramers, and/or higher oligomers of one or more C₅ to C₂₄ olefin
10 monomers, or one or more C₅ to C₂₄ alpha-olefin monomers, or one or more C₅ to C₂₄ linear alpha-olefin monomers. In an embodiment, an alpha-olefin with alkyl substituent at least 2 carbons away from the olefinic double bond can also be used. In an embodiment, the PAOs according to the instant disclosure comprise a mixture of many different oligomers. In an embodiment, the smallest oligomers from these
15 alpha-olefins may have carbon number ranging from C₁₀ to C₂₀. These small oligomers are usually too light for most high performance fluids application. They are usually separated from the higher oligomers with carbon number of greater than C₂₀, for example C₂₄ and higher which may be useful as high performance fluids.

In an embodiment, the separated C₁₀ to C₂₀ oligomers or the corresponding
20 paraffins after hydrogenation can be used in specialty applications, such as drilling fluids, solvents, paint thinner, etc with excellent biodegradability, toxicity, viscosities, etc. The high performance fluid fraction in the C₂₀ or C₃₀ and higher fractions typically have lower viscosities making them beneficial for some applications, such as better fuel economy, better biodegradability, better low temperature flow properties,
25 or lower volatility. The higher viscosity products, usually having much higher average degree of polymerization, have very low amounts of C₂₀ or C₃₀ component. These high viscosity fluids are excellent blend stocks for lube application to improve the viscosity. Because of their usually narrow molecular weight distribution, they have superior shear stability. Because of their unique chemical composition, they
30 have excellent viscometrics and unexpected low traction properties. These higher viscosity PAOs can be used as superior blend stocks. They can be blend stocks with any of the Group I, II, III, IV+, GTL and Group V fluids to give the optimum viscometrics, solvency, high and low temperature lubricity, etc. When further blended

with additives, including antioxidants, anitwear additives, friction modifiers, dispersants, detergents, corrosion inhibitors, defoamants, extreme pressure additives, seal swell additives, and optionally viscosity modifiers, etc. Description of typical additives can be found in "Lubricant Additives" Chemistry and Applications, ed. L. R.

5 Rudnick, Marcel Dekker, Inc., New York, 2003.

In an embodiment, the PAOs according to the instant disclosure, including those of low viscosity (such as those with a KV100 of 10 cSt or less), are suitable for high performance automotive engine oil formulations either by themselves or by blending with other fluids, such as Group II, Group 11+, Group III, Group 111+ or
10 lube base stocks derived from hydroisomerization of wax fractions from Fisher-Tropsch hydrocarbon synthesis from syn gas, or other Group IV or Group V base stocks. PAOs having KV100s from 3 cSt to 8 cSt are also preferred grades for high performance automotive engine oil or industrial oil formulations. The PAOs of 40 to 1000 cSt according to the instant disclosure may be used as blend stock with Group I,
15 II, III, III+ or GTL derived lube base stocks for use in industrial and automotive engine or gear oil, or high KV100 grades of 3 to 1000 cSt which are desirable for use as blend stock with Gr I, II, III, III+ or GTL derived lube base stocks for use in industrial and automotive engine or gear oil. They are also suitable for use in personal care applications, such as blends with soaps, detergents, other emollients, for use in
20 personal care creams, lotions, sticks, shampoos, detergents, etc.

In an embodiment any polyalpha olefin described herein may have a viscosity index (VI) of 100 or more, or 120 or more, or 130 or more, alternately, from 120 to 450, alternately the viscosity index is at least about 165, alternately at least about 187, alternately at least about 200, alternately at least about 252. For many lower viscosity
25 fluids made from 1-decene or 1-decene equivalent feeds (KV100 of 3 to 10 cSt), the preferred VI range is from 100 to 180. Viscosity index is determined according to ASTM Method D 2270-93 [1998].

In an embodiment any polyalpha olefin produced herein may have a vinylene content of at least 50 %, based upon total unsaturation, or at least 60%, or at least
30 70%, or at least 80 %, or at least 85%, or at least 90%, or at least 94 %, or at least 98%, as determined by ¹H NMR.

Unless otherwise indicated Mw, Mn, MWD are determined by GPC as described above.

In an embodiment, the amount of allyl chain ends, vinylene content, and the like may be determined using ^1H NMR at 120°C using deuterated tetrachloroethane as the solvent on a 500 MHz machine and in selected cases confirmed by ^{13}C NMR. Literature values have been reported for proton and carbon assignments where neat perdeuterated tetrachloroethane is used for proton spectra and a 50:50 mixture of normal and perdeuterated tetrachloroethane is used for carbon spectra; all spectra are recorded at 100°C on a BRUKER AM 300 spectrometer operating at 300 MHz for proton and 75.43 MHz for carbon, for vinyl terminated propylene oligomers, as in *J. American Chemical Soc.*, 114, 1992, pp. 1025-1032.

The term "allyl chain end" (also referred to as "allylic vinyl group" or "allylic vinyl end group") is defined to be a polymer having at least one terminus represented by $(\text{CH}_2=\text{CH}-\text{CH}_2\text{-polymer})$ according to the following formula:

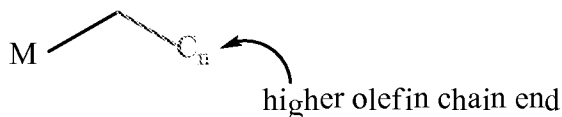


where M represents the polymer chain.

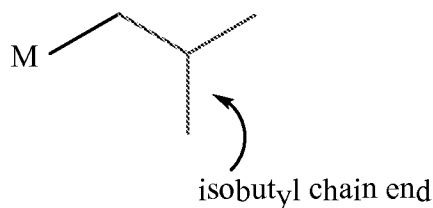
The term "vinylidene chain end" is defined to be a polymer having at least one terminus represented by $(\text{CH}_3-\text{C}(=\text{CH}_2)-\text{CH}_2\text{-polymer})$.

The term "vinylene chain end" is defined to be a polymer having at least one terminus represented by $(\text{CH}_3-\text{C}=\text{CH}_2-\text{CH}_2\text{-polymer})$.

Vinyl terminated polymers typically also have a saturated chain end, also referred to as a methyl end. In polymerizations comprising C_4 or greater monomers (or "higher olefin" monomers), the saturated chain end may be a C_4 or greater (or "higher olefin") chain end, as shown in the formula below:



where M represents the polymer chain and n is an integer selected from 4 to 40. This is especially true when there is substantially no ethylene or propylene in the polymerization. In an ethylene/ C_4 or greater monomer) copolymerization, the polymer chain may initiate growth in an ethylene monomer, thereby generating a saturated chain end which is an ethyl chain end. In polymerizations where propylene is present, the polymer chain may initiate growth in a propylene monomer, thereby generating an isobutyl chain end. An "isobutyl chain end" is defined to be an end or terminus of a polymer, represented as shown in the formula below:



where M represents the polymer chain. Isobutyl chain ends are determined according to the procedure set out in WO 2009/155471.

Mn (^1H NMR) is determined according to the following NMR method. ^1H NMR data are collected at either room temperature or 120°C (for purposes of the claims, 120°C shall 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 400 MHz is used). Data are recorded using a maximum pulse width of 45°C , 8 seconds between pulses and signal averaging 120 transients. Spectral signals are integrated and the number of unsaturation types per 1000 carbons are 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.

Unsaturated Type	Region (ppm)	Number of hydrogens per structure
Vinyl	4.95-5.10	2
Vinylidene	4.70-4.84	2
Vinylene	5.31-5.55	2
Trisubstituted	5.11-5.30	1

Differential Scanning Calorimetry (DSC)

Crystallization temperature (T_c), melting temperature (or melting point, T_m), glass transition temperature (T_g) and heat of fusion (H_f) are measured using Differential Scanning Calorimetry (DSC) on a commercially available instrument (e.g., TA Instruments 2920 DSC). Typically, 6 to 10 mg of molded polymer or plasticized polymer are sealed in an aluminum pan and loaded into the instrument at room temperature. Data are acquired by heating the sample to at least 30°C above its melting temperature, typically 220°C for polypropylene, at a heating rate of $10^\circ\text{C}/\text{min}$. The sample is held for at least 5 minutes at this temperature to destroy its thermal history. Then the sample is cooled from the melt to at least 50°C below the crystallization temperature, typically -100°C for polypropylene, at a cooling rate of $20^\circ\text{C}/\text{min}$. The sample is held at this temperature for at least 5 minutes, and finally

heated at 10°C/min to acquire additional melting data (second heat). The endothermic melting transition (first and second heat) and exothermic crystallization transition are analyzed according to standard procedures. The melting temperatures (T_m) reported are the peak melting temperatures from the second heat unless otherwise specified.

- 5 For polymers displaying multiple peaks, the melting temperature is defined to be the peak melting temperature from the melting trace associated with the largest endothermic calorimetric response (as opposed to the peak occurring at the highest temperature). Likewise, the crystallization temperature is defined to be the peak crystallization temperature from the crystallization trace associated with the largest
10 exothermic calorimetric response (as opposed to the peak occurring at the highest temperature).

