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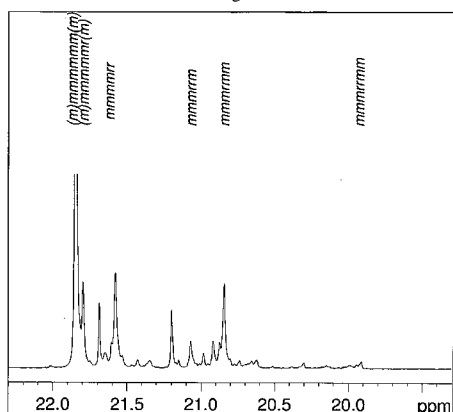
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(54) Title: MULTI-BLOCK COPOLYMER PROCESS USING POLAR SOLVENTS

(57) Abstract: A process for forming a high molecular weight, multi-block copolymer comprising two or more chemically distinguishable segments or blocks, the process comprising polymerizing one or more olefin monomers in the presence of a chain shuttling agent and a catalyst composition comprising two or more olefin polymerization catalysts capable of preparing polymers having differing chemical or physical properties under equivalent polymerization conditions, or a catalyst composition comprising at least one olefin polymerization catalyst containing multiple active catalyst sites capable of preparing polymers having differing chemical or physical properties

Fig. 1



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## MULTI-BLOCK COPOLYMER PROCESS USING POLAR SOLVENTS

Background of the Invention

The present invention relates to a process for preparing multi-block copolymers employing  
5 polar solvents. Multi-block copolymers and polymeric blends comprising the same are usefully  
employed in the preparation of solid articles such as moldings, films, sheets, and foamed objects by  
molding, extruding, or other processes, and are useful as components or ingredients in laminates,  
polymeric blends, and other end uses. The polymers comprise two or more differing regions or  
10 segments (blocks) differing in physical or chemical properties, such as crystallinity, tacticity, chain  
branching, and/or monomer insertion errors, thereby causing the polymer to possess unique physical  
properties. The resulting products are used in the manufacture of components for automobiles, such  
as profiles, bumpers and trim parts; packaging materials; electric cable insulation, adhesives, and  
other applications.

It is known in the art to prepare multi-block copolymers from one or more monomers by the  
15 use of chain shuttling agents under suitable polymerization techniques, especially continuous  
solution polymerization conditions at relatively high monomer conversions. Preferred processes  
employ two catalysts having differing comonomer incorporation properties and a chain shuttling  
agent such as organoaluminum and organozinc compounds. Examples include WO2005/904025,  
WO2005/904026, and WO2005/904027, as well as Science, 312, 714-719 (2006). Solvents for the  
20 foregoing processes generally include C<sub>4-10</sub> hydrocarbons, especially alkanes such as hexane or  
mixtures of alkanes, as well as one or more of the monomers employed in the polymerization. In  
addition, toluene was employed in WO2005/904025 in designed experiments to identify suitable  
catalysts for chain shuttling polymerizations. In general, chain shuttling properties of aluminum  
compounds, especially trialkyl aluminum compounds, were found to be inferior to those of dialkyl  
25 zinc compounds under the conditions tested in these studies.

It would be desirable if there were provided an improved process for preparing multi-block  
copolymers, especially linear multi-block copolymers of ethylene and one or more C<sub>3-10</sub>  $\alpha$ -olefins, or  
propylene, 4-methyl-1-pentene, or another C<sub>4</sub> or higher  $\alpha$ -olefin(s), mixtures of two or more C<sub>3-10</sub>  $\alpha$ -  
olefins, and mixtures of ethylene, and/or propylene with a conjugated or non-conjugated C<sub>4-20</sub> diene,  
30 by the use of a shuttling agent under chain shuttling polymerization conditions, characterized by  
improved efficiency and productivity. In addition, it would be desirable to provide such an  
improved process that is capable of preparing multi-block copolymers, especially linear multi-block  
copolymers, having improved (more narrow) molecular weight distribution employing  
organoaluminum chain shuttling agents, especially trialkylaluminum compounds. Finally, it would

be desirable to provide an improved process for preparing any of the foregoing desirable polymer products in a highly productive, continuous solution polymerization process.

#### Summary of the Invention

5           According to the present invention there are now provided a process for forming a high molecular weight, multi-block copolymer comprising two or more chemically distinguishable segments or blocks, the process comprising polymerizing one or more olefin monomers in the presence of a chain shuttling agent and a catalyst composition comprising:

                  two or more olefin polymerization catalysts capable of preparing polymers having differing  
10           chemical or physical properties under equivalent polymerization conditions,

                  or

                  a catalyst composition comprising at least one olefin polymerization catalyst containing multiple active catalyst sites capable of preparing polymers having differing chemical or physical properties;

15           characterized in that the polymerization is conducted in the presence of a solvent comprising a polar, aprotic organic liquid compound, having a dielectric constant greater than 2.4, preferably greater than or equal to 2.8, most preferably greater than or equal to 3.0.

                  Preferably, the foregoing process takes the form of a continuous solution process for forming multi-block copolymers, preferably linear, multi-block copolymers, of ethylene and one or  
20           more C<sub>4-20</sub> olefins, and most especially ethylene and propylene, ethylene and a C<sub>4-8</sub>  $\alpha$ -olefin, or propylene and an optional C<sub>4-8</sub>  $\alpha$ -olefin, using multiple catalysts under the foregoing polymerization conditions. Under continuous solution polymerization conditions at high monomer conversion, especially ethylene, in the presence of the foregoing solvents, shuttling from the chain shuttling agent to the catalyst is more advantaged compared to chain growth, due, it is believed to  
25           stabilization of the shuttling agent/ polymeryl pair combination, leading to highly efficient formation of multi-block copolymers, increased polymer molecular weights, and narrow molecular weight distributions (Mw/Mn). Surprisingly, the chain shuttling properties of organoaluminum compounds, especially trialkylaluminums, under the present reaction conditions is generally superior to those obtainable by use of dialkylzinc chain shuttling agents. An additional benefit from  
30           the use of the present polar aprotic solvents is a reduction of solution viscosity during the polymerization, allowing the attainment of increased conversions and solids contents in the reactor.

#### Brief Description of the Drawings

Figure 1 is the <sup>1</sup>H NMR spectrum of polymer prepared according to comparative A.

Figure 2 is the  $^1\text{H}$  NMR spectrum of polymer prepared according to Example 1.

### Detailed Description of the Invention

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table  
5 of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a  
Group or Groups shall be to the Group or Groups reflected in this Periodic Table of the Elements  
using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the  
context, or customary in the art, all parts and percents are based on weight and all test methods are  
current as of the filing date hereof. For purposes of United States patent practice, the contents of  
10 any patent, patent application, or publication referenced herein are hereby incorporated by reference  
in their entirety (or the equivalent US version thereof is so incorporated by reference) especially  
with respect to the disclosure of synthetic techniques, definitions (to the extent not inconsistent with  
any definitions provided herein) and general knowledge in the art.

The term “comprising” and derivatives thereof is not intended to exclude the presence of  
15 any additional component, step or procedure, whether or not the same is disclosed herein. In order  
to avoid any doubt, all compositions claimed herein through use of the term “comprising” may  
include any additional additive, adjuvant, or compound whether polymeric or otherwise, unless  
stated to the contrary. In contrast, the term, “consisting essentially of” excludes from the scope of  
any succeeding recitation any other component, step or procedure, excepting those that are not  
20 essential to operability. The term “consisting of” excludes any component, step or procedure not  
specifically delineated or listed. The term “or”, unless stated otherwise, refers to the listed  
members individually as well as in any combination.

The term “polymer”, includes both conventional homopolymers, that is, homogeneous  
polymers prepared from a single monomer, and copolymers (interchangeably referred to herein as  
25 interpolymers), meaning polymers prepared by reaction of at least two monomers or otherwise  
containing chemically differentiated segments or blocks therein even if formed from a single  
monomer. More specifically, the term “polyethylene” includes homopolymers of ethylene and  
copolymers of ethylene and one or more  $\text{C}_{3-8}$   $\alpha$ -olefins in which ethylene comprises at least 50 mole  
percent. The term “propylene copolymer” or “propylene interpolymers” means a copolymer  
30 comprising propylene and optionally one or more copolymerizable comonomers, wherein propylene  
comprises a plurality of the polymerized monomer units of at least one block or segment in the  
polymer (the crystalline block), preferably at least 90 mole percent, more preferably at least 95 mole  
percent, and most preferably at least 98 mole percent. A polymer made primarily from a different  
 $\alpha$ -olefin, such as 4-methyl-1-pentene would be named similarly. The term “crystalline” if

employed, refers to a polymer or polymer block that possesses a first order transition or crystalline melting point ( $T_m$ ) as determined by differential scanning calorimetry (DSC) or equivalent technique. The term may be used interchangeably with the term "semicrystalline". The term "amorphous" refers to a polymer lacking a crystalline melting point or to one having a heat of fusion ( $\Delta H_f$ ) less than 1 J/g as determined by DSC as described here-in-after. The term, "isotactic" or "syndiotactic" is defined as polymer repeat units having at least 70 percent isotactic or syndiotactic pentads as determined by  $^{13}\text{C}$ -NMR analysis. "Highly isotactic" or "highly syndiotactic" is defined as polymer blocks having at least 90 percent isotactic or syndiotactic pentads. The term "tactic" is defined as polymer repeat units that are either isotactic or syndiotactic and the term "highly tactic" refers to polymer repeat units that are either highly isotactic or highly syndiotactic.

The term "multi-block copolymer" or "segmented copolymer" refers to a polymer comprising two or more chemically distinct regions or segments (referred to as "blocks") preferably joined in a linear manner (linear multi-block copolymer), that is, a polymer comprising chemically differentiated units which are joined end-to-end with respect to polymerized ethylenic functionality, rather than in pendent or grafted fashion.

As used herein, the term "noncoordinating" means a substance (solvent, anion, cocatalyst or cocatalyst remnant) which either does not coordinate to the catalyst precursor and the active catalytic species derived therefrom, or which is only weakly coordinated to such complexes or species, thereby remaining sufficiently labile to be displaced by an olefin, such that the ability of the catalyst to polymerize the olefin is not prevented. The material also should not interfere with the desired polymeryl exchange between the chain shuttling agent and the active catalyst(s), for example, by irreversibly reacting with the chain shuttling agent to produce an inert product incapable of chain transfer.

It has been discovered that polar solvents are surprisingly advantaged for use in the processes described in the instant invention, especially noncoordinating, polar, aprotic solvents. As is well-known in the field, a solvent that carries hydrogen attached to oxygen as in a hydroxyl group, nitrogen as in an amine group, or, more generally, any molecular solvent that contains dissociable  $\text{H}^+$  cations is a protic solvent. The molecules of such solvents can donate a proton. Conversely, aprotic solvents cannot donate a proton. Common examples of protic solvents include water, methanol, ethanol, formic acid, and hydrogen fluoride. Polar aprotic solvents generally have similar ion dissolving power as do protic solvents but lack a dissociable  $\text{H}^+$  cation. These solvents generally have high dielectric constants and high polarity.

The dielectric constant,  $\epsilon_r$ , of a material under given conditions is a measure of the extent to which it concentrates electrostatic lines of flux. It is the ratio of the amount of stored electrical energy when a potential is applied, relative to the permittivity of a vacuum, also called relative permittivity. For the purposes of this invention, the values for dielectric constants are those

5 measured at 20 °C, according to the formula:  $\epsilon_r = \frac{\epsilon_s}{\epsilon_o}$ ,

where  $\epsilon_s$  is the static permittivity of the material, and  $\epsilon_o$  is vacuum permittivity. Vacuum permittivity is derived from Maxwell's equations by relating the electric field intensity E to the electric flux density D. In vacuum (free space), the permittivity  $\epsilon$  is  $\epsilon_o$ , and  $\epsilon_r$  equals 1.

The dielectric constant  $\epsilon_r$  can be measured for static electric fields as follows: first the  
10 capacitance of a test capacitor  $C_o$  is measured with vacuum between its plates. Then, the substance to be measured is placed between the plates of the capacitor and the capacitance,  $C_x$  is measured. The dielectric constant can be then calculated as:

$$\epsilon_r = \frac{C_x}{C_o}$$

While not wishing to be held to any particular theory of operation, it is believed that  
15 suitable solvents for use herein are non-coordinating, polar, aprotic compounds having sufficient polarity to help in stabilizing the presumed 4-center intermediate formed between the shuttling agent and the active catalyst, without adversely affecting the polymerization process or preventing polymerization from taking place. Additionally, it is believed that the use of solvents having  
20 elevated polarity or dielectric constant weaken the interaction of the active catalyst site(s) with counterions resulting from the activation process, leading to an increased relative rate of chain shuttling. Preferred solvents possess a dielectric constant from 2.5 to 50, more preferably from 2.8 to 25.0 and most preferably from 3.0 to 20.

Examples of suitable solvents for use herein include hydrocarbons, especially o-xylene, ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene,  
25 isopropylbenzene, 1-methyl-2-ethylbenzene, and 1,2-diethylbenzene, as well as heteroatom containing compounds, including chlorobenzene, o-dichlorobenzene, chlorotoluene, 1-chloroethane, dichloromethane, 1,2-dichloroethane, 1-chloroethene, 1-chloropropane, 1,1-dichloroethane, 1-chlorobutane, 1-chloropentane, 1-chlorohexane, 1,1,1-trifluoroethane, difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-  
30 trifluoropropane, 1,1,1-trifluorobutane, 1,1,1-trifluoropentane, 1,1,1-trifluorohexane, 1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane, fluorocyclobutane, difluorocyclobutane,

trifluorocyclobutane, pentafluorocyclobutane, fluorocyclohexane, 1,2-difluorocyclohexane, 1,3-difluorocyclohexane, fluorobenzene, o-difluorobenzene, m-difluorobenzene, p-difluorobenzene, fluorotoluene, difluorotoluene, 1-chloro-1-fluoroethane, 1,2-dichlorofluoroethane, dichlorofluoromethane, difluorochloromethane, 2-trifluoromethylpropane, tetrahydrofuran, methyl  
5 t-butyl ether, 2-butanone, diethylether, 1,2-dimethoxyethane, ethylene glycol dibutyl ether; diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, dichloromethane, 1,4-dioxane, chloroform, sulfolane, dimethylformamide, and dimethylether.

Mixtures of the foregoing polar, aprotic compounds may be employed as well as mixtures of one or more polar, aprotic compounds with one or more non- or less- polar organic compounds,  
10 such as one or more organic compounds having a dielectric constant less than 2.4.