Areas under the DSC curve are used to determine the heat of transition (heat of fusion, H_f , upon melting or heat of crystallization, H_c , upon crystallization), which can be used to calculate the degree of crystallinity (also called the percent
15 crystallinity). The percent crystallinity (X%) is calculated using the formula: [area under the curve (in J/g) / H° (in J/g)] * 100, where H° is the ideal heat of fusion for a perfect crystal of the homopolymer of the major monomer component. These values for H° are to be obtained from the *Polymer Handbook, Fourth Edition*, published by John Wiley and Sons, New York 1999, except that a value of 290 J/g is used for
20 H° (polyethylene), a value of 140 J/g is used for H° (polybutene), and a value of 207 J/g is used for H° (polypropylene).

Heat of melting (H_m) is determined using the DSC procedure above except that the sample is cooled to -100°C, held for 5 minutes then heated at 10°C/min to 200 °C. H_m is measured on the first melt, not the second melt. The H_m sample must have
25 been aged at least 48 hours at room temperature and should not be heated to destroy thermal history.

Ethylene and other monomer content may be determined by ASTM D 5017-96, except that the minimum signal-to-noise should be 10,000:1. Propylene content in propylene copolymers is determined by following the approach of Method 1 in Di
30 Martino and Kelchermans, *J. Appl. Polym. Sci.* 56, 1781 (1995), and using peak assignments from Zhang, *Polymer* 45, 2651 (2004) for higher olefin comonomers.

M_n , M_w , and M_z may also be measured by using a Gel Permeation Chromatography (GPC) method using a High Temperature Size Exclusion

Chromatograph (SEC, either from Waters Corporation or Polymer Laboratories), equipped with a differential refractive index detector (DRI). Experimental details, are described in: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001) and references therein. Three
5 Polymer Laboratories PLgel 10mm Mixed-B 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 135°C. Solvent for the SEC experiment is prepared by dissolving 6 grams of butylated hydroxy toluene as an antioxidant in 4 liters of Aldrich reagent
10 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 SEC. 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.
15 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 135°C. The injection concentration is from 1.0 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
20 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 concentration, c , at each point in the chromatogram is calculated from the baseline-subtracted DRI signal, I_{DRI} , using the following equation:

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

25 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 135°C and $\lambda = 690$ nm. For purposes of this invention and the claims thereto $(dn/dc) = 0.104$ for propylene polymers and ethylene polymers, and 0.1 otherwise. Units of parameters used throughout this description of the SEC method are: concentration is
30 expressed in g/cm³, molecular weight is expressed in g/mol, and intrinsic viscosity is expressed in dL/g.

Blends

In another embodiment, the PAO 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, polyesters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and/or polyisobutylene.

In an embodiment, the PAO is present in the above blends, at from 10 to 99 wt%, based upon the weight of the polymers in the blend, preferably 0.5 to 95 wt%, or at least 1 to 90 wt%, or at least 2 to 80 wt%, or at least 5 to 70 wt%, or at least 10 to 60 wt%, or at least 20 to 50 wt%.

The blends described above may be produced by mixing the PAOs 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.

The blends may be formed using conventional equipment and methods, such as by dry blending the individual components and subsequently melt mixing in a mixer, or by mixing the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which may include a compounding extruder and a side-arm extruder used directly downstream of a polymerization process, which may include blending powders or pellets of the resins at the hopper of the film extruder. Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives are well known in the art, and can include, for example: fillers; antioxidants (e.g., hindered phenolics such as IRGANOX 1010 or IRGANOX 1076 available from Ciba-

Geigy); phosphites (e.g., IRGAFOS 168 available from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates, and hydrogenated rosins; UV stabilizers; heat stabilizers; anti-blocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; talc; and the like.

The compositions described herein (preferably PAO compositions) may also be used in the preparation of 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. The PAO compositions described above may also be used in the preparation of nonwoven fabrics and fibers.

EMBODIMENTS

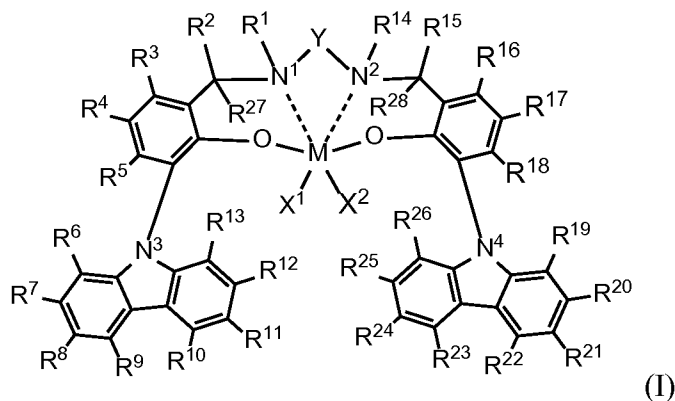
Accordingly, the instant disclosure relates to the following embodiments:

A. A process comprising:

contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin comprising at least 50 mol% C₅ to C₂₄ olefin;

the catalyst system comprising an activator and a catalyst compound according to Formula I, Formula II, Formula III, or a combination thereof:

Formula I being represented by:



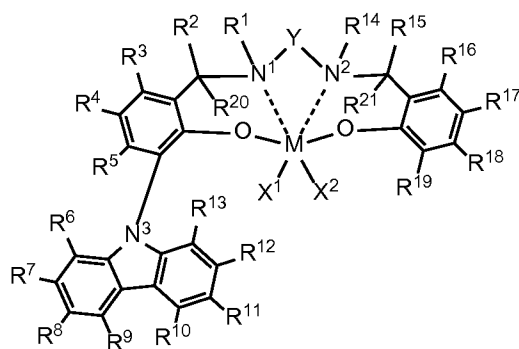
where M is a Group 3, 4, 5 or 6 transition metal;
each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional

group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X^1 and X^2 join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, provided, however, where M is trivalent then X^2 is not present;

each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}$, and R^{28} is, independently, a hydrogen, a C_1 - C_{40} hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or two or more of R^1 to R^{28} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, or a combination thereof, or a combination thereof; and

Y is a divalent C_1 to C_{20} hydrocarbyl;

Formula II being represented by:



(II)

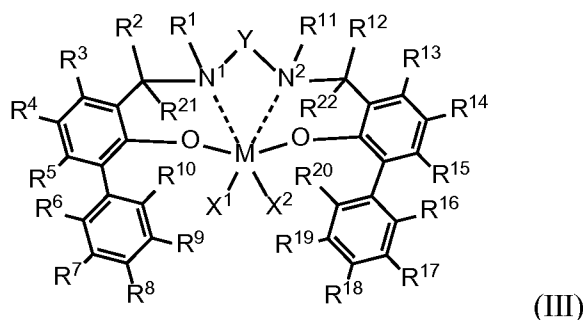
where M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C_1 to C_{20} hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X^1 and X^2 join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, provided, however, where M is trivalent then X^2 is not present;

each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}$, and R^{21} is, independently, a hydrogen, a C_1 - C_{40} hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R^1 to R^{21} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, or a combination thereof; subject to the proviso that R^{19} is not a carbazole or a substituted carbazole radical, and

Y is a divalent C_1 to C_{20} hydrocarbyl radical;

Formula III being represented by:



where M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements,

5 or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the

10 elements, or two or more of R¹ to R²² may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof;

at least one of R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁶, R¹⁷, R¹⁸, R¹⁹, or R²⁰ comprise fluorine; and

Y is a divalent C₁ to C₂₀ hydrocarbyl radical.

15 B. The process of Embodiment A, wherein two or more of R¹ to R²⁸ of Formula I, R¹ to R²¹ of Formula II, R¹ to R²² of Formula III, or a combination thereof, independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure.

20 C. The process of any one of Embodiments A-B, wherein M of Formula I, Formula II, Formula III, or a combination thereof is Hf, Ti, or Zr.

D. The process of any one of Embodiments A-C, wherein each X of Formula I, Formula II, Formula III, or a combination thereof is, independently, a halogen or a C₁ to C₇ hydrocarbyl radical.

E. The process of any one of Embodiments A-D, wherein each X of Formula I, Formula II, Formula III, or a combination thereof is a benzyl radical.

F. The process of any one of Embodiments A-E, wherein each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}$ and R^{28} of Formula (I), each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}$, and R^{21} of Formula (II), $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}$, and R^{22} of Formula (III), or a combination thereof are, independently, hydrogen, a halogen, or a C_1 to C_{30} hydrocarbyl radical.

G. The process of any one of Embodiments A-F, wherein each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}$ and R^{28} of Formula (I), each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}$, and R^{21} of Formula (II), $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}$, and R^{22} of Formula (III), or a combination thereof are, independently, hydrogen, a halogen, or a C_1 to C_{10} hydrocarbyl radical.

H. The process of any one of Embodiments A-G, wherein one or more of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}, R^{22}, R^{23}, R^{24}, R^{25}, R^{26}, R^{27}$, and R^{28} of Formula I is a methyl radical, a fluoride, or a combination thereof.

I. The process of any one of Embodiments A-H, wherein the catalyst compound is according to Formula I wherein,

25 M is Zr;
 X^1 and X^2 are benzyl radicals;
 R^1 and R^{14} are methyl radicals;
 R^2 through R^{13} and R^{15} through R^{28} are hydrogen; and
Y is $-CH_2CH_2-$.