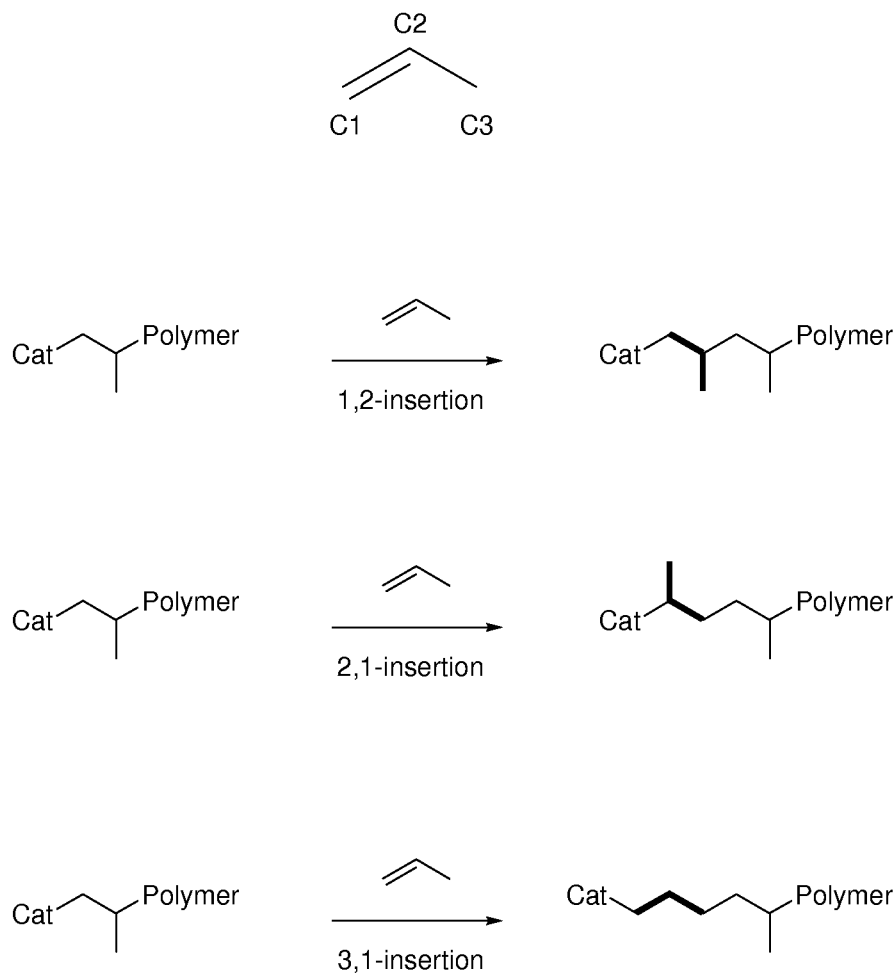
Suitable olefin monomers for use in the present invention include linear and cyclic compounds containing one or more ethylenic unsaturations that are capable of polymerization or copolymerization using coordination polymerization catalysts. The present process is ideally suited for the polymerization of a single  $C_{2-20}$  olefin, especially ethylene, as well as the polymerization of  
15 two or more  $C_{2-20}$   $\alpha$ -olefins, especially ethylene and a  $C_{3-8}$   $\alpha$ -olefin, or for the polymerization of one or more  $C_{2-20}$   $\alpha$ -olefins in combination with one or more  $C_{4-20}$  cycloolefins or diolefins. Suitable monomers for use according to the present invention preferably include ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, or other aliphatic  $C_{4-20}$   $\alpha$ -olefin, and optionally one or more copolymerizable ethylenically unsaturated compounds, especially a conjugated or non-  
20 conjugated diene, provided that the object of the invention, preparation of a multi-block copolymer containing blocks of differing chemical properties, is obtained. Examples of suitable comonomer combinations include ethylene and straight-chain or branched  $\alpha$ -olefins of 3 to 20, preferably 3 to 8 carbon atoms, such as propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-  
25 octadecene and 1-eicosene; cycloolefins of 3 to 30, preferably 3 to 20 carbon atoms, such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene; diolefins and multi-olefins, such as butadiene, isoprene, 4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene,  
30 ethylidene norbornene, vinyl norbornene, dicyclopentadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene, and 5,9-dimethyl-1,4,8-decatriene; aromatic vinyl compounds such as mono or polyalkylstyrenes (including styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylstyrene, m-ethylstyrene and p-ethylstyrene), and functional group-containing derivatives, such as methoxystyrene, ethoxystyrene, vinylbenzoic acid, methyl



vinylbenzoate, vinylbenzyl acetate, hydroxystyrene, o-chlorostyrene, p-chlorostyrene, divinylbenzene, 3-phenylpropene, 4-phenylpropene,  $\alpha$ -methylstyrene, vinylchloride, 1,2-difluoroethylene, 1,2-dichloroethylene, tetrafluoroethylene, and 3,3,3-trifluoro-1-propene. Highly desirably, the polymers comprise in polymerized form ethylene, propylene and/or 1-octene.

5           Highly preferably the multi-block copolymer prepared according to the present process possesses a molecular weight distribution, Mw/Mn, of less than 3.0, preferably less than 2.5, most preferably less than 2.0. In some embodiments of the invention some of the blocks are crystalline while others are amorphous, for example blocks of high density polyethylene and blocks of linear  
10           low density polyethylene. In other embodiments of the invention some of the blocks are tactic, especially isotactic, more preferably highly isotactic, and others are atactic. In still other  
15           embodiments of the invention, some blocks are highly regular, isotactic polypropylene and other blocks contain irregularities, especially blocks comprising polypropylene containing regio-irregular monomer insertions which are 3,1-insertions, leading to chain straightening of the resulting polymer. The resulting blocks are relatively amorphous, compared to the tactic polypropylene blocks.

          The difference in various monomer addition geometries herein is illustrated by the following diagram using propylene as a representative monomer, with the active catalyst site designated as Cat and the previously formed polymer chain designated by Polymer:



Because the respective distinguishable segments or blocks are joined into single polymer chains, the polymer cannot be completely fractionated using standard selective extraction techniques. For example, polymers containing regions that are high density polyethylene (for example ethylene homopolymer) and regions or blocks that are low density polyethylene (for example ethylene/C<sub>3-8</sub>  $\alpha$ -olefin copolymers) or polymers with highly tactic blocks and blocks containing regio-irregular 2,1- or 3,1-monomer insertion cannot be completely selectively extracted or fractionated using differing solvents. In a preferred embodiment the quantity of extractable polymer using either a dialkyl ether- or an alkane- solvent is less than 10 percent, preferably less than 7 percent, more preferably less than 5 percent and most preferably less than 2 percent of the total polymer weight.

As used herein with respect to a chemical compound, unless specifically indicated otherwise, the singular includes all isomeric forms and vice versa (for example, "hexane", includes all isomers of hexane individually or collectively). The terms "compound" and "complex" are used interchangeably herein to refer to organic-, inorganic- and organometal compounds. The term,

“atom” refers to the smallest constituent of an element regardless of ionic state, that is, whether or not the same bears a charge or partial charge or is bonded to another atom. The term “heteroatom” refers to an atom other than carbon or hydrogen. Preferred heteroatoms include: F, Cl, Br, N, O, P, B, S, Si, Sb, Al, Sn, As, Se and Ge.

5           The term, “hydrocarbyl” refers to univalent substituents containing only hydrogen and carbon atoms, including branched or unbranched, saturated or unsaturated, cyclic, polycyclic or noncyclic species. Examples include alkyl-, cycloalkyl-, alkenyl-, alkadienyl-, cycloalkenyl-, cycloalkadienyl-, aryl-, and alkynyl- groups. “Substituted hydrocarbyl” refers to a hydrocarbyl group that is substituted with one or more nonhydrocarbyl substituent groups. The terms,  
10           “heteroatom containing hydrocarbyl” or “heterohydrocarbyl” refer to univalent groups in which at least one atom other than hydrogen or carbon is present along with one or more carbon atom and one or more hydrogen atoms. The term “heterocarbyl” refers to groups containing one or more carbon atoms and one or more heteroatoms and no hydrogen atoms. The bond between the carbon atom and any heteroatom as well as the bonds between any two heteroatoms, may be a single or  
15           multiple covalent bond or a coordinating or other donative bond. Thus, an alkyl group substituted with a heterocycloalkyl-, aryl- substituted heterocycloalkyl-, heteroaryl-, alkyl- substituted heteroaryl-, alkoxy-, aryloxy-, dihydrocarbylboryl-, dihydrocarbylphosphino-, dihydrocarbylamino-, trihydrocarbysilyl-, hydrocarbylthio-, or hydrocarbyselene- group is within the scope of the term heteroalkyl. Examples of suitable heteroalkyl groups include cyanomethyl-, benzoylmethyl-, (2-  
20           pyridyl)methyl-, and trifluoromethyl- groups.

          As used herein the term “aromatic” refers to a polyatomic, cyclic, conjugated ring system containing  $(4\delta+2)$   $\pi$ -electrons, wherein  $\delta$  is an integer greater than or equal to 1. The term “fused” as used herein with respect to a ring system containing two or more polyatomic, cyclic rings means that with respect to at least two rings thereof, at least one pair of adjacent atoms is included in both  
25           rings. The term “aryl” refers to a monovalent aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. Examples of aromatic ring(s) include phenyl, naphthyl, anthracenyl, and biphenyl, among others.

          “Substituted aryl” refers to an aryl group in which one or more hydrogen atoms bound to  
30           any carbon is replaced by one or more functional groups such as alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, alkylhalos (for example,  $\text{CF}_3$ ), hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked

to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in benzophenone or oxygen as in diphenylether or nitrogen in diphenylamine.

The term, "shuttling agent" refers to a compound that is capable of causing polymeryl exchange between at least two different active catalyst sites of the catalyst or catalysts included in the composition under the conditions of the polymerization. That is, transfer of a polymer fragment occurs both to and from one or more of the active catalyst sites. In contrast to a shuttling agent, a "chain transfer agent" causes termination of polymer chain growth and amounts to a one-time transfer of growing polymer from the catalyst to the transfer agent. Preferably, the shuttling agent has an activity ratio  $R_{A-B}/R_{B-A}$  of from 0.01 and 100, more preferably from 0.1 to 10, most preferably from 0.5 to 2.0, and most highly preferably from 0.8 to 1.2, wherein  $R_{A-B}$  is the rate of polymeryl transfer from catalyst A active site to catalyst B active site via the shuttling agent, and  $R_{B-A}$  is the rate of reverse polymeryl transfer, that is, the rate of exchange starting from the catalyst B active site to catalyst A active site via the shuttling agent. Desirably, the intermediate formed between the shuttling agent and the polymeryl chain is sufficiently stable that chain termination is relatively rare. Desirably, less than 90 percent, preferably less than 75 percent, more preferably less than 50 percent and most desirably less than 10 percent of shuttle-polymeryl products are terminated prior to attaining 3 distinguishable polymer segments or blocks. Ideally, the rate of chain shuttling (defined by the time required to transfer a polymer chain from a catalyst site to the chain shuttling agent and then back to a catalyst site) is equivalent to or faster than the rate of polymer termination, greater than or equal to 10-, or even greater than or equal to 100 times faster than the rate of polymer termination. This permits polymer block formation on the same time scale as polymer propagation.

By selecting different combinations of catalysts having differing polymerization ability, and by pairing various shuttling agents or mixtures of agents with these catalyst combinations, polymer products having segments of different properties, different block lengths, and different numbers of such segments or blocks in each copolymer can be prepared. For example, if the activity of the shuttling agent is low relative to the catalyst polymer chain propagation rate of one or more of the catalysts, longer block length multi-block copolymers and polymer blends may be obtained. Contrariwise, if shuttling is very fast relative to polymer chain propagation, a copolymer having a more random chain structure and shorter block lengths is obtained. An extremely fast shuttling agent may produce a multi-block copolymer having substantially random copolymer properties. By proper selection of both catalyst mixture and shuttling agent, relatively pure block copolymers, copolymers containing relatively large polymer segments or blocks, and/or blends of the foregoing with various homopolymers and/or copolymers can be obtained. By use of the polar aprotic

solvents according to the present invention, higher molecular weight multi-block copolymers having relatively longer block lengths are readily obtainable.

Highly desirably, multi-block copolymers prepared according to the present invention have an average number of blocks or segments per average chain (as defined as the average number of blocks of different composition divided by the Mn of the polymer) greater than 3.0 more preferably greater than 3.5, even more preferably greater than 4.0, and less than 25, preferably less than 15, more preferably less than 10.0, most preferably less than 8.0 are formed according to the invention. Mw and Mn for the purposes of this invention is determined using gel permeation chromatography (GPC) as elaborated here-in-after.

10 Suitable shuttling agents for use herein include Group 1, 2, 12 or 13 metal compounds or complexes containing at least one C<sub>1-20</sub> hydrocarbyl group, preferably hydrocarbyl substituted aluminum, gallium or zinc compounds containing from 1 to 12 carbons in each hydrocarbyl group, and reaction products thereof with a proton source. Preferred hydrocarbyl groups are alkyl groups, preferably linear or branched, C<sub>2-8</sub> alkyl groups. Most preferred shuttling agents for use in the present invention are trialkyl aluminum compounds having from 1 to 8 carbons in each alkyl group. Examples include: triethylaluminum, tri(i-propyl) aluminum, tri(i-butyl) aluminum, tri(n-hexyl) aluminum, tri(n-octyl) aluminum, triethyl gallium, diethyl zinc, diisobutyl zinc and dioctyl zinc. Additional suitable shuttling agents include the reaction product or mixture formed by combining the foregoing organometal compound, preferably a tri(C<sub>1-8</sub>) alkyl aluminum or di(C<sub>1-8</sub>) alkyl zinc 15 compound with less than a stoichiometric quantity (relative to the number of hydrocarbyl groups) of a secondary amine or a hydroxyl compound, especially bis(trimethylsilyl)amine, t-butyl(dimethyl)siloxane, 2-hydroxymethylpyridine, di(n-pentyl)amine, 2,6-di(t-butyl)phenol, ethyl(1-naphthyl)amine, bis(2,3,6,7-dibenzo-1-azacycloheptaneamine), or 2,6-diphenylphenol. Desirably, sufficient amine or hydroxyl reagent is used such that one hydrocarbyl group remains per metal atom. The primary reaction products of the foregoing combinations most desired for use in the present invention as shuttling agents are n-octylaluminum di(bis(trimethylsilyl)amide), i-propylaluminum bis(dimethyl(t-butyl)siloxide), and n-octylaluminum di(pyridinyl-2-methoxide), i-butylaluminum bis(dimethyl(t-butyl)siloxane), i-butylaluminum bis(di(trimethylsilyl)amide), n-octylaluminum di(pyridine-2-methoxide), i-butylaluminum bis(di(n-pentyl)amide), n-octylaluminum bis(2,6-di-t-butylphenoxide), n-octylaluminum di(ethyl(1-naphthyl)amide), ethylaluminum bis(t-butyl)dimethylsiloxide, ethylaluminum di(bis(trimethylsilyl)amide), ethylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide), n-octylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide), n-octylaluminum bis(dimethyl(t-butyl)siloxide), ethylzinc (2,6-

diphenylphenoxide), and ethylzinc (t-butoxide). Especially preferred shuttling agents are trimethyl aluminum, triethyl aluminum and tri i-propyl aluminum.

It will be appreciated by the skilled artisan that a suitable shuttling agent for one catalyst or catalyst combination may not necessarily be as good or even satisfactory for use with a different  
5 catalyst or catalyst combination. Some potential shuttling agents may adversely affect the performance of one or more catalysts and may be undesirable for use for that reason as well. Accordingly, the activity of the chain shuttling agent desirably is balanced with the catalytic activity of the catalysts to achieve the desired polymer properties. In some embodiments of the invention, best results may be obtained by use of shuttling agents having a chain shuttling activity (as  
10 measured by the average number of blocks per number average molecular weight ( $M_n$ ) of the polymer chain) that is less than is possible using more active chain shuttling agents.

Generally however, preferred shuttling agents possess the highest rates of reversible polymer transfer as well as the highest transfer efficiencies (reduced incidences of chain termination). Such shuttling agents may be used in reduced reactor concentrations and still achieve  
15 the desired degree of shuttling. In addition, such shuttling agents result in production of relatively shorter polymer block lengths and/or more blocks per average polymer chain. Highly desirably, chain shuttling agents with a single exchange site are employed due to the fact that the effective molecular weight of the polymer in the reactor is lowered, thereby reducing viscosity of the reaction mixture and consequently reducing operating costs. For the purposes of this invention, the term  
20 "single exchange site" refers to a chain shuttling agent that, during the chain shuttling polymerization reaction, has a single alkyl or polymeryl group that can reversibly exchange with growing polymeryl groups on the active polymerization catalyst species. For example, diethyl zinc has two exchange sites, presumably giving dipolymerylzinc specie during the exchange process. An example of a single exchange site chain shuttling agent would be  $\text{EtZn-L}$ , where L is a ligand that is  
25 not exchanged, yet does not prevent the reversible exchange of the remaining polymeryl group.