30

J. The process of any one of Embodiments A-I, wherein the catalyst compound is according to Formula I wherein,

M is Zr;

X^1 and X^2 are benzyl radicals;
 R^1 , R^4 , R^{14} and R^{17} are methyl radicals;
 R^2 , R^3 , R^5 through R^{13} , R^{15} , R^{16} , R^{18} through R^{28} are hydrogen; and
 Y is $-\text{CH}_2\text{CH}_2-$.

5

K. The process of any one of Embodiments A-J, wherein the catalyst compound is according to Formula I wherein,

M is Zr ;
 X^1 and X^2 are benzyl radicals;
 R^1 and R^{14} are methyl radicals;
 R^4 and R^{17} are fluoro groups;
 R^2 , R^3 , R^5 through R^{13} , R^{15} , R^{16} , R^{18} through R^{28} are hydrogen; and
 Y is $-\text{CH}_2\text{CH}_2-$.

10

15 L. The process of any one of Embodiments A-K, wherein the catalyst compound is according to Formula I wherein,

M is Zr ;
 X^1 and X^2 are benzyl radicals;
 R^1 , R^4 , R^{14} and R^{17} are methyl radicals;
 R^8 , R^{11} , R^{21} and R^{24} are tert-butyl radicals;
 R^2 , R^3 , R^5 , R^6 , R^7 , R^9 , R^{10} , R^{12} , R^{13} , R^{15} , R^{16} , R^{18} , R^{19} , R^{20} , R^{22} , R^{23} , R^{25} and
 R^{26} through R^{28} are hydrogen; and
 Y is $-\text{CH}_2\text{CH}_2-$.

20

25 M. The process of any one of Embodiments A-L, wherein the catalyst compound is according to Formula I wherein,

M is Zr ;
 X^1 and X^2 are benzyl radicals;
 R^1 , R^4 , R^{14} and R^{17} are methyl radicals;
 R^8 , R^{11} , R^{21} and R^{24} are mesityl radicals;
 R^2 , R^3 , R^5 , R^6 , R^7 , R^9 , R^{10} , R^{12} , R^{13} , R^{15} , R^{16} , R^{18} , R^{19} , R^{20} , R^{22} , R^{23} , R^{25} and
 R^{26} through R^{28} are hydrogen; and
 Y is $-\text{CH}_2\text{CH}_2-$.

30

N. The process of any one of Embodiments A-M, wherein the catalyst compound is according to Formula II wherein one or more of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , and R^{21} is a methyl radical, a
5 bromide, an adamantyl radical, or a combination thereof.

O. The process of any one of Embodiments A-N, wherein the catalyst compound is according to Formula II wherein,

M is Zr;

10 X^1 and X^2 are benzyl radicals;

R^1 and R^{14} are methyl radicals;

R^2 through R^{13} , R^{15} , R^{16} , R^{18} , R^{20} and R^{21} are hydrogen;

R^{17} and R^{19} are bromine; and

Y is $-\text{CH}_2\text{CH}_2-$.

15

P. The process of any one of Embodiments A-O, wherein the catalyst compound is according to Formula II wherein,

M is Zr;

X^1 and X^2 are benzyl radicals;

20 R^1 , R^{14} and R^{17} are methyl radicals;

R^2 through R^{13} , R^{15} , R^{16} , R^{18} , R^{20} , and R^{21} are hydrogen;

R^{19} is a 1-adamantyl radical; and

Y is $-\text{CH}_2\text{CH}_2-$.

25 Q. The process of any one of Embodiments A-P, wherein the catalyst compound is according to Formula II wherein,

M is Hf;

X^1 and X^2 are benzyl radicals;

R^1 and R^{14} and R^{17} are methyl radicals;

30 R^2 through R^{13} , R^{15} , R^{16} , R^{18} , R^{20} and R^{21} are hydrogen;

R^{19} is a 1-adamantyl radical; and

Y is $-\text{CH}_2\text{CH}_2-$.

R. The process of any one of Embodiments A-Q, wherein the catalyst compound is according to Formula III wherein one or more of $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}$, and R^{22} is a methyl radical, a fluoride, or a combination thereof.

5

S. The process of any one of Embodiments A-R, wherein the catalyst compound is according to Formula III wherein,

M is Ti;

X^1 and X^2 are benzyl radicals;

10 R^1 and R^{11} are methyl radicals;

$R^2, R^3, R^5, R^{12}, R^{13}, R^{15}, R^{21}$ and R^{22} are hydrogen;

$R^4, R^6, R^7, R^8, R^9, R^{10}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}$, and R^{20} are fluorine; and

Y is $-\text{CH}_2\text{CH}_2-$.

15 T. The process of any one of Embodiments A-S, wherein the catalyst compound is according to Formula III wherein,

M is Ti;

X^1 and X^2 are benzyl radicals;

R^1, R^4, R^{11} and R^{14} are methyl radicals;

20 $R^2, R^3, R^5, R^{12}, R^{13}, R^{15}, R^{21}$ and R^{22} are hydrogen;

$R^6, R^7, R^8, R^9, R^{10}, R^{16}, R^{17}, R^{18}, R^{19}$, and R^{20} are fluorine; and

Y is $-\text{CH}_2\text{CH}_2-$.

25 U. The process of any one of Embodiments A-T, wherein the catalyst compound is according to Formula III wherein,

M is Zr;

X^1 and X^2 are benzyl radicals;

R^1 and R^{11} are methyl radicals;

$R^2, R^3, R^5, R^{12}, R^{13}, R^{15}, R^{21}$ and R^{22} are hydrogen;

30 $R^4, R^6, R^7, R^8, R^9, R^{10}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}$, and R^{20} are fluorine; and

Y is $-\text{CH}_2\text{CH}_2-$.

V. The process of any one of Embodiments A-U, wherein the catalyst compound is according to Formula III wherein,

M is Zr;

X^1 and X^2 are benzyl radicals;

5 R^1 , R^4 , R^{11} and R^{14} are methyl radicals;

R^2 , R^3 , R^5 , R^{12} , R^{13} , R^{15} , R^{21} and R^{22} are hydrogen;

R^6 , R^7 , R^8 , R^9 , R^{10} , R^{16} , R^{17} , R^{18} , R^{19} , and R^{20} are fluorine; and

Y is $-\text{CH}_2\text{CH}_2-$.

10 W. The process of any one of Embodiments A-V, wherein Y of Formula I, Formula II, Formula III, or a combination thereof is $-\text{CH}_2\text{CH}_2-$ or 1,2-cyclohexylene.

X. The process of any one of Embodiments A-W, wherein Y of Formula I, Formula II, Formula III, or a combination thereof is $-\text{CH}_2\text{CH}_2\text{CH}_2-$.

15

Y. The process of any one of Embodiments A-X, wherein Y of Formula I, Formula II, Formula III, or a combination thereof is a C_1 - C_{40} divalent hydrocarbyl radical comprising a linker backbone comprising from 1 to 18 carbon atoms bridging between nitrogen atoms N^1 and N^2 .

20

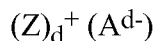
Z. The process of any one of Embodiments A-Y, wherein Y of Formula I, Formula II, Formula III, or a combination thereof is a C_1 - C_{40} divalent hydrocarbyl radical comprising O, S, $\text{S}(\text{O})$, $\text{S}(\text{O})_2$, $\text{Si}(\text{R}')_2$, $\text{P}(\text{R}')$, N, $\text{N}(\text{R}')$, or a combination thereof, wherein each R' is independently a C_1 - C_{18} hydrocarbyl radical.

25

A1. The process of any one of Embodiments A-Z, wherein the activator comprises alumoxane, a non-coordinating anion activator, or a combination thereof.

30 B1. The process of any one of Embodiments A-A1, wherein the activator comprises alumoxane and the alumoxane is present at a ratio of 1 mole aluminum or more to mole of catalyst compound.

C1. The process of any one of Embodiments A-B1, wherein the activator is represented by the formula:



wherein Z is (L-H), or a reducible Lewis Acid, wherein L is a neutral Lewis
5 base;

H is hydrogen;

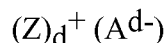
(L-H)⁺ is a Bronsted acid;

A^{d-} is a non-coordinating anion having the charge d-; and

d is an integer from 1 to 3.

10

D1. The process of any one of Embodiments A-C1, wherein the activator is represented by the formula:



wherein A^{d-} is a non-coordinating anion having the charge d-;

15

d is an integer from 1 to 3, and

Z is a reducible Lewis acid represented by the formula: (Ar₃C⁺), where Ar is aryl radical, an aryl radical substituted with a heteroatom, an aryl radical substituted with one or more C₁ to C₄₀ hydrocarbyl radicals, an aryl radical substituted with one or more functional groups comprising elements from
20 Groups 13 – 17 of the periodic table of the elements, or a combination thereof.

E1. The process of any one of Embodiments A-D1, wherein the activator is selected from the group consisting of:

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

F1. The process of any one of Embodiments A-E1, wherein the temperature is
 20 from about 0 °C to about 300 °C, the pressure is from about 0.35 MPa to about 10
 MPa, the time is from about 0.1 minutes to about 24 hours, or a combination thereof.

G1. The process of any one of Embodiments A-F1, wherein the temperature is
 from about 50 °C to about 150 °C.