Suitable catalysts for use herein include any compound or combination of compounds that is adapted for preparing polymers of the desired composition or type. Both heterogeneous and homogeneous catalysts may be employed. Examples of heterogeneous catalysts include the well known Ziegler-Natta compositions, especially Group 4 metal halides supported on Group 2 metal  
30 halides or mixed halides and alkoxides and the well known chromium or vanadium based catalysts. Preferably however, for ease of use and for production of narrow molecular weight polymer segments in solution, the catalysts for use herein are homogeneous catalysts comprising a relatively pure organometallic compound or metal complex, especially compounds or complexes based on metals selected from Groups 3-10 or the Lanthanide series of the Periodic Table of the Elements. It

is preferred that any catalyst employed herein, not significantly detrimentally affect the performance of the other catalyst under the conditions of the present polymerization. Desirably, no catalyst is reduced in activity by greater than 25 percent, more preferably greater than 10 percent under the conditions of the present polymerization.

5 By catalyst activity reduction, it is meant that it is desirable that the presence of a second (or more) catalyst species in the reactor does not reduce the catalytic efficiency of the other catalyst species. This can be determined, for example, by independently evaluating each catalyst species in the absence of the other(s), under the same conditions of stirring, temperature, solvent, monomer type and concentrations, and in the absence of chain shuttling agents. The activity of each catalyst  
10 as run independently of other catalysts can then be compared to the case where the catalysts are combined in the reactor under the same conditions of stirring, temperature, solvent, monomer type and concentrations, and in the absence of chain shuttling agents. In this case, the products of each type of catalyst species can generally be separated by some procedure and quantified. For example, in the absence of a chain shuttling agent, the product resulting from the use of two distinct catalysts  
15 often results in a bimodal molecular weight distribution, which can be evaluated using standard GPC techniques and the amount of each component quantified using standard deconvolution techniques which are well known in the art. If two hypothetical transition metal containing catalysts, Catalyst A and Catalyst B, were determined to have a catalyst activity of 100,000 gram polymer per gram of transition metal added to the reactor and 200,000 gram polymer per gram of  
20 transition metal added to the reactor respectively when run independently, and 100,000 g/g and 180,000 g/g respectively when run together, Catalyst A will have reduced the activity of Catalyst B by 10 percent.

Suitable metal complexes for use herein include complexes of transition metals selected from Groups 3 to 15 of the Periodic Table of the Elements containing one or more delocalized,  
25  $\pi$ -bonded ligands or Lewis base ligands. Examples include metallocene, half-metallocene, constrained geometry, and pyridylamine, or other monodentate or multidentate base complexes. The complexes are generically depicted by the formula:  $MK_kX_xZ_z$ , or a dimer thereof, wherein  
M is a metal selected from Groups 3-15, preferably 3-10, more preferably 4-8, and most preferably Group 4 of the Periodic Table of the Elements;

30 K independently each occurrence is a group containing delocalized  $\pi$ -electrons or one or more electron pairs through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two or more K groups may be joined together forming a bridged structure, and further optionally one or more K groups may be bound to Z, to X or to both Z and X;

X independently each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X groups may be bonded together thereby forming a divalent or polyvalent anionic group, and, further optionally, one or more X groups and one or more Z groups may be bonded together thereby forming a moiety that is bound to M in a polydentate fashion with formally anionic and formally neutral donor atoms;

Z independently each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one electron pair through which Z is coordinated to M;

k is an integer from 0 to 3;

x is an integer from 1 to 4;

z is a number from 0 to 3; and

the sum,  $k+x$ , is equal to the formal oxidation state of M.

Suitable metal complexes include those containing from 1 to 3  $\pi$ -bonded anionic or neutral ligand groups, which may be cyclic or non-cyclic delocalized  $\pi$ -bonded anionic ligand groups. Exemplary of such  $\pi$ -bonded groups are conjugated or nonconjugated, cyclic or non-cyclic diene and dienyl groups, allyl groups, boratabenzene groups, phosphole, and arene groups. By the term " $\pi$ -bonded" is meant that the ligand group is bonded to the transition metal by a sharing of electrons from a partially delocalized  $\pi$ -bond.

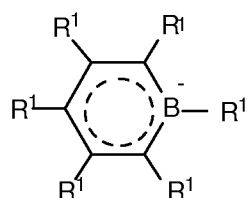
Each atom in the delocalized  $\pi$ -bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl-substituted heteroatoms wherein the heteroatom is selected from Group 14-16 of the Periodic Table of the Elements, and such hydrocarbyl-substituted heteroatom radicals further substituted with a Group 15 or 16 hetero atom containing moiety. In addition two or more such radicals may together form a fused ring system, including partially or fully hydrogenated fused ring systems, or they may form a metallocycle with the metal. Included within the term "hydrocarbyl" are  $C_{1-20}$  straight, branched and cyclic alkyl radicals,  $C_{6-20}$  aromatic radicals,  $C_{7-20}$  alkyl-substituted aromatic radicals, and  $C_{7-20}$  aryl-substituted alkyl radicals. Suitable hydrocarbyl-substituted heteroatom radicals include mono-, di- and tri-substituted radicals of boron, silicon, germanium, nitrogen, phosphorus or oxygen wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. Examples include N,N-dimethylamino, pyrrolidinyl, trimethylsilyl, triethylsilyl, t-butyl dimethylsilyl, methyl di(t-butyl)silyl, triphenylgermyl, and trimethylgermyl groups. Examples of Group 15 or 16 hetero atom containing moieties include amino, phosphino, alkoxy, or alkylthio moieties or divalent derivatives thereof, for example, amide, phosphide, alkyleneoxy or alkylene thio



groups bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group,  $\pi$ -bonded group, or hydrocarbyl- substituted heteroatom.

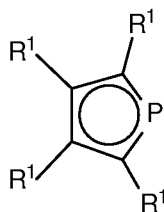
Examples of suitable anionic, delocalized  $\pi$ -bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups, phosphole, and boratabenzyl groups, as well as inertly substituted derivatives thereof, especially C<sub>1-10</sub> hydrocarbyl- substituted or tris(C<sub>1-10</sub> hydrocarbyl)silyl- substituted derivatives thereof. By “inertly substituted derivative” it is meant that the substituent does not contain functionality that reacts with any catalyst or cocatalyst component or chain shuttling agent in the reaction mixture, thereby reducing catalyst or chain-shuttling activity. Preferred anionic delocalized  $\pi$ -bonded groups are cyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetramethylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, tetrahydrofluorenyl, octahydrofluorenyl, 1-indacenyl, 3-pyrrolidinoindenyl, 3,4-(cyclopenta(*l*))phenanthren-1-yl, and tetrahydroindenyl.

The boratabenzenyl ligands are anionic ligands which are boron containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in Organometallics, 14,1, 471-480 (1995). Preferred boratabenzenyl ligands correspond to the formula:



wherein R<sup>1</sup> is an inert substituent, preferably selected from the group consisting of hydrogen, hydrocarbyl, silyl, halo or germyl, said R<sup>1</sup> having up to 20 atoms not counting hydrogen, and optionally two adjacent R<sup>1</sup> groups may be joined together. In complexes involving divalent derivatives of such delocalized  $\pi$ -bonded groups one atom thereof is bonded by means of a covalent bond or a covalently bonded divalent group to another atom of the complex thereby forming a bridged system.

Phospholes are anionic ligands that are phosphorus containing analogues to a cyclopentadienyl group. They are previously known in the art having been described by WO 98/50392, and elsewhere. Preferred phosphole ligands correspond to the formula:



wherein R<sup>1</sup> is as previously defined.

Preferred transition metal complexes for use herein correspond to the formula: MK<sub>k</sub>X<sub>x</sub>Z<sub>z</sub>, or a dimer thereof, wherein:

5 M is a Group 4 metal;

K is a group containing delocalized  $\pi$ -electrons through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two K groups may be joined together forming a bridged structure, and further optionally one K may be bound to X or Z;

10 X independently each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X and one or more K groups are bonded together to form a metallocycle, and further optionally one or more X and one or more Z groups are bonded together thereby forming a moiety that is bound to M in a polydentate fashion with formally anionic and formally neutral donor atoms;

15 Z independently each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one electron pair through which Z is coordinated to M;

k is an integer from 0 to 3;

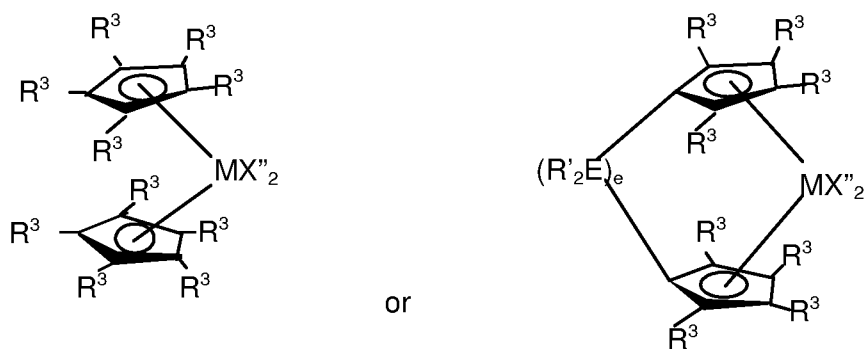
x is an integer from 1 to 4;

z is a number from 0 to 3; and

the sum, k+x, is equal to the formal oxidation state of M.

20 Preferred complexes include those containing either one or two K groups. The latter complexes include those containing a bridging group linking the two K groups. Preferred bridging groups are those corresponding to the formula (ER'<sub>2</sub>)<sub>e</sub> wherein E is silicon, germanium, tin, or carbon, R' independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms, and e is  
25 1 to 8. Preferably, R' independently each occurrence is methyl, ethyl, propyl, benzyl, tert-butyl, phenyl, methoxy, ethoxy or phenoxy.

Examples of the complexes containing two K groups are compounds corresponding to the formula:



wherein:

M is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the +2 or +4 formal oxidation state;

5  $R^3$  in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said  $R^3$  having up to 20 non-hydrogen atoms, or adjacent  $R^3$  groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system, and

10  $X''$  independently each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two  $X''$  groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized  $\pi$ -electrons to M, whereupon M is in the +2 formal oxidation state, and

$R'$ , E and e are as previously defined.

Exemplary bridged ligands containing two  $\pi$ -bonded groups are:

15 dimethylbis(cyclopentadienyl)silane, dimethylbis(tetramethylcyclopentadienyl)silane, dimethylbis(2-ethylcyclopentadien-1-yl)silane, dimethylbis(2-t-butylcyclopentadien-1-yl)silane, 2,2-bis(tetramethylcyclopentadienyl)propane, dimethylbis(inden-1-yl)silane, dimethylbis(tetrahydroinden-1-yl)silane, dimethylbis(flouren-1-yl)silane, dimethylbis(tetrahydrofluoren-1-yl)silane, dimethylbis(2-methyl-4-phenylinden-1-yl)-silane,

20 dimethylbis(2-methylinden-1-yl)silane, dimethyl(cyclopentadienyl)(fluoren-1-yl)silane, dimethyl(cyclopentadienyl)(octahydrofluoren-1-yl)silane, dimethyl(cyclopentadienyl)(tetrahydrofluoren-1-yl)silane, (1, 1, 2, 2-tetramethyl)-1, 2-bis(cyclopentadienyl)disilane, (1, 2-bis(cyclopentadienyl)ethane, and dimethyl(cyclopentadienyl)-1-(fluoren-1-yl)methane.

25 Preferred  $X''$  groups are selected from hydride, hydrocarbyl, silyl, germyl, halohydrocarbyl, halosilyl, silylhydrocarbyl and aminohydrocarbyl groups, or two  $X''$  groups together form a divalent derivative of a conjugated diene or else together they form a neutral,  $\pi$ -bonded, conjugated diene. Most preferred  $X''$  groups are  $C_{1-20}$  hydrocarbyl groups.

Examples of metal complexes of the foregoing formula suitable for use in the present invention include:

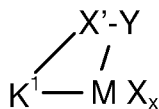
- bis(cyclopentadienyl)zirconiumdimethyl,
- bis(cyclopentadienyl)zirconium dibenzyl,
- 5 bis(cyclopentadienyl)zirconium methyl benzyl,
- bis(cyclopentadienyl)zirconium methyl phenyl,
- bis(cyclopentadienyl)zirconiumdiphenyl,
- bis(cyclopentadienyl)titanium-allyl,
- bis(cyclopentadienyl)zirconiummethoxymethylmethoxide,
- 10 bis(cyclopentadienyl)zirconiummethylchloride,
- bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
- bis(pentamethylcyclopentadienyl)titaniumdimethyl,
- bis(indenyl)zirconiumdimethyl,
- indenyfluorenyl zirconiumdimethyl,
- 15 bis(indenyl)zirconiummethyl(2-(dimethylamino)benzyl),
- bis(indenyl)zirconiummethyltrimethylsilyl,
- bis(tetrahydroindenyl)zirconiummethyltrimethylsilyl,
- bis(pentamethylcyclopentadienyl)zirconiummethylbenzyl,
- bis(pentamethylcyclopentadienyl)zirconiumdibenzyl,
- 20 bis(pentamethylcyclopentadienyl)zirconiummethoxymethylmethoxide,
- bis(pentamethylcyclopentadienyl)zirconiummethylchloride,
- bis(methylethylcyclopentadienyl)zirconiumdimethyl,
- bis(butylcyclopentadienyl)zirconiumdibenzyl,
- bis(t-butylcyclopentadienyl)zirconiumdimethyl,
- 25 bis(ethyltetramethylcyclopentadienyl)zirconiumdimethyl,
- bis(methylpropylcyclopentadienyl)zirconiumdibenzyl,
- bis(trimethylsilylcyclopentadienyl)zirconiumdibenzyl,
- dimethylsilylbis(cyclopentadienyl)zirconiumdichloride,
- dimethylsilylbis(cyclopentadienyl)zirconiumdimethyl,
- 30 dimethylsilylbis(tetramethylcyclopentadienyl)titanium (III) allyl
- dimethylsilylbis(t-butylcyclopentadienyl)zirconiumdichloride,
- dimethylsilylbis(n-butylcyclopentadienyl)zirconiumdichloride,
- (dimethylsilylbis(tetramethylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,
- (dimethylsilylbis(n-butylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,

dimethylsilylbis(indenyl)zirconiumdichloride,  
 dimethylsilylbis(indenyl)zirconiumdimethyl,  
 dimethylsilylbis(2-methylindenyl)zirconiumdimethyl,  
 dimethylsilylbis(2-methyl-4-phenylindenyl)zirconiumdimethyl,  
 5 dimethylsilylbis(2-methylindenyl)zirconium-1,4-diphenyl-1,3-butadiene,  
 dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium (II) 1,4-diphenyl-1,3-butadiene,  
 dimethylsilylbis(4,5,6,7-tetrahydroinden-1-yl)zirconiumdichloride,  
 dimethylsilylbis(4,5,6,7-tetrahydroinden-1-yl)zirconiumdimethyl,  
 dimethylsilylbis(tetrahydroindenyl)zirconium(II) 1,4-diphenyl-1,3-butadiene,  
 10 dimethylsilylbis(tetramethylcyclopentadienyl)zirconium dimethyl  
 dimethylsilylbis(fluorenyl)zirconiumdimethyl,  
 dimethylsilylbis(tetrahydrofluorenyl)zirconium bis(trimethylsilyl),  
 ethylenebis(indenyl)zirconiumdichloride,  
 ethylenebis(indenyl)zirconiumdimethyl,  
 15 ethylenebis(4,5,6,7-tetrahydroindenyl)zirconiumdichloride,  
 ethylenebis(4,5,6,7-tetrahydroindenyl)zirconiumdimethyl,  
 (isopropylidene)(cyclopentadienyl)(fluorenyl)zirconiumdibenzyl, and  
 dimethylsilyl(tetramethylcyclopentadienyl)(fluorenyl)zirconium dimethyl.

A further class of metal complexes utilized in the present invention corresponds to the  
 20 preceding formula:  $MK_kZ_zX_x$ , or a dimer thereof, wherein M, K, X, x and z are as previously  
 defined, k is one, and Z is a substituent of up to 50 non-hydrogen atoms that together with K forms  
 a metallocycle with M.

Preferred Z substituents include groups containing up to 30 non-hydrogen atoms comprising  
 at least one atom that is oxygen, sulfur, boron or a member of Group 14 of the Periodic Table of the  
 25 Elements directly attached to K, and a different atom, selected from the group consisting of  
 nitrogen, phosphorus, oxygen or sulfur that is covalently bonded to M.

More specifically this class of Group 4 metal complexes used according to the present  
 invention includes "constrained geometry catalysts" corresponding to the formula:



30 wherein:

M is titanium or zirconium, preferably titanium in the +2, +3, or +4 formal oxidation state;

$K^1$  is a delocalized,  $\pi$ -bonded ligand group optionally substituted with from 1 to 5  $R^2$  groups,

$R^2$  in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said  $R^2$  having up to 20 non-  
5 hydrogen atoms, or adjacent  $R^2$  groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

each X is independently a halo, hydride, hydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 non-hydrogen atoms, or two X groups together form a neutral  $C_{5-30}$  conjugated diene or a divalent derivative thereof;

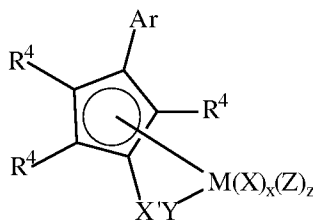
10 x is 1 or 2;

Y is -O-, -S-, -NR'-, -PR'-; and

X' is  $SiR'_2$ ,  $CR'_2$ ,  $SiR'_2SiR'_2$ ,  $CR'_2CR'_2$ ,  $CR'=CR'$ ,  $CR'_2SiR'_2$ , or  $GeR'_2$ , wherein

$R'$  independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said  $R'$  having up to 30 carbon or silicon atoms.

15 Specific examples of the foregoing constrained geometry metal complexes include compounds corresponding to the formula:



wherein,

Ar is an aryl group of from 6 to 30 atoms not counting hydrogen;

20  $R^4$  independently each occurrence is hydrogen, Ar, or a group other than Ar selected from hydrocarbyl, trihydrocarbysilyl, trihydrocarbylgermyl, halide, hydrocarbyloxy, trihydrocarbysiloxy, bis(trihydrocarbysilyl)amino, di(hydrocarbyl)amino, hydrocarbadiylamino, hydrocarbylimino, di(hydrocarbyl)phosphino, hydrocarbadiylphosphino, hydrocarbysulfido, halo-substituted hydrocarbyl, hydrocarbyloxy- substituted hydrocarbyl, trihydrocarbysilyl- substituted  
25 hydrocarbyl, trihydrocarbysiloxy- substituted hydrocarbyl, bis(trihydrocarbysilyl)amino- substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino- substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbysulfido- substituted hydrocarbyl, said R group having up to 40 atoms not counting hydrogen atoms, and optionally two adjacent  $R^4$   
30 groups may be joined together forming a polycyclic fused ring group;

M is titanium;

X' is  $\text{SiR}^6_2$ ,  $\text{CR}^6_2$ ,  $\text{SiR}^6_2\text{SiR}^6_2$ ,  $\text{CR}^6_2\text{CR}^6_2$ ,  $\text{CR}^6=\text{CR}^6$ ,  $\text{CR}^6_2\text{SiR}^6_2$ ,  $\text{BR}^6$ ,  $\text{BR}^6\text{L}$ , or  $\text{GeR}^6_2$ ;

Y is -O-, -S-,  $-\text{NR}^5_2$ ,  $-\text{PR}^5_2$ ;  $-\text{NR}^5_2$ , or  $-\text{PR}^5_2$ ;

$\text{R}^5$ , independently each occurrence, is hydrocarbyl, trihydrocarbysilyl, or  
 5 trihydrocarbysilylhydrocarbyl, said  $\text{R}^5$  having up to 20 atoms other than hydrogen, and optionally  
 two  $\text{R}^5$  groups or  $\text{R}^5$  together with Y or Z form a ring system;

$\text{R}^6$ , independently each occurrence, is hydrogen, or a member selected from hydrocarbyl,  
 hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl,  $-\text{NR}^5_2$ , and combinations thereof, said  $\text{R}^6$   
 10 having up to 20 non-hydrogen atoms, and optionally, two  $\text{R}^6$  groups or  $\text{R}^6$  together with Z forms a  
 ring system;

Z is a neutral diene or a monodentate or polydentate Lewis base optionally bonded to  $\text{R}^5$ ,  
 $\text{R}^6$ , or X;

X is hydrogen, a monovalent anionic ligand group having up to 60 atoms not counting  
 hydrogen, or two X groups are joined together thereby forming a divalent ligand group;

15 x is 1 or 2; and

z is 0, 1 or 2.

Preferred examples of the foregoing metal complexes are substituted at both the 3- and 4-  
 positions of a cyclopentadienyl or indenyl group with an Ar group.

Examples of the foregoing metal complexes include:

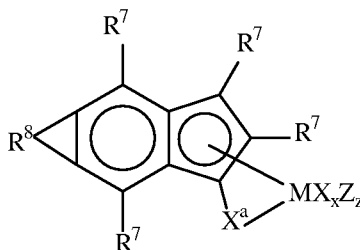
20 (3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,  
 (3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,  
 (3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,3-diphenyl-1,3-  
 butadiene;  
 (3-(pyrrol-1-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,  
 25 (3-(pyrrol-1-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,  
 (3-(pyrrol-1-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-  
 diphenyl-1,3-butadiene;  
 (3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,  
 (3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,  
 30 (3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-  
 diphenyl-1,3-butadiene;  
 (3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,  
 (3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,  
 (3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,3-

- pentadiene;
- (3-(3-N,N-dimethylamino)phenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
- (3-(3-N,N-dimethylamino)phenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
- 5 (3-(3-N,N-dimethylamino)phenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
- (3-(4-methoxyphenyl)-4-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
- 10 (3-(4-methoxyphenyl)-4-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl, (3-(4-methoxyphenyl)-4-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
- (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
- (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
- 15 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
- (3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
- (3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
- 20 (3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
- 2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
- 25 2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
- 2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
- ((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silane titanium dichloride,
- 30 ((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silane titanium dimethyl,
- ((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;



- (2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,  
 (2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,  
 (2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-  
 diphenyl-1,3-butadiene;
- 5 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,  
 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,  
 (3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-  
 diphenyl-1,3-butadiene;
- (2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,  
 10 (2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,  
 (2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-  
 diphenyl-1,3-butadiene;
- (2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,  
 (2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl, and  
 15 (2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-  
 diphenyl-1,3-butadiene.

Additional examples of suitable metal complexes for use herein are polycyclic complexes corresponding to the formula:



- 20 where M is titanium in the +2, +3 or +4 formal oxidation state;  
 $R^7$  independently each occurrence is hydride, hydrocarbyl, silyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl-substituted  
 25 hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino-substituted hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl, hydrocarbylene-phosphino-substituted hydrocarbyl, or hydrocarbylsulfido-substituted hydrocarbyl, said  $R^7$  group having up to 40 atoms not counting hydrogen, and optionally two or more of the foregoing groups may together  
 30 form a divalent derivative;

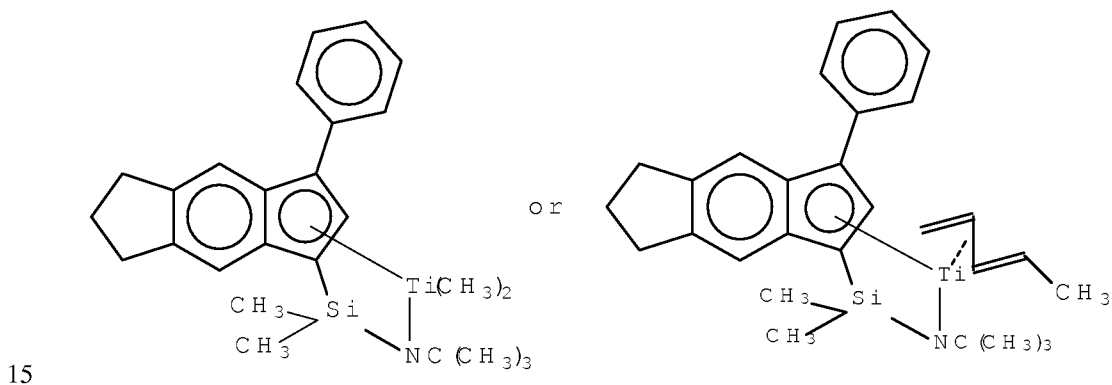
$R^8$  is a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused system with the remainder of the metal complex, said  $R^8$  containing from 1 to 30 atoms not counting hydrogen;

$X^a$  is a divalent moiety, or a moiety comprising one  $\sigma$ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said  $X^a$  comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

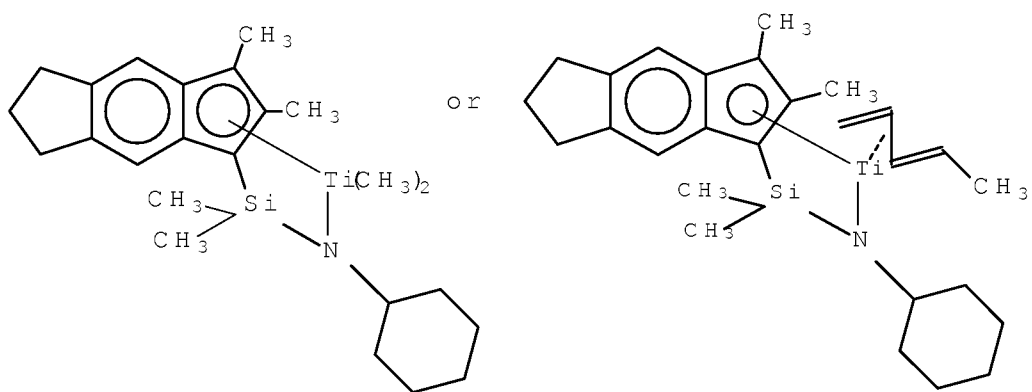
X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized,  $\pi$ -bound ligand groups and optionally two X groups together form a divalent ligand group;

10 Z independently each occurrence is a neutral ligating compound having up to 20 atoms; x is 0, 1 or 2; and z is zero or 1.

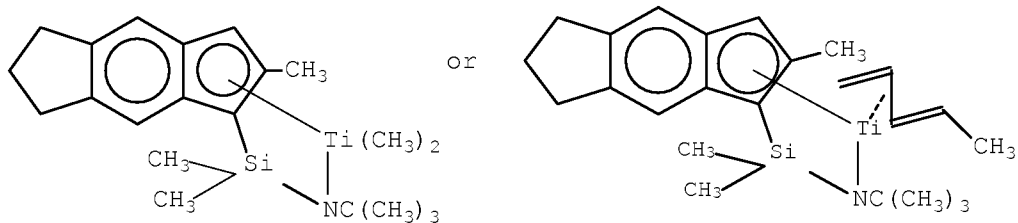
Preferred examples of such complexes are 3-phenyl-substituted s-indecenyl complexes corresponding to the formula:



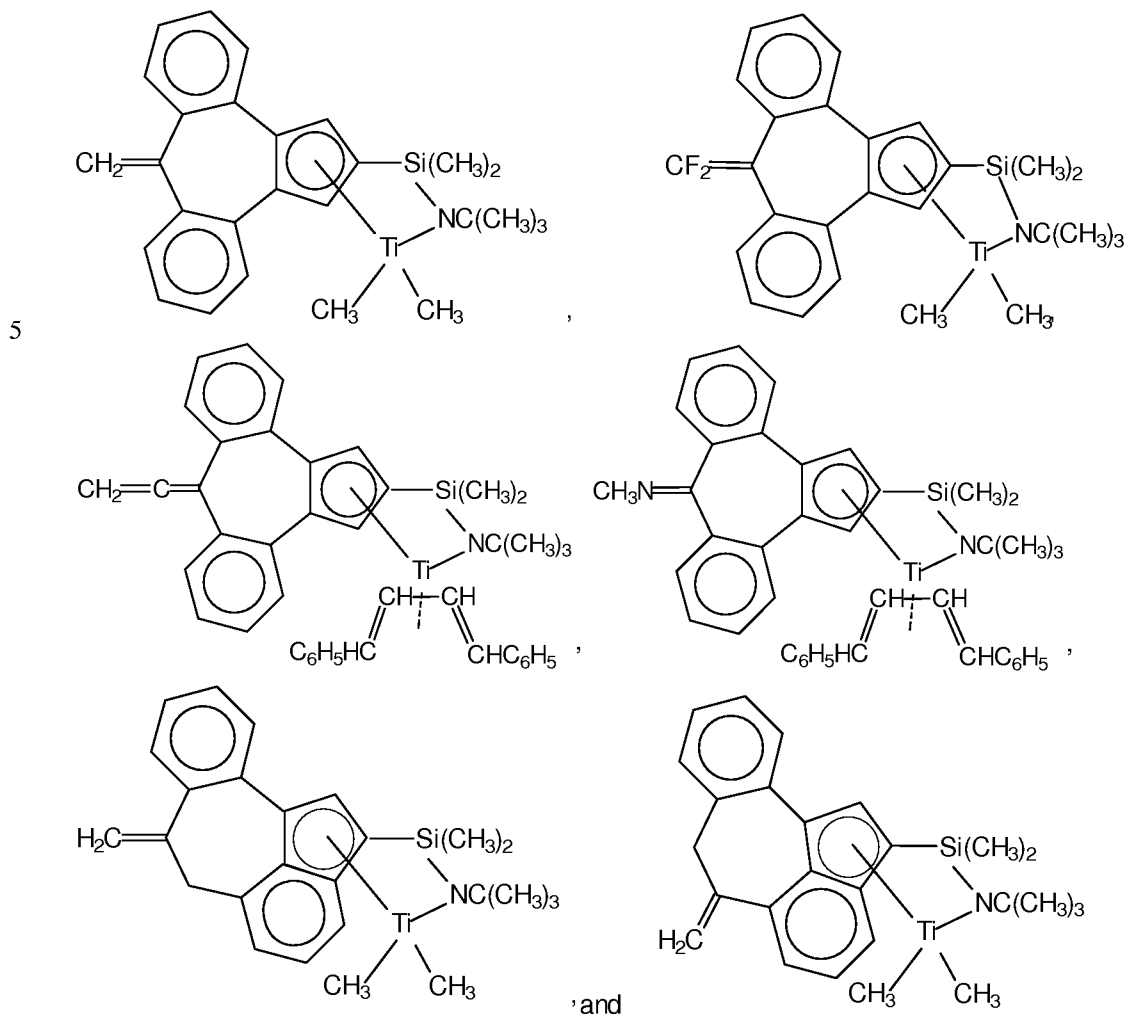
2,3-dimethyl-substituted s-indecenyl complexes corresponding to the formulas:



or 2-methyl-substituted s-indecenyl complexes corresponding to the formula:



Additional examples of metal complexes that are usefully employed according to the present invention include those of the formula:



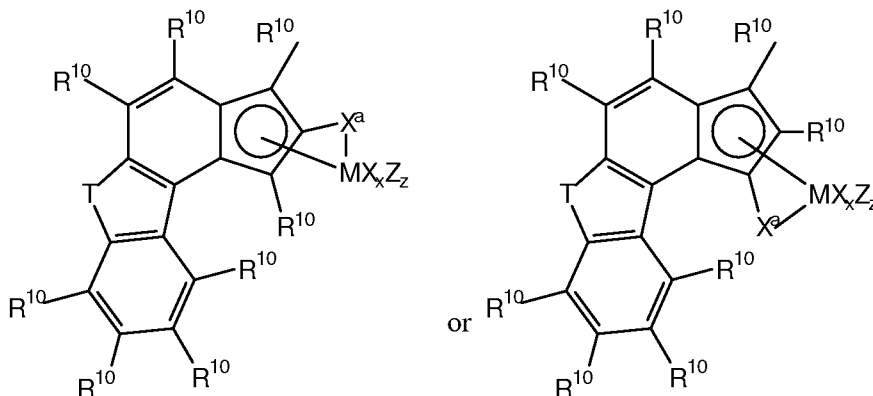
Specific metal complexes include:

- 10 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylanamide  
titanium (II) 1,4-diphenyl-1,3-butadiene,  
(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylanamide  
titanium (II) 1,3-pentadiene,

- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,
- 5 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,
- 10 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,
- (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,
- (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-
- 15 dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,
- (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,
- (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,
- 20 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,
- 25 (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide
- 30 titanium (IV) dichloride,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,
- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,

- (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,  
 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,  
 5 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,  
 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,  
 10 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,  
 (8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl, and mixtures thereof, especially mixtures of positional isomers.