25

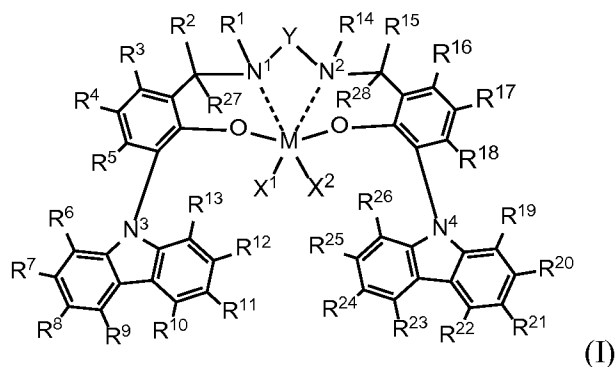
H1. The process of any one of Embodiments A-G1, wherein the polyalphaolefin
 comprises at least 50 mole% decene.

I1. The process of any one of Embodiments A-H1, wherein the polyalphaolefin
 30 comprises at least 75 mole% C₈ to C₂₄ olefin.

J1. The process of any one of Embodiments A-I1, wherein the polyalphaolefin
 comprises:

- a) less than 300 ppm of the Group 3, 4, 5, or 6 metal, as determined by ASTM 5185;
- b) less than 100 ppm of a Group 13 metal, as determined by ASTM 5185;
- c) an Mw of 100,000 g/mol or less;
- 5 d) an Mn of 50,000 g/mol or less;
- e) an Mw/Mn of greater than 1 and less than 5;
- f) a pour point of less than 0°C, as determined according to ASTM D97;
- g) a kinematic viscosity at 40°C from about 4 to about 50,000 cSt, as determined according to ASTM D445;
- 10 h) a kinematic viscosity at 100°C from about 1.5 to about 5,000 cSt, as determined according to ASTM D445;
- i) a flash point of 150 °C or more, as determined according to ASTM D56;
- j) a dielectric constant of 2.5 or less (1 kHz at 23°C), as determined according to ASTM 924;
- 15 k) a specific gravity of 0.75 to 0.96 g/cm³, as determined according to ASTM D4052;
- l) a viscosity index (VI) of 100 or more, as determined according to ASTM D2270-93[1998];
- m) a vinylene content of at least 50 %, based upon total unsaturation, as determined by ¹H NMR;
- 20 or a combination thereof.

- K1. A polyalphaolefin comprising:
- at least 50 mol% C₅ to C₂₄ olefin, the polymer produced by a process
- 25 comprising:
- contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin, the catalyst system comprising an activator and a catalyst compound according to Formula I, Formula II, Formula III, or a combination thereof:
- 30 Formula I being represented by:



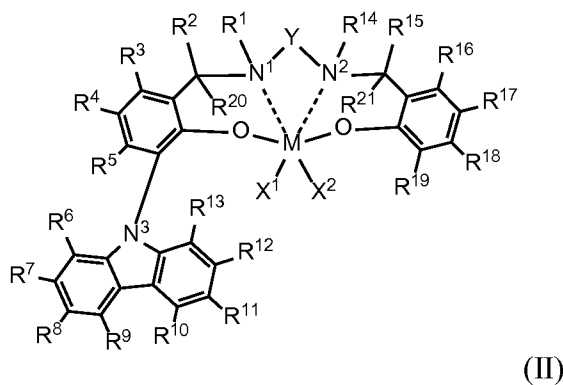
where M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷, and R²⁸ is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²⁸ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof, or a combination thereof; and

Y is a divalent C₁ to C₂₀ hydrocarbyl;

Formula II being represented by:



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

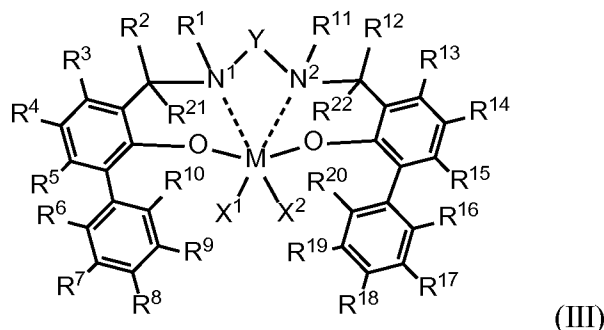
each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹,

R^{20} , and R^{21} is, independently, a hydrogen, a C_1 - C_{40} hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R^1 to R^{21} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, or a combination thereof; subject to the proviso that R^{19} is not a carbazole or a substituted carbazole radical, and

Y is a divalent C_1 to C_{20} hydrocarbyl radical;

Formula III being represented by:



where M is a Group 3, 4, 5 or 6 transition metal;

- each X is, independently, a univalent C_1 to C_{20} hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X^1 and X^2 join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, provided, however, where M is trivalent then X^2 is not present;
- each $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, R^{20}, R^{21}$, and R^{22} is, independently, a hydrogen, a C_1 - C_{40} hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R^1 to R^{22} may independently join together to form a C_4 to C_{62} cyclic or polycyclic ring structure, or a combination thereof;
- at least one of $R^6, R^7, R^8, R^9, R^{10}, R^{16}, R^{17}, R^{18}, R^{19}$, or R^{20} comprise fluorine; and
- Y is a divalent C_1 to C_{20} hydrocarbyl radical; or
- a polyalphaolefin produced according to the process of any one of Embodiments A – J1.

L1. The polyalphaolefin according to Embodiment K1, comprising at least 50 mole% decene.

M1. The polyalphaolefin according to any one of Embodiments K1-L1, wherein the polyalphaolefin comprises at least 75 mole% C_8 to C_{24} olefin.

N1. The polyalphaolefin according to any one of Embodiments K1-M1, wherein the polyalphaolefin comprises:

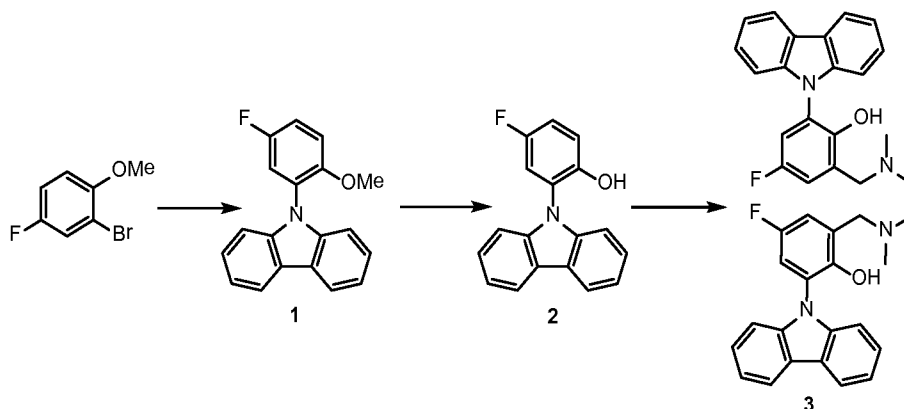
- a) less than 300 ppm of the Group 3, 4, 5, or 6 metal, as determined by ASTM 5185;
 - b) less than 100 ppm of a Group 13 metal, as determined by ASTM 5185;
 - c) an Mw of 100,000 g/mol or less;
 - d) an Mn of 50,000 g/mol or less;
 - e) an Mw/Mn of greater than 1 and less than 5;
 - f) a pour point of less than 0°C, as determined according to ASTM D97;
 - g) a kinematic viscosity at 40°C from about 4 to about 50,000 cSt, as determined according to ASTM D445;
 - h) a kinematic viscosity at 100°C from about 1.5 to about 5,000 cSt, as determined according to ASTM D445;
 - i) a flash point of 150 °C or more, as determined according to ASTM D56;
 - j) a dielectric constant of 2.5 or less (1 kHz at 23°C), as determined according to ASTM 924;
 - k) a specific gravity of 0.75 to 0.96 g/cm³, as determined according to ASTM D4052;
 - l) a viscosity index (VI) of 100 or more, as determined according to ASTM D2270-93[1998];
 - m) a vinylene content of at least 50 %, based upon total unsaturation, as determined by ¹H NMR;
- or a combination thereof.

EXAMPLES

The foregoing discussion can be further described with reference to the following non-limiting examples. Two illustrative catalyst compounds (**A** and **B**), each according to one or more embodiments described, were synthesized and some were used to polymerize olefins. All reactions were carried out under a purified nitrogen atmosphere using standard glovebox, high vacuum or Schlenk techniques, unless otherwise noted. All solvents used were anhydrous, de-oxygenated and

purified according to known procedures. All starting materials were either purchased from Aldrich and purified prior to use or prepared according to procedures known to those skilled in the art.

Synthesis of Compounds A - B:



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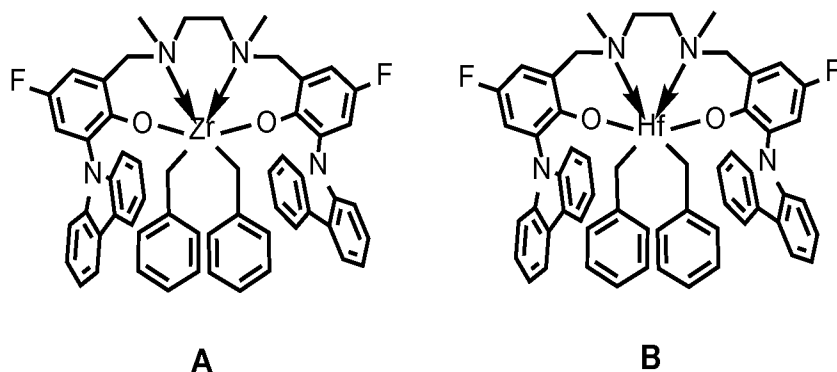
9-(5-Fluoro-2-methoxyphenyl)-9H-carbazole (1): 2-Bromo-4-fluoroanisole (20 g, 10 mmol, 1 equiv) and carbazole (18.4 g, 11 mmol, 1.1 equiv) were dissolved in 1,4-dioxane (200 mL). Potassium phosphate tribasic hydrate (46 g, 20 mmol, 2 equiv), copper(I) iodide (1 g, 0.5 mmol, 0.05 equiv) and 1,2-diaminopropane (1 mL, 1.3 mmol, 0.13 equiv) were added and the reaction was refluxed for 18 hours. The reaction was cooled to room temperature and filtered through celite. The filtrate was concentrated under reduced pressure and the residue was purified over silica gel (250 g), eluting with gradient of 0 to 10% ethyl acetate in heptanes to give compound **1** (7.6 g, 26% yield) as an off white solid that was contaminated with carbazole. This material was used subsequently.

2-(9H-Carbazol-9-yl)-4-fluorophenol (2): A 1.0 M boron tribromide solution in dichloro-methane (60 mL, 60 mmol, 3 equiv) was added dropwise over 30 minutes at -78 °C to a solution of compound **1** (5.8 g, 20 mmol, 1 equiv) in dichloromethane (60 mL). The reaction was stirred at -78 °C for 4 hours, when ¹H-NMR indicated that the reaction was complete. The reaction was poured into saturated sodium bicarbonate (100 mL) and the pH adjusted to 8 with 10% sodium hydroxide. The layers were separated and the aqueous phase was extracted with dichloro-methane (3 x 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified over silica gel (100g), eluting with a gradient of 60 to 100% dichloromethane in heptanes. The product

containing fractions were combined, concentrated under reduced pressure and triturated with 20% methyl *tert*-butyl ether in heptanes (10 mL) to give compound **2** (4.3 g, 78% yield) as a white solid.

6,6'-((Ethane-1,2-diylbis(methylazanediyl))bis(methylene))bis(2-(9*H*-carbazol-9-yl)-4-fluorophenol) (3**):**

A mixture of compound **2** (1.5 g, 5.4 mmol, 2 equiv), paraformaldehyde (716 mg, 5.4 mmol, 2 equiv), N,N'-dimethylethylenediamine (300 μ L, 2.7 mmol, 1 equiv) and anhydrous ethanol (20 mL) was refluxed for 18 hours (reaction was ~60% complete after 2 hours). The reaction was cooled to room temperature, then concentrated under reduced pressure. The residue was purified over silica gel (50g), eluting with a gradient of 60 to 100% dichloromethane in heptanes to give compound **3** (640 mg, 34% yield) as a white solid.



[6,6'-((Ethane-1,2-diylbis(methylazanediyl))bis(methylene))bis(2-(9*H*-carbazol-9-yl)-4-fluorophenol)]zirconium(IV)dibenzyl (A**):**

Under a nitrogen atmosphere, a toluene solution (5 mL) of **3** (107 mg, 0.17 mmol) was added to a yellow toluene solution (5 mL) of ZrBn₄ (77 mg, 0.17 mmol), forming a deep yellow solution. After stirring at room temperature for 15 minutes, the solvent was removed to give a yellow sticky solid. The product was washed with pentane and dried under vacuum to give compound **A** as a yellow solid (yield 135 mg, 88%). Compound **B** was made in a similar manner compound **3** and hafnium tetrabenzyl.

Polymerization Process: All reactions were performed under an inert nitrogen atmosphere. Solvents were anhydrous grade from Sigma Aldrich which were sparged with nitrogen and stored over alumina beads (activated at 300°C) before use. Deuterated solvents were obtained from Cambridge Isotope Laboratories (Andover, MA) and dried over 3 Å molecular sieves. All other reagents were obtained from Sigma Aldrich (St. Louis, MO) and used as received,

unless otherwise noted. All ^1H NMR data was collected on a Bruker AVANCE III 400 MHz spectrometer running TopspinTM 3.0 software at room temperature (approx 23°C). Tetrachloroethane- d_2 was used as a solvent (chemical shift of 5.98 ppm was used as a reference) for all materials.

5 Polymerization 1

Catalyst **A** (11.3 mg) and $(\text{C}_6\text{H}_5)_3\text{C}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ (11.4 mg) were combined in ~2 mL of toluene in a 20 mL vial. In a 100 mL round bottom flask 50 μL of tri-*n*-octylaluminum was combined with 15.3 grams of 1-hexene (NaK dried). The catalyst solution was added and the reaction was placed in an oil bath at 45 °C and left
10 overnight. 14.3 grams of polyhexene was isolated after drying under vacuum.

Polymerization 2

Catalyst **A** (5.8 mg) and $(\text{C}_6\text{H}_5)_3\text{C}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ (5.8 mg) were combined in ~2 mL of toluene in a 20 mL vial. In a 100 mL round bottom flask 20 μL of tri-*n*-octylaluminum was combined with 6.86 grams of 1-hexene (NaK dried). The catalyst
15 solution was added and the reaction was placed in an oil bath at 80 °C for 3 hours. 6.11 grams of polyhexene was isolated after drying under vacuum.

Polymerization 3

Catalyst **A** (5.3 mg) and $(\text{C}_6\text{H}_5)_3\text{C}^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ (5.3 mg) were combined in ~2 mL of toluene in a 20 mL vial. In a 100 mL round bottom flask 20 μL of tri-*n*-
20 octylaluminum was combined with 6.78 grams of 1-hexene (NaK dried). The catalyst solution was added and the reaction was placed in an oil bath at 45 °C and left overnight. 6.2 grams of polyhexene was isolated after drying under vacuum.

Table 1. Polymerization Results for Compound A with 1-hexene.

Polymerization	1	2	3
Temperature (°C)	45	80	100
Reaction Time (hr)	16	3	3
Yield (g)	14.3	6.11	6.21
Conversion (%)	92.8	89.1	91.5
Mn (g/mol)	4000	4600	4500
Vinylene (%)	95.2	98.8	95.1
Vinylidene (%)	4.7	1.2	4.7

25 Polymerization 4

Compound **B** (10 μmol) was dissolved in 1 mL of 1-hexene and added to a stirred solution of MAO (500 equiv) in 4 mL 1-hexene at room temperature. The

resulting mixture was stirred until the resulting polymer solution had become viscous. The polymer was treated with acidified methanol solution (5% HCl solution) and extracted with chloroform.

Polymerization 5

Compound **B** (10 μ mol) was dissolved in 1 mL of 1-hexene and added to a stirred solution of $B(C_6F_5)_3$ (1.5 equiv) in 4 mL 1-hexene. The resulting mixture was stirred at room temperature until the resulting polymer solution had become viscous. The polymer was dried from monomer in vacuum. The ^{13}C NMR for the poly-(1-hexene) made with Compound **B**/ $B(C_6F_5)_3$ is shown in Figure 2.

Polymerization 6

Compound **B** (10 μ mol) was dissolved in 0.5 mL of toluene and added to a stirred solution of MAO (500 equiv), 1 g vinylcyclohexane in 5 mL toluene were added. The resulting mixture was stirred for 1 hour. The poly-vinylcyclohexane (poly-VCH) was treated with acidified methanol solution (5% HCl solution), filtered and dried in air. The ^{13}C NMR for the poly-(1-hexene) made with Compound **B**/MAO is shown in Figure 1.

Table 2. Polymerization Results for Compound B with 1-hexene and vinylcyclohexane.

Monomer	Activator	Catalyst Amt (mg)	Time (hr)	Polymer Amt (g)	Activity (g/mmol/hr)	Tacticity [mmmm]
1-hexene	MAO	10	1	3.36	336	62.7
1-hexene	$B(C_6F_5)_3$	10	1	2.94	294	94.1
VCH	MAO	10	1	1.00	100	ND

Note: ND = Not determined

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As the data show, the catalyst compounds, catalyst systems, and polymerization processes disclosed herein provide novel and improved catalyst and systems for the polymerization of olefins, which in an embodiment produce polymers having improved properties, such as high polymer melting point, high polymer molecular weights, an increased conversion and/or comonomer incorporation, which may further include a significant amount of long chain branching and/or a significant amount of vinyl termination.

The catalysts in an embodiment provide improvement in catalyst activity, produce polymers with improved properties or both. In an embodiment crystallographic techniques indicate that the appended ring system or systems (e.g.,

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the carbazole ring systems) are oriented transversely, e.g., perpendicular, to the phenol rings. In an embodiment these catalysts have a structure to provide a broad corridor for the polymeryl moiety to reside and for the monomer to insert during the polymerization process. As such, catalysts according to one embodiment of the
5 instant disclosure provide for an ability to control one or more characteristics of polymerization, tacticity, comonomer insertion, and the like.