- 15 Further illustrative examples of metal complexes for use according to the present invention correspond to the formula:



where M is titanium in the +2, +3 or +4 formal oxidation state;

T is  $-NR^9-$  or  $-O-$ ;

- 20  $R^9$  is hydrocarbyl, silyl, germyl, dihydrocarbylboryl, or halohydrocarbyl or up to 10 atoms not counting hydrogen;

- $R^{10}$  independently each occurrence is hydrogen, hydrocarbyl, trihydrocarbysilyl, trihydrocarbysilylhydrocarbyl, germyl, halide, hydrocarbyloxy, hydrocarbysiloxy, hydrocarbysilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino,  
 25 hydrocarbylene-phosphino, hydrocarbysulfido, halo- substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl- substituted hydrocarbyl, hydrocarbysiloxy- substituted hydrocarbyl, hydrocarbysilylamino- substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl,

hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said R<sup>10</sup> group having up to 40 atoms not counting hydrogen atoms, and optionally two or more of the foregoing adjacent R<sup>10</sup> groups may together form a divalent derivative thereby forming a saturated or unsaturated fused ring;

X<sup>a</sup> is a divalent moiety lacking in delocalized  $\pi$ -electrons, or such a moiety comprising one  $\sigma$ -bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said X' comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic ligand groups bound to M through delocalized  $\pi$ -electrons or two X groups together are a divalent anionic ligand group;

Z independently each occurrence is a neutral ligating compound having up to 20 atoms;

x is 0, 1, 2, or 3; and

z is 0 or 1.

Highly preferably T is =N(CH<sub>3</sub>), X is halo or hydrocarbyl, x is 2, X' is dimethylsilane, z is 0, and R<sup>10</sup> each occurrence is hydrogen, a hydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, hydrocarbyleneamino, dihydrocarbylamino- substituted hydrocarbyl group, or hydrocarbyleneamino- substituted hydrocarbyl group of up to 20 atoms not counting hydrogen, and optionally two R<sup>10</sup> groups may be joined together.

Illustrative metal complexes of the foregoing formula that may be employed in the practice of the present invention further include the following compounds:

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(II) 1,4-diphenyl-1,3-butadiene,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(II) 1,3-pentadiene,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(III) 2-(N,N-dimethylamino)benzyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(IV) dichloride,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(IV) dimethyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium

(IV) dibenzyl,

- (t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),
- (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
- 5 (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,
- (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- 10 (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,
- (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,
- (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl,
- 15 (cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),
- (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
- 20 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,
- (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
- 25 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,
- (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,
- (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl,
- 30 (t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),

- (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,  
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,  
5 (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,  
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,  
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,  
10 (cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl; and  
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl).
- 15 Illustrative Group 4 metal complexes that may be employed in the practice of the present invention further include:
- (tert-butylamido)(1,1-dimethyl-2,3,4,9,10-η-1,4,5,6,7,8-hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,  
(tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10-η-1,4,5,6,7,8-hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,  
20 (tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl) dimethylsilanetitanium dibenzyl,  
(tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)dimethylsilanetitanium dimethyl,  
(tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl,  
(tert-butylamido)(tetramethyl-η<sup>5</sup>-indenyl)dimethylsilanetitanium dimethyl,  
25 (tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)dimethylsilane titanium (III) 2-(dimethylamino)benzyl;  
(tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)dimethylsilanetitanium (III) allyl,  
(tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)dimethylsilanetitanium (III) 2,4-dimethylpentadienyl,  
30 (tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene,  
(tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl)dimethylsilanetitanium (II) 1,3-pentadiene,  
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-

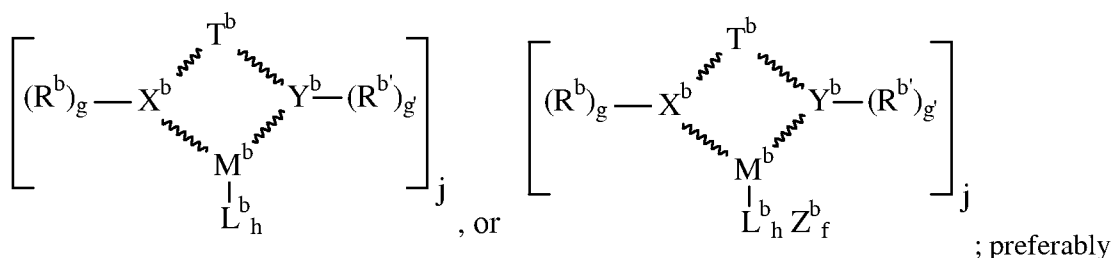


- butadiene,  
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,  
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-  
 butadiene,  
 5 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) isoprene,  
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,  
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)  
 2,3-dimethyl-1,3-butadiene,  
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)  
 10 isoprene  
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dimethyl  
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dibenzyl  
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,  
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,  
 15 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-  
 1,3-butadiene,  
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,  
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dimethyl,  
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dibenzyl,  
 20 (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II)  
 1,4-diphenyl-1,3-butadiene,  
 (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,  
 (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethyl- silanetitanium (IV)  
 25 1,3-butadiene,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (IV)  
 2,3-dimethyl-1,3-butadiene,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (IV)  
 isoprene,  
 30 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethyl- silanetitanium (II)  
 1,4-dibenzyl-1,3-butadiene,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium (II)  
 2,4-hexadiene,  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethyl- silanetitanium (II)

3-methyl-1,3-pentadiene,  
 (tert-butylamido)(2,4-dimethylpentadien-3-yl)dimethylsilanetitaniumdimethyl,  
 (tert-butylamido)(6,6-dimethylcyclohexadienyl)dimethylsilanetitaniumdimethyl,  
 (tert-butylamido)(1,1-dimethyl-2,3,4,9,10-η-1,4,5,6,7,8-hexahydronaphthalen-4-  
 5 yl)dimethylsilanetitaniumdimethyl,  
 (tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10-η-1,4,5,6,7,8-hexahydronaphthalen-4-  
 yl)dimethylsilanetitaniumdimethyl  
 (tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl methylphenylsilanetitanium (IV)  
 dimethyl,  
 10 (tert-butylamido)(tetramethyl-η<sup>5</sup>-cyclopentadienyl methylphenylsilanetitanium (II)  
 1,4-diphenyl-1,3-butadiene,  
 1-(tert-butylamido)-2-(tetramethyl-η<sup>5</sup>-cyclopentadienyl)ethanediyltitanium (IV)  
 dimethyl, and  
 1-(tert-butylamido)-2-(tetramethyl-η<sup>5</sup>-cyclopentadienyl)ethanediyl-titanium (II) 1,4-diphenyl-1,3-  
 15 butadiene.

Other delocalized, π-bonded complexes, especially those containing other Group 4 metals,  
 will, of course, be apparent to those skilled in the art, and are disclosed among other places in:  
 WO 03/78480, WO 03/78483, WO 02/92610, WO 02/02577, US 2003/0004286 and US  
 Patents 6,515,155, 6,555,634, 6,150,297, 6,034,022, 6,268,444, 6,015,868, 5,866,704, and  
 20 5,470,993.

Additional examples of metal complexes that are usefully employed as catalysts in the  
 present invention are complexes of polyvalent Lewis bases corresponding to the formula:






halogen, alkoxy, aryloxy, alkoxy carbonyl, aryloxy carbonyl, di(hydrocarbyl)amine, tri(hydrocarbyl)silyl, and nitrile groups. Preferred  $Z^b$  groups include triphenylphosphine, tetrahydrofuran, pyridine, and 1,4-diphenylbutadiene;

f is an integer from 1 to 3;

5 two or three of  $T^b$ ,  $R^b$  and  $R^{b'}$  may be joined together to form a single or multiple ring structure;

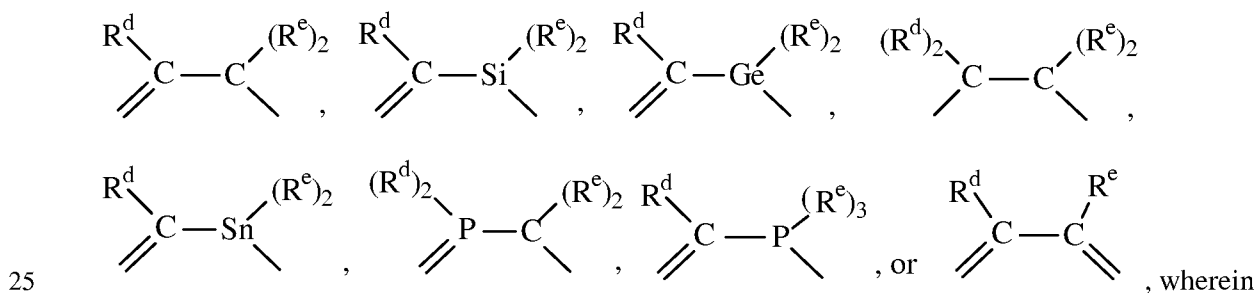
h is an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3;

10  indicates any form of electronic interaction, especially coordinate or covalent bonds, including multiple bonds, arrows signify coordinate bonds, and dotted lines indicate optional double bonds.

In one embodiment, it is preferred that  $R^b$  have relatively low steric hindrance with respect to  $X^b$ . In this embodiment, most preferred  $R^b$  groups are straight chain alkyl groups, straight chain alkenyl groups, branched chain alkyl groups wherein the closest branching point is at least 3 atoms removed from  $X^b$ , and halo, dihydrocarbylamino, alkoxy or trihydrocarbylsilyl substituted derivatives thereof. Highly preferred  $R^b$  groups in this embodiment are  $C_{1-8}$  straight chain alkyl groups.

At the same time, in this embodiment  $R^{b'}$  preferably has relatively high steric hindrance with respect to  $Y^b$ . Non-limiting examples of suitable  $R^{b'}$  groups for this embodiment include alkyl or alkenyl groups containing one or more secondary or tertiary carbon centers, cycloalkyl, aryl, 20 alkaryl, aliphatic or aromatic heterocyclic groups, organic or inorganic oligomeric, polymeric or cyclic groups, and halo, dihydrocarbylamino, alkoxy or trihydrocarbylsilyl substituted derivatives thereof. Preferred  $R^{b'}$  groups in this embodiment contain from 3 to 40, more preferably from 3 to 30, and most preferably from 4 to 20 atoms not counting hydrogen and are branched or cyclic.

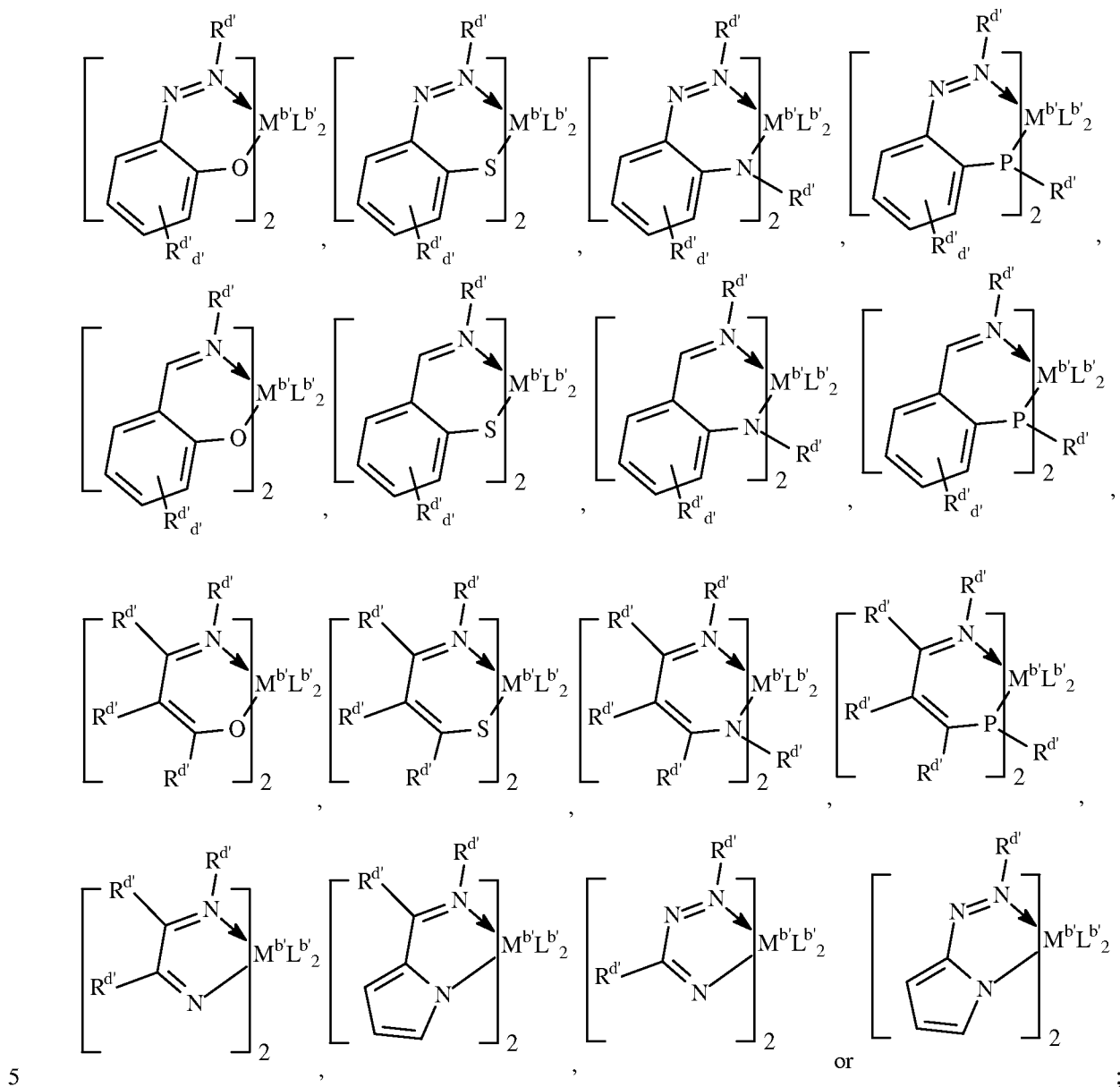
Examples of preferred  $T^b$  groups are structures corresponding to the following formulas:



Each  $R^d$  is  $C_{1-10}$  hydrocarbyl group, preferably methyl, ethyl, n-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. Each  $R^e$  is  $C_{1-10}$  hydrocarbyl, preferably methyl, ethyl, n-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. In addition, two or more  $R^d$  or  $R^e$  groups, or mixtures of  $R^d$  and  $R^e$  groups may together form a polyvalent derivative of a

hydrocarbyl group, such as, 1,4-butylene, 1,5-pentylene, or a multicyclic, fused ring, polyvalent hydrocarbyl- or heterohydrocarbyl- group, such as naphthalene-1,8-diyl.

Preferred examples of the foregoing polyvalent Lewis base complexes include:



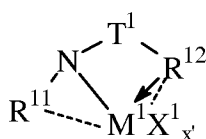
wherein  $R^{d'}$  each occurrence is independently selected from the group consisting of hydrogen and  $C_{1-50}$  hydrocarbyl groups optionally containing one or more heteroatoms, or inertly substituted derivative thereof, or further optionally, two adjacent  $R^{d'}$  groups may together form a divalent bridging group;

10  $d'$  is 4;

$M^b$  is a Group 4 metal, preferably titanium or hafnium, or a Group 10 metal, preferably Ni or Pd;

$L^{b'}$  is a monovalent ligand of up to 50 atoms not counting hydrogen, preferably halide or hydrocarbyl, or two  $L^{b'}$  groups together are a divalent or neutral ligand group, preferably a  $C_{2-50}$  hydrocarbylene, hydrocarbadiyl or diene group.

The polyvalent Lewis base complexes for use in the present invention include Group 4  
5 metal derivatives, especially hafnium derivatives, of hydrocarbylamine substituted heteroaryl compounds, said complexes corresponding to the formula:



wherein:

$R^{11}$  is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly  
10 substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen or a divalent derivative thereof;

$T^1$  is a divalent bridging group of from 1 to 41 atoms other than hydrogen, preferably 1 to 20 atoms other than hydrogen, and most preferably a mono- or di-  $C_{1-20}$  hydrocarbyl substituted methylene or silane group; and

$R^{12}$  is a  $C_{5-20}$  heteroaryl group containing Lewis base functionality, especially a pyridin-2-  
15 yl- or substituted pyridin-2-yl group or a divalent derivative thereof;

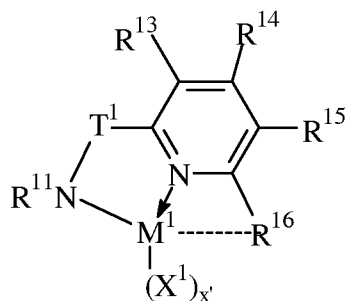
$M^1$  is a Group 4 metal, preferably hafnium;

$X^1$  is an anionic, neutral or dianionic ligand group;

$x'$  is a number from 0 to 5 indicating the number of such  $X^1$  groups; and

20 bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

Preferred complexes are those wherein ligand formation results from hydrogen elimination from the amine group and optionally from the loss of one or more additional groups, especially from  $R^{12}$ . In addition, electron donation from the Lewis base functionality, preferably an electron  
25 pair, provides additional stability to the metal center. Preferred metal complexes correspond to the formula:

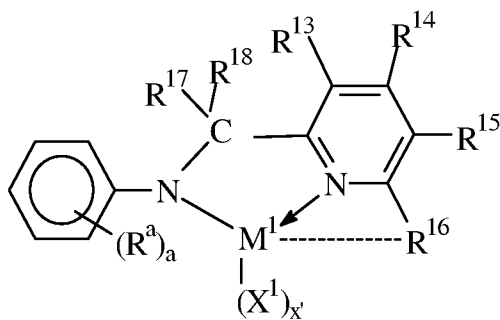


, wherein

$M^1$ ,  $X^1$ ,  $x'$ ,  $R^{11}$  and  $T^1$  are as previously defined,

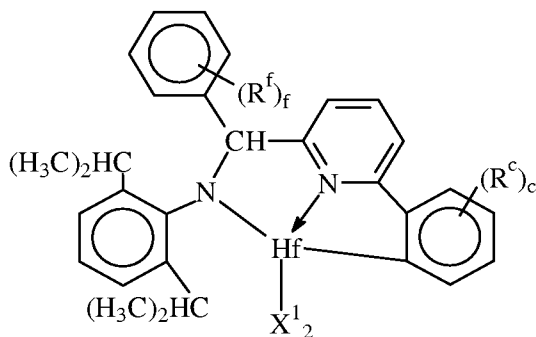
- $R^{13}$ ,  $R^{14}$ ,  $R^{15}$  and  $R^{16}$  are hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, or silyl group of up to 20 atoms not counting hydrogen, or adjacent  $R^{13}$ ,  $R^{14}$ ,  $R^{15}$  or  $R^{16}$  groups may be joined together thereby forming fused ring derivatives, and
- bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

More preferred examples of the foregoing metal complexes correspond to the formula:



, wherein

- $M^1$ ,  $X^1$ , and  $x'$  are as previously defined,
- $R^{13}$ ,  $R^{14}$ ,  $R^{15}$  and  $R^{16}$  are as previously defined, preferably  $R^{13}$ ,  $R^{14}$ , and  $R^{15}$  are hydrogen, or  $C_{1-4}$  alkyl, and  $R^{16}$  is  $C_{6-20}$  aryl, most preferably naphthalenyl;
- $R^a$  independently each occurrence is  $C_{1-4}$  alkyl, and  $a$  is 1-5, most preferably  $R^a$  in two ortho- positions to the nitrogen is isopropyl or t-butyl;
- $R^{17}$  and  $R^{18}$  independently each occurrence are hydrogen, halogen, or a  $C_{1-20}$  alkyl or aryl group, most preferably one of  $R^{17}$  and  $R^{18}$  is hydrogen and the other is a  $C_{6-20}$  aryl group, especially 2-isopropyl, phenyl or a fused polycyclic aryl group, most preferably an anthracenyl group, and
- covalent bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.
- Highly preferred metal complexes for use herein as one of the catalysts herein correspond to the formula:

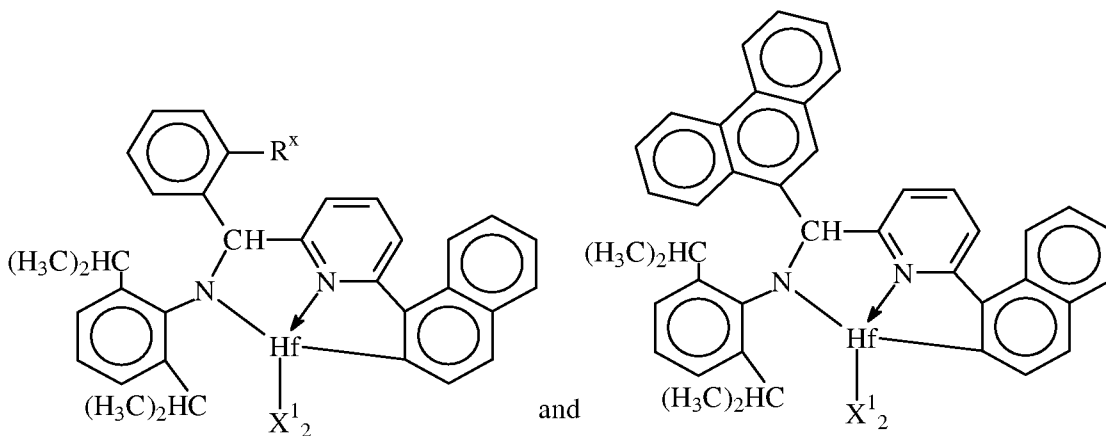


wherein  $X^1$  each occurrence is halide, N,N-dimethylamido, or  $C_{1-4}$  alkyl, and preferably each occurrence  $X^1$  is methyl;

$R^f$  independently each occurrence is hydrogen, halogen,  $C_{1-20}$  alkyl, or  $C_{6-20}$  aryl, or two adjacent  $R^f$  groups are joined together thereby forming a ring, and  $f$  is 1-5; and

$R^c$  independently each occurrence is hydrogen, halogen,  $C_{1-20}$  alkyl, or  $C_{6-20}$  aryl, or two adjacent  $R^c$  groups are joined together thereby forming a ring, and  $c$  is 1-5.

Additional examples of metal complexes for use according to the present invention are complexes of the following formulas:



10

wherein  $R^x$  is  $C_{1-4}$  alkyl or cycloalkyl, preferably methyl, isopropyl, t-butyl or cyclohexyl; and

$X^1$  each occurrence is halide, N,N-dimethylamido, or  $C_{1-4}$  alkyl, preferably methyl.

Examples of metal complexes of the foregoing type include:

15

[N-(2,6-di(1-methylethyl)phenyl)amido](o-tolyl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido](o-tolyl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

20

[N-(2,6-di(1-methylethyl)phenyl)amido](o-tolyl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;



[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

5 [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;

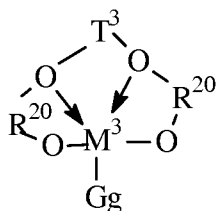
[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

10 [N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido); and

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)( $\alpha$ -naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride.

Under the reaction conditions used to prepare the metal complexes used in the present invention, the hydrogen of the 2-position of the  $\alpha$ -naphthalene group substituted at the 6-position of the pyridin-2-yl group is subject to elimination, thereby uniquely forming metal complexes wherein the metal is covalently bonded to both the resulting amide group and to the 2-position of the  $\alpha$ -naphthalenyl group, as well as stabilized by coordination to the pyridinyl nitrogen atom through the electron pair of the nitrogen atom.

Additional suitable metal complexes include compounds corresponding to the formula:



20

, where:

$R^{20}$  is an aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen, or a polyvalent derivative thereof;

$T^3$  is a hydrocarbylene or silane group having from 1 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof;

25

$M^3$  is a Group 4 metal, preferably zirconium or hafnium;

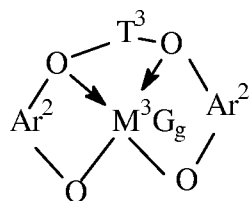
G is an anionic, neutral or dianionic ligand group; preferably a halide, hydrocarbyl or dihydrocarbylamide group having up to 20 atoms not counting hydrogen;

g is a number from 1 to 5 indicating the number of such G groups; and

bonds and electron donative interactions are represented by lines and arrows respectively.

30

Preferably, such complexes correspond to the formula:



, wherein:

$T^3$  is a divalent bridging group of from 2 to 20 atoms not counting hydrogen, preferably a substituted or unsubstituted,  $C_{3-6}$  alkylene group; and

$Ar^2$  independently each occurrence is an arylene or an alkyl- or aryl-substituted arylene group of from 6 to 20 atoms not counting hydrogen;

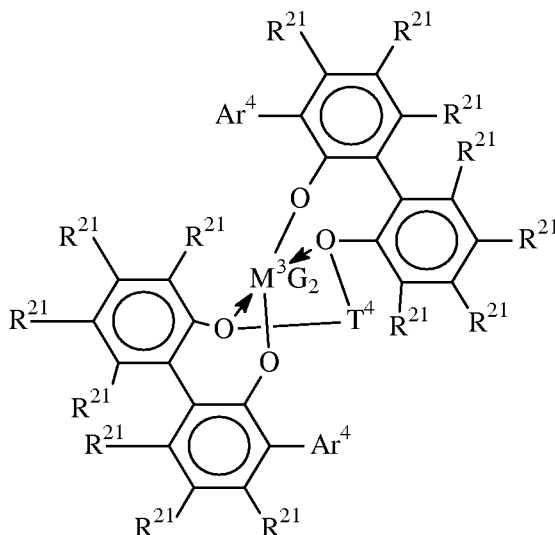
$M^3$  is a Group 4 metal, preferably hafnium or zirconium;

$G$  independently each occurrence is an anionic, neutral or dianionic ligand group;

$g$  is a number from 1 to 5 indicating the number of such  $X$  groups; and

electron donative interactions are represented by arrows.

Preferred examples of metal complexes of foregoing formula include the following compounds:



where  $M^3$  is Hf or Zr;

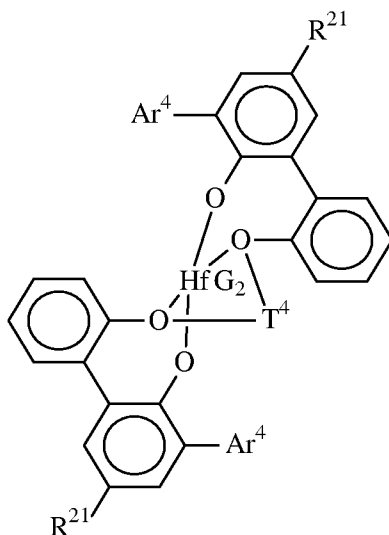
$Ar^4$  is  $C_{6-20}$  aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, 3,5-di(t-butyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl, and

$T^4$  independently each occurrence comprises a  $C_{3-6}$  alkylene group, a  $C_{3-6}$  cycloalkylene group, or an inertly substituted derivative thereof;

$R^{21}$  independently each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbysilyl, or trihydrocarbysilylhydrocarbyl of up to 50 atoms not counting hydrogen; and

G, independently each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 G groups together are a divalent derivative of the foregoing hydrocarbyl or trihydrocarbylsilyl groups.

Especially preferred are compounds of the formula:



5

wherein Ar<sup>4</sup> is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, 3,5-di(t-butyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl,

R<sup>21</sup> is hydrogen, halo, or C<sub>1-4</sub> alkyl, especially methyl or t-butyl

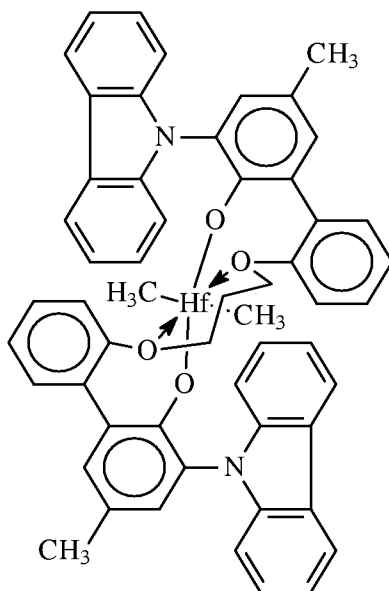
R<sup>21</sup> is hydrogen, halo, or C<sub>1-4</sub> alkyl, especially methyl

10

T<sup>4</sup> is propan-1,3-diyl, butan-1,4-diyl, cyclohexyl, dimethylene(cyclohexan-1,2-diyl), dimethylene(cyclohex-3-en-1,2-diyl), and

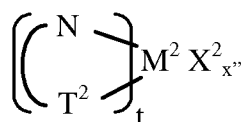
G is chloro, methyl or benzyl.

Other suitable metal complexes are those of the formula:



The foregoing polyvalent Lewis base complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of the Group 4 metal and the neutral polyfunctional ligand source. In addition, the complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding Group 4 metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum. Other techniques may be used as well. These complexes are known from the disclosures of, among others, US patents 5 6,320,005, 6,103,657, WO 02/38628, WO 03/40195, and US 04/0220050.

Additional suitable metal complexes include Group 4-10 metal derivatives corresponding to 10 the formula:



wherein

$\text{M}^2$  is a metal of Groups 4-10 of the Periodic Table of the elements, preferably Group 4 metals, Ni(II) or Pd(II), most preferably zirconium;

15  $\text{T}^2$  is a nitrogen, oxygen or phosphorus containing group;

$\text{X}^2$  is halo, hydrocarbyl, or hydrocarbyloxy;

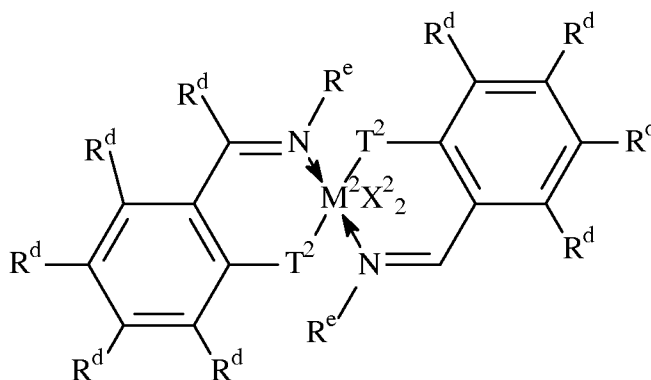
$t$  is one or two;

$x''$  is a number selected to provide charge balance;

and  $\text{T}^2$  and  $\text{N}$  are linked by a bridging ligand.