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
10 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.
15 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
20 group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

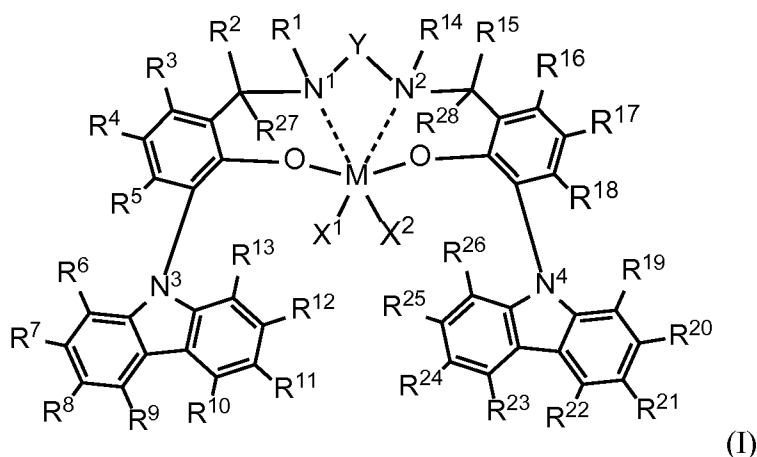
CLAIMS:

What is claimed is:

1. A process comprising:

- 5 contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin comprising at least 50 mol% C₅ to C₂₄ olefin; the catalyst system comprising an activator and a catalyst compound according to Formula I, Formula II, Formula III, or a combination thereof:

10 Formula I being represented by:



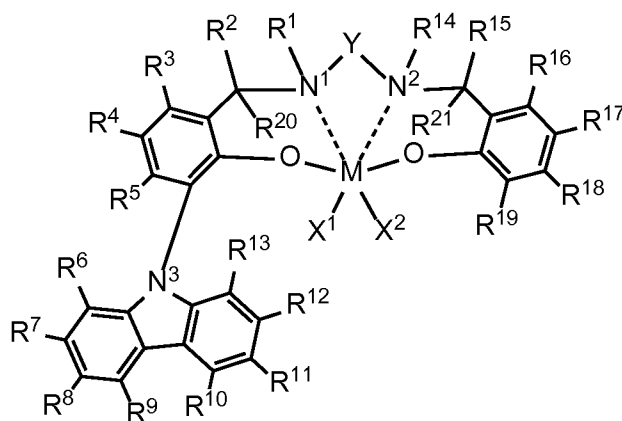
M is a Group 3, 4, 5 or 6 transition metal;

15 each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

20 each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷, and R²⁸ is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²⁸ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof, or a combination thereof; and

25 Y is a divalent C₁ to C₂₀ hydrocarbyl;

Formula II being represented by:



(II)

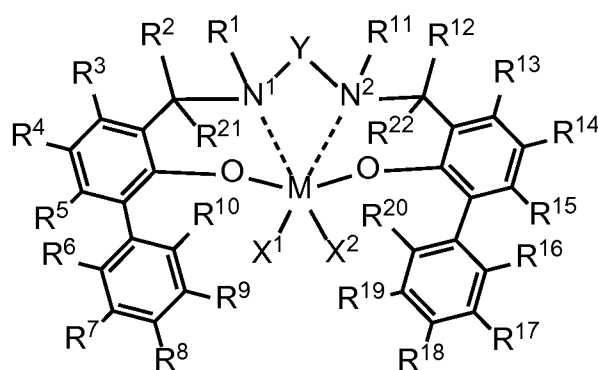
where M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, and R²¹ is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²¹ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof; subject to the proviso that R¹⁹ is not a carbazole or a substituted carbazole radical, and

Y is a divalent C₁ to C₂₀ hydrocarbyl radical;

Formula III being represented by:



(III)

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

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²² may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof;

at least one of R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁶, R¹⁷, R¹⁸, R¹⁹, or R²⁰ comprise fluorine; and

Y is a divalent C₁ to C₂₀ hydrocarbyl radical.

2. The process of claim 1, wherein two or more of R¹ to R²⁸ of Formula I, R¹ to R²¹ of Formula II, R¹ to R²² of Formula III, or a combination thereof, independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure.

3. The process of claim 1, wherein M of Formula I, Formula II, Formula III, or a combination thereof is Hf, Ti, or Zr.

4. The process of claim 1, wherein each X of Formula I, Formula II, Formula III, or a combination thereof is, independently, a halogen or a C₁ to C₇ hydrocarbyl radical.

5. The process of claim 1, wherein each X of Formula I, Formula II, Formula III, or a combination thereof is a benzyl radical.

6. The process of claim 1, wherein each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷ and R²⁸ of Formula (I), each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶,

R^{17} , R^{18} , R^{19} , R^{20} , and R^{21} of Formula (II), R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , and R^{22} of Formula (III), or a combination thereof are, independently, hydrogen, a halogen, or a C_1 to C_{30} hydrocarbyl radical.

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7. The process of claim 1, wherein each R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} and R^{28} of Formula (I), each R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , and R^{21} of Formula (II), R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , and R^{22} of Formula (III), or a combination thereof are, independently, hydrogen, a halogen, or a C_1 to C_{10} hydrocarbyl radical.

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8. The process of claim 1, wherein the catalyst compound is according to Formula I where one or more of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} , and R^{28} is a methyl radical, a fluoride, or a combination thereof.

15

9. The process of claim 1, wherein the catalyst compound is according to Formula I where,

20

M is Zr;

X^1 and X^2 are benzyl radicals;

R^1 and R^{14} are methyl radicals;

R^2 through R^{13} and R^{15} through R^{28} are hydrogen; and

25

Y is $-CH_2CH_2-$.

10. The process of claim 1, wherein the catalyst compound is according to Formula I where,

30

M is Zr;

X^1 and X^2 are benzyl radicals;

R^1 , R^4 , R^{14} and R^{17} are methyl radicals;

R^2 , R^3 , R^5 through R^{13} , R^{15} , R^{16} , R^{18} through R^{28} are hydrogen; and

Y is $-CH_2CH_2-$.

11. The process of claim 1, wherein the catalyst compound is according to Formula I where,

M is Zr;

5 X¹ and X² are benzyl radicals;

R¹ and R¹⁴ are methyl radicals;

R⁴ and R¹⁷ are fluoro groups;

R², R³, R⁵ through R¹³, R¹⁵, R¹⁶, R¹⁸ through R²⁸ are hydrogen; and

Y is -CH₂CH₂-.

10

12. The process of claim 1, wherein the catalyst compound is according to Formula I where,

M is Zr;

X¹ and X² are benzyl radicals;

15 R¹, R⁴, R¹⁴ and R¹⁷ are methyl radicals;

R⁸, R¹¹, R²¹ and R²⁴ are tert-butyl radicals;

R², R³, R⁵, R⁶, R⁷, R⁹, R¹⁰, R¹², R¹³, R¹⁵, R¹⁶, R¹⁸, R¹⁹, R²⁰, R²², R²³, R²⁵ and R²⁶ through R²⁸ are hydrogen; and

Y is -CH₂CH₂-.

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13. The process of claim 1, wherein the catalyst compound is according to Formula I where,

M is Zr;

X¹ and X² are benzyl radicals;

25 R¹, R⁴, R¹⁴ and R¹⁷ are methyl radicals;

R⁸, R¹¹, R²¹ and R²⁴ are mesityl radicals;

R², R³, R⁵, R⁶, R⁷, R⁹, R¹⁰, R¹², R¹³, R¹⁵, R¹⁶, R¹⁸, R¹⁹, R²⁰, R²², R²³, R²⁵ and R²⁶ through R²⁸ are hydrogen; and

Y is -CH₂CH₂-.

30

14. The process of claim 1, wherein the catalyst compound is according to Formula II where one or more of R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, and R²¹ is a methyl radical, a bromide, an adamantyl

radical, or a combination thereof.

15. The process of claim 1, wherein the catalyst compound is according to Formula II where,

- 5 M is Zr;
 X^1 and X^2 are benzyl radicals;
 R^1 and R^{14} are methyl radicals;
 R^2 through R^{13} , R^{15} , R^{16} , R^{18} , R^{20} and R^{21} are hydrogen;
 R^{17} and R^{19} are bromine; and
 10 Y is $-\text{CH}_2\text{CH}_2-$.

16. The process of claim 1, wherein the catalyst compound is according to Formula II where,

- M is Zr;
 15 X^1 and X^2 are benzyl radicals;
 R^1 , R^{14} and R^{17} are methyl radicals;
 R^2 through R^{13} , R^{15} , R^{16} , R^{18} , R^{20} , and R^{21} are hydrogen;
 R^{19} is a 1-adamantyl radical; and
 Y is $-\text{CH}_2\text{CH}_2-$.

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17. The process of claim 1, wherein the catalyst compound is according to Formula II where,

- M is Hf;
 X^1 and X^2 are benzyl radicals;
 25 R^1 and R^{14} and R^{17} are methyl radicals;
 R^2 through R^{13} , R^{15} , R^{16} , R^{18} , R^{20} and R^{21} are hydrogen;
 R^{19} is a 1-adamantyl radical; and
 Y is $-\text{CH}_2\text{CH}_2-$.

- 30 18. The process of claim 1, wherein the catalyst compound is according to Formula III where one or more of R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , and R^{22} is a methyl radical, a fluoride, or a combination thereof.