Such catalysts have been previously disclosed in *J. Am. Chem. Soc.*, 118, 267-268 (1996), *J. Am. Chem. Soc.*, 117, 6414 -6415 (1995), and *Organometallics*, 16, 1514-1516, (1997), among other disclosures.

Preferred examples of the foregoing metal complexes are aromatic diimine or aromatic dioximine complexes of Group 4 metals, especially zirconium, corresponding to the formula:



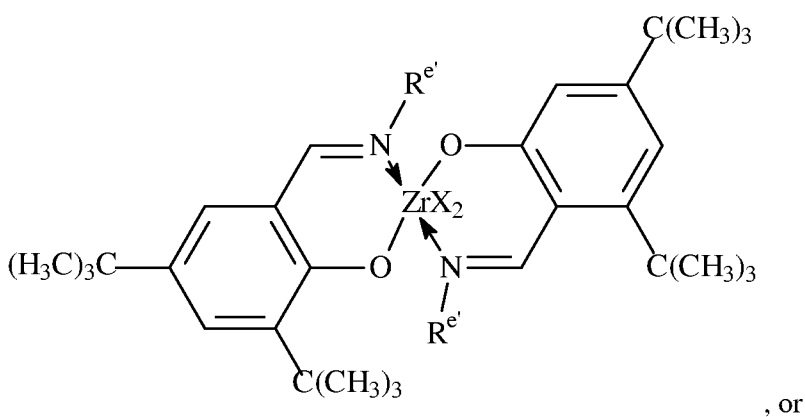
wherein;

$M^2$ ,  $X^2$  and  $T^2$  are as previously defined;

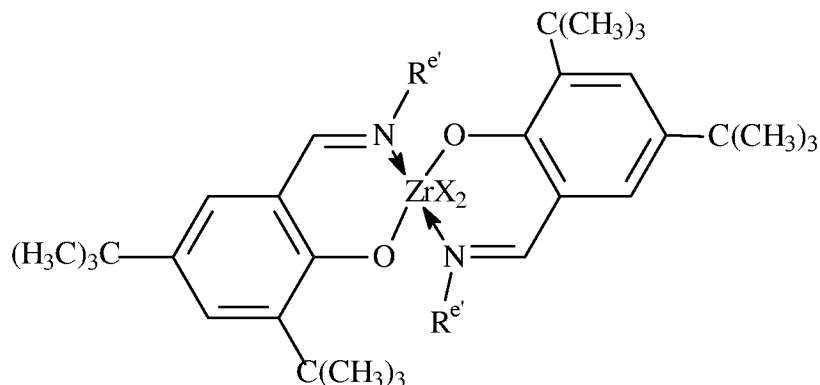
$R^d$  independently each occurrence is hydrogen, halogen, or  $R^e$ ; and

$R^e$  independently each occurrence is  $C_{1-20}$  hydrocarbyl or a heteroatom-, especially a F, N, S or P- substituted derivative thereof, more preferably  $C_{1-10}$  hydrocarbyl or a F or N substituted derivative thereof, most preferably alkyl, dialkylaminoalkyl, pyrrolyl, piperidenyl, perfluorophenyl, cycloalkyl, (poly)alkylaryl, or aralkyl.

Most preferred examples of the foregoing metal complexes for use as a catalyst herein are aromatic dioximine complexes of zirconium, corresponding to the formula:



, or



wherein;

$X^2$  is as previously defined, preferably  $C_{1-10}$  hydrocarbyl, most preferably methyl or benzyl;

and

5  $R^{e'}$  is methyl, isopropyl, t-butyl, cyclopentyl, cyclohexyl, 2-methylcyclohexyl, 2,4-dimethylcyclohexyl, 2-pyrrolyl, N-methyl-2-pyrrolyl, 2-piperidenyl, N-methyl-2-piperidenyl, benzyl, o-tolyl, 2,6-dimethylphenyl, perfluorophenyl, 2,6-di(isopropyl)phenyl, or 2,4,6-trimethylphenyl.

The foregoing complexes also include certain phosphinimine complexes are disclosed in  
10 EP-A-890581. These complexes correspond to the formula:  $[(R^f)_3-P=N]_f M(K^2)(R^f)_{3-f}$ , wherein:

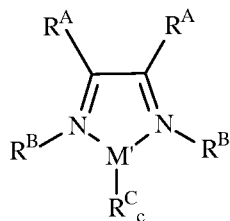
$R^f$  is a monovalent ligand or two  $R^f$  groups together are a divalent ligand, preferably  $R^f$  is hydrogen or  $C_{1-4}$  alkyl;

$M$  is a Group 4 metal,

$K^2$  is a group containing delocalized  $\pi$ -electrons through which  $K^2$  is bound to  $M$ , said  $K^2$   
15 group containing up to 50 atoms not counting hydrogen atoms, and

$f$  is 1 or 2.

Additional suitable metal complexes include metal complexes corresponding to the  
formula:

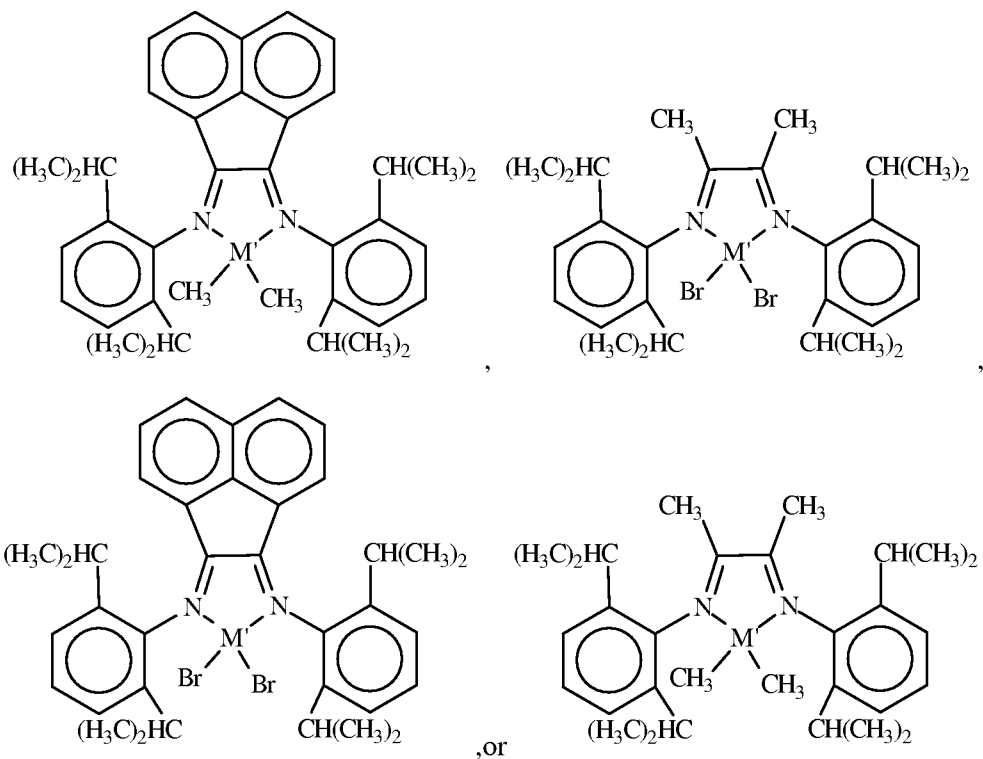


20 where  $M'$  is a metal of Groups 4-13, preferably Groups 8-10, most preferably Ni or Pd;

$R^A$ ,  $R^B$  and  $R^C$  are univalent or neutral substituents, which also may be joined together to form one or more divalent substituents, and

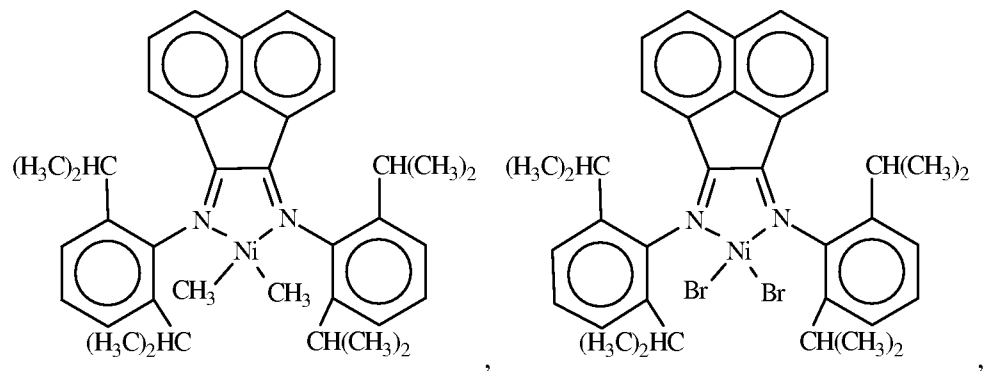
$c$  is a number chosen to balance the charge of the metal complex.

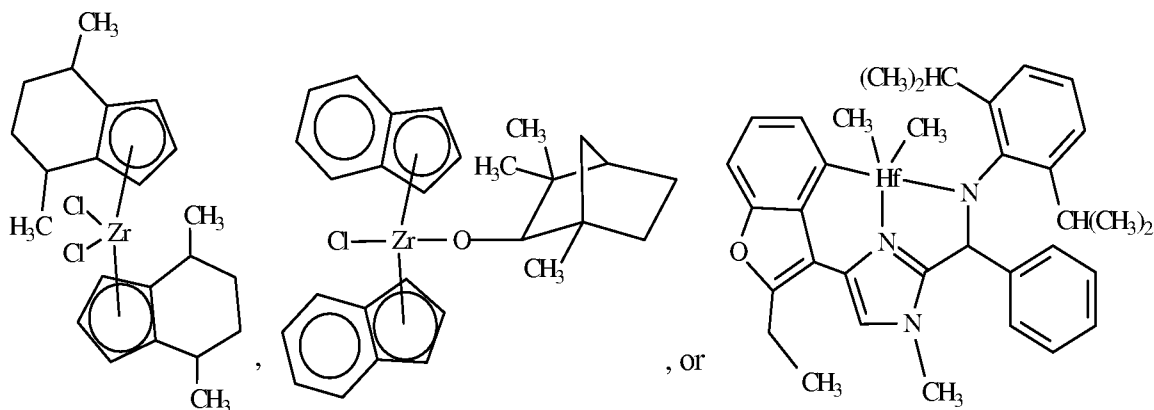
Preferred examples of the foregoing metal complexes for use as catalysts are compounds corresponding to the formula:



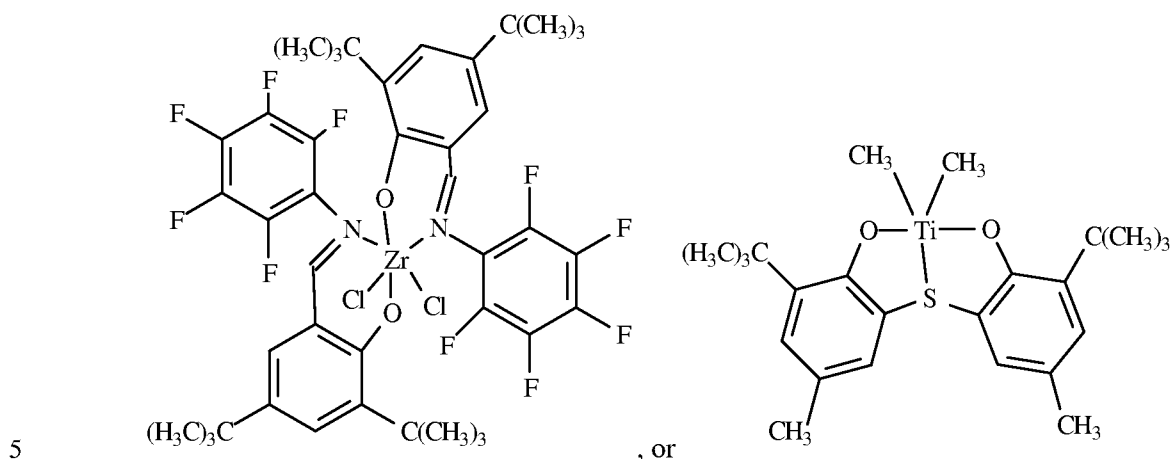
5 wherein  $M'$  is Pd or Ni.

Preferred examples of the foregoing metal complexes are compounds corresponding to the formulas:





Metal complexes capable of increased 2,1-monomer insertion include compounds of the formulas:



Through use of the foregoing metal complexes, regio-irregular branching may be induced in the multi-block copolymers by the use of catalysts that result in “chain-walking” in the resulting polymer. For example, certain homogeneous bridged bis indenyl- or partially hydrogenated bis indenyl- zirconium catalysts, disclosed by Kaminski, *et al.*, J. Mol. Catal. A: Chemical, 102 (1995) 59-65; Zambelli, *et al.*, Macromolecules, 1988, 21, 617-622; or Dias, *et al.*, J. Mol. Catal. A: Chemical, 185 (2002) 57-64 may be used to prepare branched copolymers, including hyper-branched polymers, from single monomers. Higher transition metal catalysts, especially nickel and palladium catalysts are also known to lead to hyper-branched polymers (the branches of which are also branched) as disclosed in Brookhart, *et al.*, J. Am. Chem. Soc., 1995, 117, 64145-6415.

Accordingly, in one embodiment of the invention a multi-block copolymer containing blocks or segments differing in the presence of such branching in combination with other segments or blocks substantially lacking such branching (especially high isotactic polymer blocks) can be produced. The presence of regio-irregular 2,1- or 3,1-monomer insertion in the multi-block



copolymers of the invention can be detected by NMR techniques. The quantity of the foregoing types of polymer moieties present in the polymers of the invention (as a portion of the blocks or segments containing the same), is normally in the range from 1 to 200, preferably 10-166 incidences per 1,000 carbons for 2,1-monomer insertions and 1-250, preferably 100-200 incidences per 1,000  
5 carbons for 3,1-monomer insertions. In addition, incidental regio-errors in the tactic polymer segment may also be present. In one embodiment, such errors are identifiable by  $^{13}\text{C}$  NMR peaks at 14.6 and 15.7 ppm, the peaks being of approximately equal intensity and representing up to 5 mole percent of such polymer segment.

Especially desired metal complexes for preparation of tactic polymer segments are the well  
10 known racemic biscyclopentadienyl complexes of Group 4 metals, such as dimethylsilane or 1,2-ethylene bridged biscyclopentadienyl zirconium complexes, and inertly substituted derivatives thereof. Examples include racemic dimethylsilane or 1,2-ethylene bisindenyl complexes of Group 4 metals, especially zirconium, such as ethylenebis(4,5,6,7-tetrahydro-1-indenyl)dimethyl zirconium or racemic ethylene bis(indenyl)dimethyl zirconium, and inertly substituted derivatives thereof.

15 Generally, the metal complex catalyst (also interchangeably referred to herein as procatalysts) may be activated to form the active catalyst composition by combination with a cocatalyst, preferably a cation forming cocatalyst comprising a relatively non-nucleophilic anion, a strong Lewis acid, or a combination thereof. In a preferred embodiment, the shuttling agent is employed both for purposes of chain shuttling and as the cocatalyst component of the catalyst  
20 composition.

The metal complexes desirably are rendered catalytically active by combination with a cation forming cocatalyst, such as those previously known in the art for use with Group 4 metal olefin polymerization complexes. Suitable cation forming cocatalysts for use herein include neutral Lewis acids, such as  $\text{C}_{1-30}$  hydrocarbyl substituted Group 13 compounds, especially  
25 tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluoro-phenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially the use of  
30 ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium- salts of compatible, noncoordinating anions, or ferrocenium-, lead- or silver salts of compatible, noncoordinating anions; and combinations of the foregoing cation forming cocatalysts and techniques. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal complexes for olefin polymerizations in the following references: EP-A-277,003,

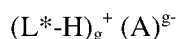
US-A-5,153,157, US-A-5,064,802, US-A-5,321,106, US-A-5,721,185, US-A-5,350,723,  
 US-A-5,425,872, US-A-5,625,087, US-A-5,883,204, US-A-5,919,983, US-A-5,783,512,  
 WO 99/15534, and WO99/42467.