19. The process of claim 1, wherein the catalyst compound is according to Formula III where,

M is Ti;

5 X^1 and X^2 are benzyl radicals;

R^1 and R^{11} are methyl radicals;

$R^2, R^3, R^5, R^{12}, R^{13}, R^{15}, R^{21}$ and R^{22} are hydrogen;

$R^4, R^6, R^7, R^8, R^9, R^{10}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}$, and R^{20} are fluorine; and

Y is $-\text{CH}_2\text{CH}_2-$.

10

20. The process of claim 1, wherein the catalyst compound is according to Formula III where,

M is Ti;

X^1 and X^2 are benzyl radicals;

15 R^1, R^4, R^{11} and R^{14} are methyl radicals;

$R^2, R^3, R^5, R^{12}, R^{13}, R^{15}, R^{21}$ and R^{22} are hydrogen;

$R^6, R^7, R^8, R^9, R^{10}, R^{16}, R^{17}, R^{18}, R^{19}$, and R^{20} are fluorine; and

Y is $-\text{CH}_2\text{CH}_2-$.

20 21. The process of claim 1, wherein the catalyst compound is according to Formula III where,

M is Zr;

X^1 and X^2 are benzyl radicals;

R^1 and R^{11} are methyl radicals;

25 $R^2, R^3, R^5, R^{12}, R^{13}, R^{15}, R^{21}$ and R^{22} are hydrogen;

$R^4, R^6, R^7, R^8, R^9, R^{10}, R^{14}, R^{16}, R^{17}, R^{18}, R^{19}$, and R^{20} are fluorine; and

Y is $-\text{CH}_2\text{CH}_2-$.

30 22. The process of claim 1, wherein the catalyst compound is according to Formula III where,

M is Zr;

X^1 and X^2 are benzyl radicals;

R^1, R^4, R^{11} and R^{14} are methyl radicals;

$R^2, R^3, R^5, R^{12}, R^{13}, R^{15}, R^{21}$ and R^{22} are hydrogen;

$R^6, R^7, R^8, R^9, R^{10}, R^{16}, R^{17}, R^{18}, R^{19}$, and R^{20} are fluorine; and

Y is $-\text{CH}_2\text{CH}_2-$.

5 23. The process of claim 1, wherein Y of Formula I, Formula II, Formula III, or a combination thereof is $-\text{CH}_2\text{CH}_2-$ or 1,2-cyclohexylene.

24. The process of claim 1, wherein Y of Formula I, Formula II, Formula III, or a combination thereof is $-\text{CH}_2\text{CH}_2\text{CH}_2-$.

10

25. The process of claim 1, wherein Y of Formula I, Formula II, Formula III, or a combination thereof is a C_1 - C_{40} divalent hydrocarbyl radical comprising a linker backbone comprising from 1 to 18 carbon atoms bridging between nitrogen atoms N^1 and N^2 .

15

26. The process of claim 1, wherein Y of Formula I, Formula II, Formula III, or a combination thereof is a C_1 - C_{40} divalent hydrocarbyl radical comprising O, S, $\text{S}(\text{O})$, $\text{S}(\text{O})_2$, $\text{Si}(\text{R}')_2$, $\text{P}(\text{R}')$, N, $\text{N}(\text{R}')$, or a combination thereof, wherein each R' is independently a C_1 - C_{18} hydrocarbyl radical.

20

27. The process of claim 1, wherein the activator comprises alumoxane, a non-coordinating anion activator, or a combination thereof.

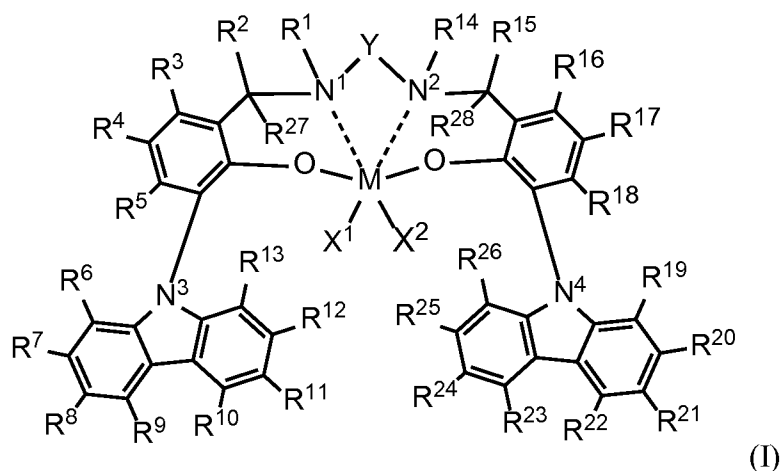
28. A polyalphaolefin comprising:

25 at least 50 mol% C_5 to C_{24} olefin, the polymer produced by a process comprising:

contacting one or more olefins with a catalyst system at a temperature, a pressure, and for a period of time sufficient to produce a polyalphaolefin, the catalyst system comprising an activator and a catalyst compound according to Formula I, Formula II, Formula III, or a combination thereof:

30

Formula I being represented by:



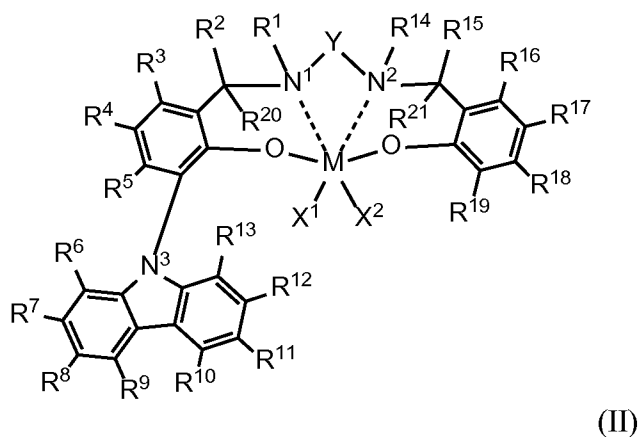
M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, R²², R²³, R²⁴, R²⁵, R²⁶, R²⁷, and R²⁸ is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²⁸ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof; and

Y is a divalent C₁ to C₂₀ hydrocarbyl;

Formula II being represented by:



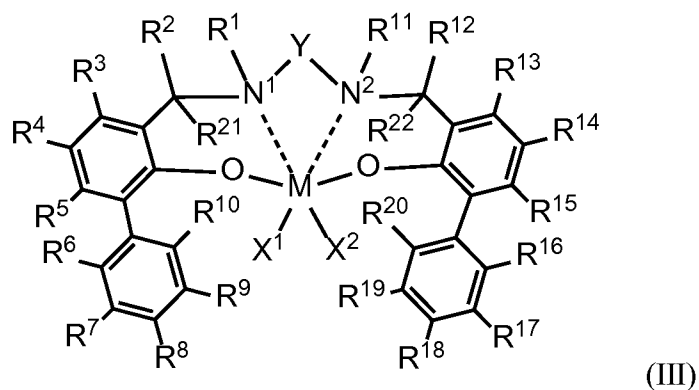
where M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, and R²¹ is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²¹ may independently join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, or a combination thereof; subject to the proviso that R¹⁹ is not a carbazole or a substituted carbazole radical, and

Y is a divalent C₁ to C₂₀ hydrocarbyl radical;

Formula III being represented by:



where M is a Group 3, 4, 5 or 6 transition metal;

each X is, independently, a univalent C₁ to C₂₀ hydrocarbyl radical, a functional group comprising elements from Groups 13 – 17 of the periodic table of the elements, or X¹ and X² join together to form a C₄ to C₆₂ cyclic or polycyclic ring structure, provided, however, where M is trivalent then X² is not present;

each R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, R¹⁵, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² is, independently, a hydrogen, a C₁-C₄₀ hydrocarbyl radical, a functional group comprising elements from Group 13 – 17 of the periodic table of the elements, or two or more of R¹ to R²² may independently join together to form a C₄ to C₆₂ cyclic or

polycyclic ring structure, or a combination thereof;
at least one of R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹⁶, R¹⁷, R¹⁸, R¹⁹, or R²⁰ comprise fluorine;
and
Y is a divalent C₁ to C₂₀ hydrocarbyl radical.

5

29. The polyalphaolefin of claim 28 comprising at least 50 mole% decene.

30. The polyalphaolefin of claim 28, wherein the polyalphaolefin comprises at least 75 mole% C₈ to C₂₄ olefin.

10

31. The polyalphaolefin of claim 28, wherein the polyalphaolefin comprises:
- a) less than 300 ppm of the Group 3, 4, 5, or 6 metal, as determined by ASTM 5185;
 - b) less than 100 ppm of a Group 13 metal, as determined by ASTM 5185;
 - 15 c) an Mw of 100,000 g/mol or less;
 - d) an Mn of 50,000 g/mol or less;
 - e) an Mw/Mn of greater than 1 and less than 5;
 - f) a pour point of less than 0°C, as determined according to ASTM D97;
 - g) a kinematic viscosity at 40°C from about 4 to about 50,000 cSt, as
 - 20 determined according to ASTM D445;
 - h) a kinematic viscosity at 100°C from about 1.5 to about 5,000 cSt, as determined according to ASTM D445;
 - i) a flash point of 150 °C or more, as determined according to ASTM D56;
 - j) a dielectric constant of 2.5 or less (1 kHz at 23°C), as determined according
 - 25 to ASTM 924;
 - k) a specific gravity of 0.75 to 0.96 g/cm³, as determined according to ASTM D4052;
 - l) a viscosity index (VI) of 100 or more, as determined according to ASTM D2270-93[1998];
 - 30 m) a vinylene content of at least 50 %, based upon total unsaturation, as determined by ¹H NMR;
- or a combination thereof.

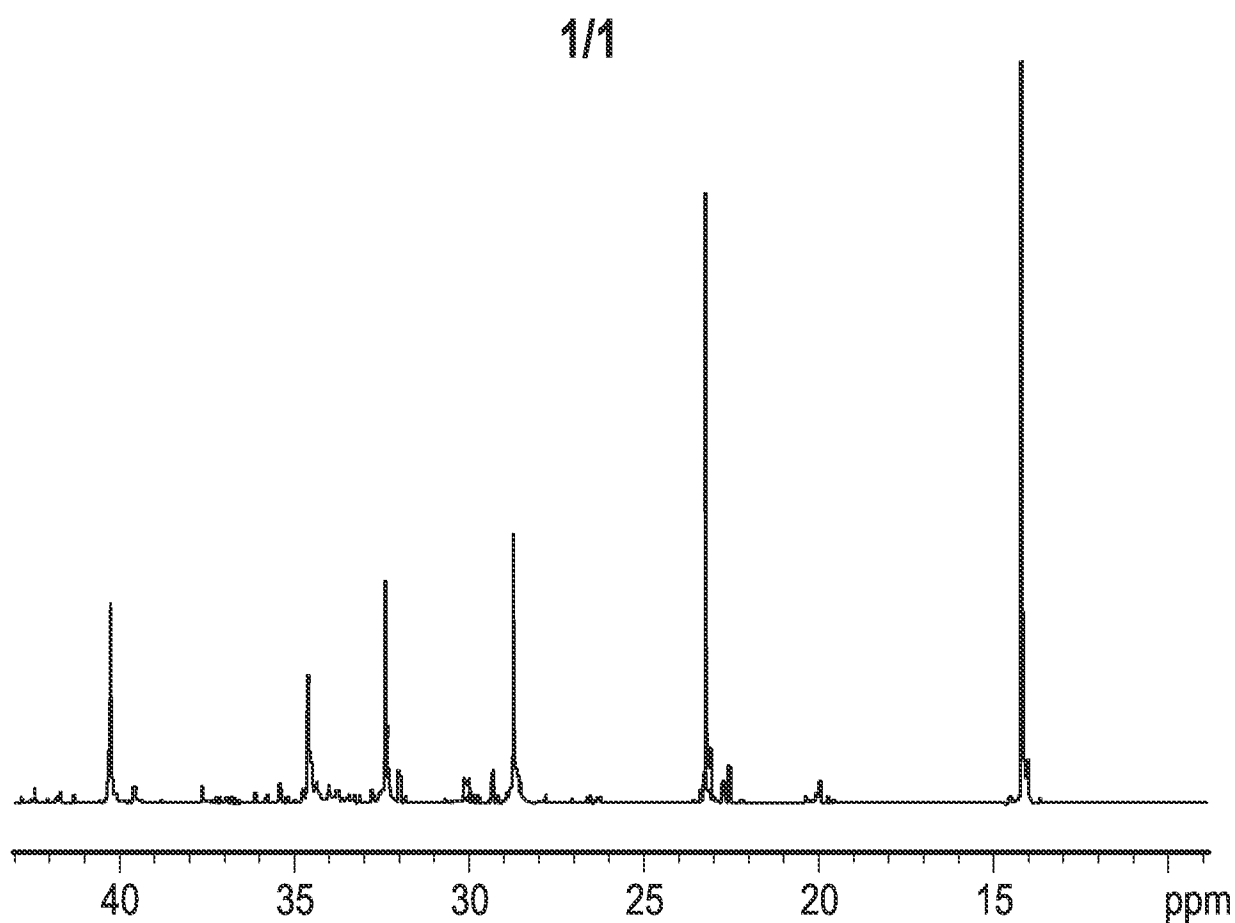


FIG. 1

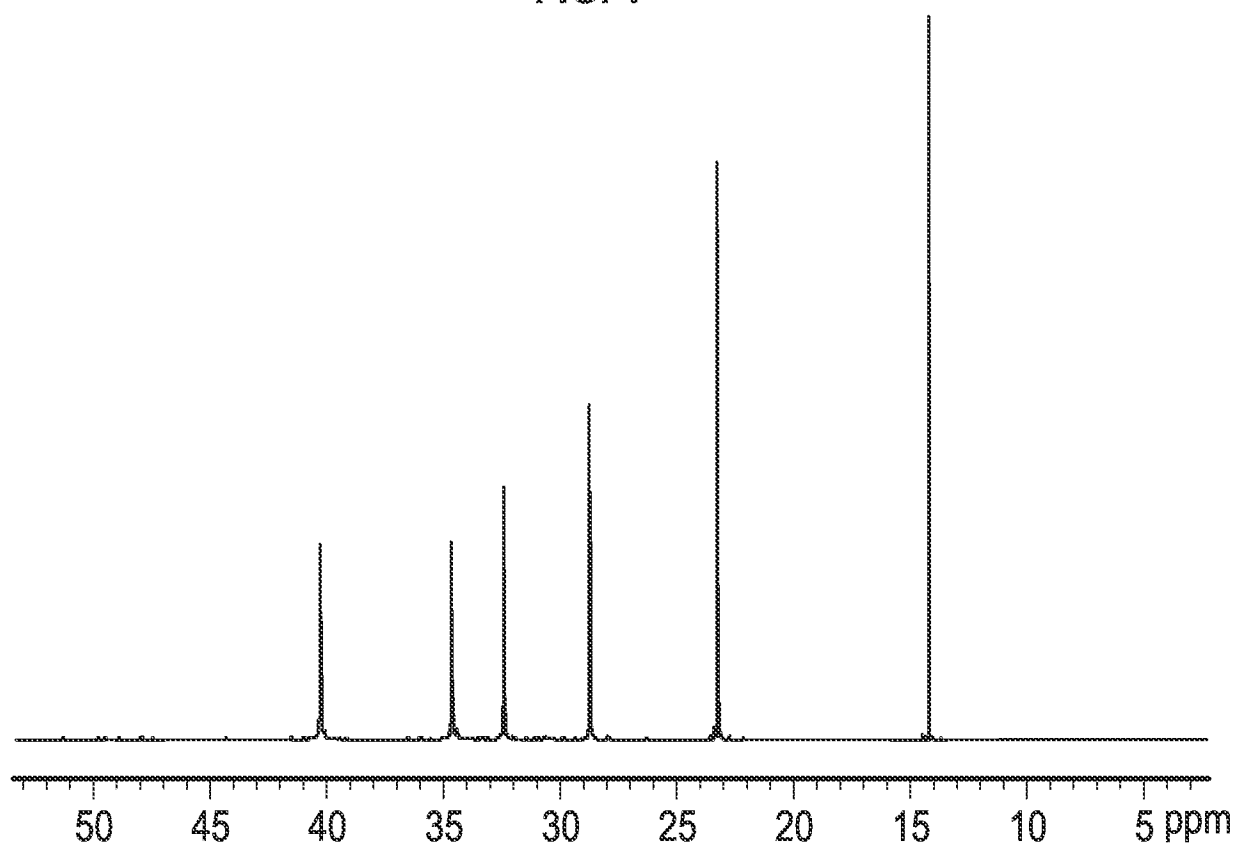


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 13/46615

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - C09B 55/00; C07C 1/00 (2013.01) USPC - 556/33,34;585/329,502 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC(8) - C09B 55/00; C07C 1/00 (2013.01) USPC - 556/33,34;585/329,502 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched IPC(8) - C09B 55/00; C07C 1/00 (2013.01) USPC - 556/33,34;585/329,502 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Minesoft Patbase, Google Scgolar, Google: Salan, salen, salalen, metallosalan, metallosalen, metallocene, olefin, carbazol, catalyst, KOL, HOLT CAMP, GIESBRECHT, (Ti or Hf or Zr), (1000 carbon atoms) w25 (long branch, t-butyl, branching w2 index, density.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2012/098521 A1 (KOL et al.) 26 July 2012 (26.07.2012) page 1, lines 5-10; page 6, page 6, lines 20-25; page 7, lines 1-5; page 7, lines 5-8; page 7, lines 16-24; page 9, lines 3-10; page 12, lines 19; page 12, line 34; page 19, lines 20-23; page 15, lines 5-13; page 28, line 14; page 29, lines 30-32; page 37, lines 17-18; page 37, line 26; page 43, lines 1-15; page 44, lines 1-15; page 51, lines 1-15; Fig 1A, 1B, 4; page 51, lines 23-28; page 41, lines 5-10; page 54, lines 15-17; claims 9, 10.	1-31
Y	US 2005/0075242 A1 (HOLT CAMP et al.) 07 April 2005 (07.04.2005) para [0004], [0029], [0031], [0032], [0047], [0071], [0141], [0382]	1-31
☐ Further documents are listed in the continuation of Box C. ☐		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 28 October 2013 (28.10.2013)		Date of mailing of the international search report 13 NOV 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774