Combinations of neutral Lewis acids, especially the combination of a trialkyl aluminum  
 5 compound having from 1 to 4 carbons in each alkyl group and a halogenated tri(hydrocarbyl)boron  
 compound having from 1 to 20 carbons in each hydrocarbyl group, especially  
 tris(pentafluorophenyl)borane, further combinations of such neutral Lewis acid mixtures with a  
 polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially  
 tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane may be used as activating  
 10 cocatalysts. Preferred molar ratios of metal complex:tris(pentafluorophenyl)-borane:alumoxane are  
 from 1:1:1 to 1:5:20, more preferably from 1:1:1.5 to 1:5:10.

Suitable ion forming compounds useful as cocatalysts in one embodiment of the present  
 invention comprise a cation which is a Bronsted acid capable of donating a proton, and a,  
 noncoordinating anion, A<sup>-</sup>.

15 Preferred anions are those containing a single coordination complex comprising a charge-  
 bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst  
 species (the metal cation) which may be formed when the procatalyst and the cocatalyst are  
 combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and  
 acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles.  
 20 Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids  
 include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions  
 which comprise coordination complexes containing a single metal or metalloid atom are, of course,  
 well known and many, particularly such compounds containing a single boron atom in the anion  
 portion, are available commercially.

25 Preferably such cocatalysts may be represented by the following general formula:



wherein:

L\* is a neutral Lewis base;

(L\*-H)<sup>+</sup> is a conjugate Bronsted acid of L\*;

30 A<sup>g-</sup> is a noncoordinating, compatible anion having a charge of g-, and  
 g is an integer from 1 to 3.

More preferably A<sup>g-</sup> corresponds to the formula: [M'Q<sub>4</sub>]<sup>-</sup>;

wherein:

M' is boron or aluminum in the +3 formal oxidation state; and

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and halo- substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxy Q groups are disclosed in US-A-5,296,433.

In a more preferred embodiment, d is one, that is, the counter ion has a single negative charge and is  $A^-$ . Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



wherein:

L\* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

Preferred Lewis base salts are ammonium salts, more preferably trialkylammonium salts containing one or more  $C_{12-40}$  alkyl groups. Most preferably, Q is each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this invention are tri-substituted ammonium salts such as:

trimethylammonium tetrakis(pentafluorophenyl) borate,  
triethylammonium tetrakis(pentafluorophenyl) borate,  
tripropylammonium tetrakis(pentafluorophenyl) borate,  
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,  
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate,  
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,  
N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate,  
N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate,  
N,N-dimethylanilinium tetrakis(4-(t-butyl)dimethylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,  
N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,  
N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate,  
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate,

N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate,  
 dimethyloctadecylammonium tetrakis(pentafluorophenyl) borate,  
 methyldioctadecylammonium tetrakis(pentafluorophenyl) borate,  
 dialkyl ammonium salts such as:

5 di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate,  
 methyloctadecylammonium tetrakis(pentafluorophenyl) borate,  
 methyloctadecylammonium tetrakis(pentafluorophenyl) borate, and  
 dioctadecylammonium tetrakis(pentafluorophenyl) borate;

tri-substituted phosphonium salts such as:

10 triphenylphosphonium tetrakis(pentafluorophenyl) borate,  
 methyldioctadecylphosphonium tetrakis(pentafluorophenyl) borate, and  
 tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate;

di-substituted oxonium salts such as:

diphenyloxonium tetrakis(pentafluorophenyl) borate,  
 15 di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and  
 di(octadecyl)oxonium tetrakis(pentafluorophenyl) borate;

di-substituted sulfonium salts such as:

di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and  
 methylcotadecylsulfonium tetrakis(pentafluorophenyl) borate.

20 Preferred (L\*-H)<sup>+</sup> cations are methyldioctadecylammonium cations,  
 dimethyloctadecylammonium cations, and ammonium cations derived from mixtures of trialkyl  
 amines containing one or 2 C<sub>14-18</sub> alkyl groups.

Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing  
 agent and a noncoordinating, compatible anion represented by the formula:

25  $(\text{Ox}^{\text{h}+})_{\text{g}}(\text{A}^{\text{g}-})_{\text{h}}$ ,

wherein:

Ox<sup>h+</sup> is a cationic oxidizing agent having a charge of h+;

h is an integer from 1 to 3; and

A<sup>g-</sup> and g are as previously defined.

30 Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted  
 ferrocenium, Ag<sup>+</sup>, or Pb<sup>+2</sup>. Preferred embodiments of A<sup>g-</sup> are those anions previously defined with  
 respect to the Bronsted acid containing activating cocatalysts, especially  
 tetrakis(pentafluorophenyl)borate.

Another suitable ion forming, activating cocatalyst comprises a compound which is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula:

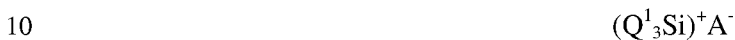


wherein:

5  $[C]^+$  is a C<sub>1-20</sub> carbenium ion; and

A<sup>-</sup> is a noncoordinating, compatible anion having a charge of -1. A preferred carbenium ion is the trityl cation, that is triphenylmethylum.

A further suitable ion forming, activating cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:



wherein:

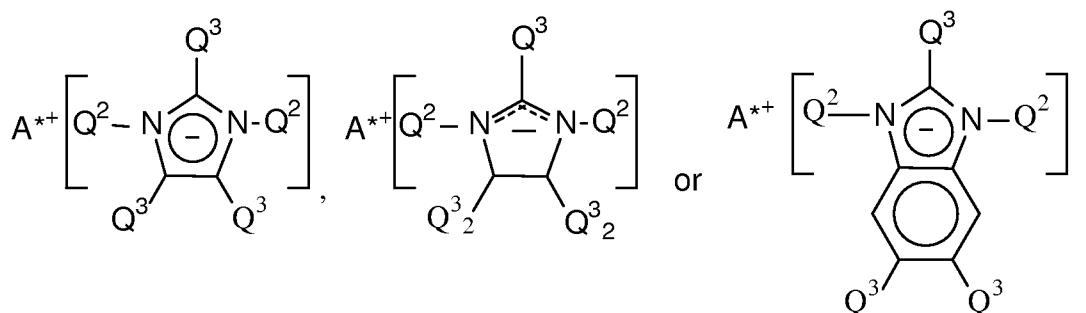
Q<sup>1</sup> is C<sub>1-10</sub> hydrocarbyl, and A<sup>-</sup> is as previously defined.

Preferred silylium salt activating cocatalysts are trimethylsilylium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate and ether substituted adducts thereof. Silylium salts have been previously generically disclosed in J. Chem Soc. Chem. Comm., 1993, 383-384, as well as Lambert, J. B., et al., Organometallics, 1994, 13, 2430-2443. The use of the above silylium salts as activating cocatalysts for addition polymerization catalysts is disclosed in US-A-5,625,087.

Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present invention. Such cocatalysts are disclosed in US-A-5,296,433.

Suitable activating cocatalysts for use herein also include polymeric or oligomeric alumoxanes, especially methylalumoxane (MAO), triisobutyl aluminum modified methylalumoxane (MMAO), or isobutylalumoxane; Lewis acid modified alumoxanes, especially perhalogenated tri(hydrocarbyl)aluminum- or perhalogenated tri(hydrocarbyl)boron modified alumoxanes, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, and most especially tris(pentafluorophenyl)borane modified alumoxanes. Such cocatalysts are previously disclosed in US Patents 6,214,760, 6,160,146, 6,140,521, and 6,696,379.

A class of cocatalysts comprising non-coordinating anions generically referred to as expanded anions, further disclosed in US Patent 6,395,671, may be suitably employed to activate the metal complexes of the present invention for olefin polymerization. Generally, these cocatalysts (illustrated by those having imidazolide, substituted imidazolide, imidazolinide, substituted imidazolinide, benzimidazolide, or substituted benzimidazolide anions) may be depicted as follows:



wherein:

$A^{++}$  is a cation, especially a proton containing cation, and preferably is a trihydrocarbyl ammonium cation containing one or two  $C_{10-40}$  alkyl groups, especially a methyl

5 (C<sub>14-20</sub> alkyl)ammonium cation,

$Q^3$ , independently each occurrence, is hydrogen or a halo, hydrocarbyl, halocarbyl, halohydrocarbyl, silylhydrocarbyl, or silyl, (including mono-, di- and tri(hydrocarbyl)silyl) group of up to 30 atoms not counting hydrogen, preferably  $C_{1-20}$  alkyl, and

$Q^2$  is tris(pentafluorophenyl)borane or tris(pentafluorophenyl)alumane).

10 Examples of these catalyst activators include trihydrocarbylammonium- salts, especially, methyl(C<sub>14-20</sub> alkyl)ammonium- salts of:

bis(tris(pentafluorophenyl)borane)imidazolide,

bis(tris(pentafluorophenyl)borane)-2-undecylimidazolide,

bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolide,

15 bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolide,

bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolide,

bis(tris(pentafluorophenyl)borane)imidazolinide,

bis(tris(pentafluorophenyl)borane)-2-undecylimidazolinide,

bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolinide,

20 bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolinide,

bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolinide,

bis(tris(pentafluorophenyl)borane)-5,6-dimethylbenzimidazolide,

bis(tris(pentafluorophenyl)borane)-5,6-bis(undecyl)benzimidazolide,

bis(tris(pentafluorophenyl)alumane)imidazolide,

25 bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolide,

bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolide,

bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolide,

bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolide,

bis(tris(pentafluorophenyl)alumane)imidazolinide,

bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide,  
bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide,  
bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide,  
bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide,  
5 bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolidine, and  
bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolidine.

Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2''-nonafluorobiphenyl)fluoroaluminate. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example,  
10 EP-A-0 573120, PCT publications WO 94/07928 and WO 95/14044 and US Patents 5,153,157 and 5,453,410. WO 98/09996 describes activating catalyst compounds with perchlorates, periodates and iodates, including their hydrates. WO 99/18135 describes the use of organoboroaluminum activators. WO 03/10171 discloses catalyst activators that are adducts of Bronsted acids with Lewis acids. Other activators or methods for activating a catalyst compound are described in for  
15 example, US Patents 5,849,852, 5,859, 653, 5,869,723, EP-A-615981, and PCT publication WO 98/32775. All of the foregoing catalyst activators as well as any other known activator for transition metal complex catalysts may be employed alone or in combination according to the present invention.

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 100:1,  
20 more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used by itself as an activating cocatalyst, is typically employed in large quantity, generally at least 100 times the quantity of metal complex on a molar basis. Tris(pentafluorophenyl)borane, when used as an activating cocatalyst is employed in a molar ratio to the metal complex of from 0.5:1 to 10:1, more preferably from 1:1 to 6:1 most preferably from 1:1 to 5:1. The remaining activating  
25 cocatalysts are generally employed in approximately equimolar quantity with the metal complex.

During the polymerization, the monomer or monomers are contacted with the activated catalyst composition according to any suitable polymerization conditions. The process is characterized by use of elevated temperatures and pressures. Hydrogen may be employed as a chain transfer agent for molecular weight control according to known techniques if desired. As in other  
30 similar polymerizations, it is highly desirable that the monomer(s) and solvents employed be of sufficiently high purity that significant catalyst deactivation does not occur. Any suitable technique for monomer purification such as devolatilization at reduced pressure, contacting with molecular sieves or high surface area alumina, or a combination of the foregoing processes may be employed. The skilled artisan will appreciate that the ratio of chain shuttling agent to one or more catalysts and

or monomers in the process of the present invention may be varied in order to produce polymers differing in one or more chemical or physical properties.

The polymerization is desirably carried out as a continuous polymerization, preferably a continuous, solution polymerization, in which catalyst components, shuttling agent(s), monomer(s), and optionally solvent, adjuvants, scavengers, and polymerization aids are continuously supplied to the reaction zone and polymer product continuously removed there from. Within the scope of the terms "continuous" and "continuously" as used in this context are those processes in which there are intermittent additions of reactants and removal of products at small regular or irregular intervals, so that, over time, the overall process is substantially continuous.

For a solution polymerization process it is desirable to employ homogeneous dispersions of the catalyst components in a liquid diluent in which the polymer is soluble under the polymerization conditions employed. One such process utilizing an extremely fine silica or similar dispersing agent to produce such a homogeneous catalyst dispersion where either the metal complex or the cocatalyst is only poorly soluble is disclosed in US-A-5,783,512. A solution process to prepare the novel polymers of the present invention, especially a continuous solution process is preferably carried out at a temperature between 80 °C and 250 °C, more preferably between 100 °C and 210 °C, and most preferably between 110 °C and 210 °C. A high pressure process is usually carried out at temperatures from 100 °C to 400 °C and at pressures above 500 bar (50 MPa). A slurry process typically uses an inert hydrocarbon diluent and temperatures of from 0 °C up to a temperature just below the temperature at which the resulting polymer becomes substantially soluble in the inert polymerization medium. Preferred temperatures in a slurry polymerization are from 30 °C, preferably from 60 °C up to 115 °C, preferably up to 100 °C. Pressures typically range from atmospheric (100 kPa) to 500 psi (3.4 MPa).

In all of the foregoing processes, continuous or substantially continuous polymerization conditions are preferably employed. The use of such polymerization conditions, especially continuous, solution polymerization processes employing two or more active polymerization catalyst species, allows the use of elevated reactor temperatures which results in the economical production of multi-block copolymers in high yields and efficiencies. Both well-mixed and plug-flow type reaction conditions may be employed. The latter conditions are preferred where tapering of the block composition is desired.

The catalyst compositions may be prepared as homogeneous compositions by addition of the metal complexes to a solvent in which the polymerization will be conducted or in a diluent compatible with the ultimate reaction mixture. The desired cocatalyst and the shuttling agent may



be combined with the catalyst composition either prior to, simultaneously with, or after combination with the monomers to be polymerized and any additional reaction diluent.

At all times, the individual ingredients as well as any active catalyst composition must be protected from oxygen and moisture. Therefore, the catalyst components, shuttling agent and  
5 activated catalysts must be prepared and stored in an oxygen and moisture free atmosphere, preferably a dry, inert gas such as nitrogen.

Without limiting in any way the scope of the invention, one means for carrying out such a polymerization process is as follows. In a stirred-tank reactor, the monomers to be polymerized are introduced continuously together with any solvent or diluent. The reactor contains a liquid phase  
10 composed substantially of monomers together with any solvent or diluent and dissolved polymer. Preferred solvents include C<sub>4-10</sub> hydrocarbons or mixtures thereof, especially alkanes such as hexane or mixtures of alkanes, as well as one or more of the monomers employed in the polymerization.

The mixture of two or more catalysts along with cocatalyst and chain shuttling agent are continuously or intermittently introduced in the reactor liquid phase or any recycled portion thereof.  
15 The reactor temperature and pressure may be controlled by adjusting the solvent/monomer ratio, the catalyst addition rate, as well as by cooling or heating coils, jackets or both. The polymerization rate is controlled by the rate of catalyst addition. The comonomer content (if any) of the polymer product is determined by the ratio of major monomer to comonomer in the reactor, which is controlled by manipulating the respective feed rates of these components to the reactor. The  
20 polymer product molecular weight is controlled, optionally, by controlling other polymerization variables such as the temperature, monomer concentration, or by the previously mentioned chain transfer agent, as is well known in the art. Upon exiting the reactor, the effluent is contacted with a catalyst kill agent such as water, steam or an alcohol. The polymer solution is optionally heated, and the polymer product is recovered by flashing off gaseous monomers as well as residual solvent  
25 or diluent at reduced pressure, and, if necessary, conducting further devolatilization in equipment such as a devolatilizing extruder. In a continuous process the mean residence time of the catalyst and polymer in the reactor generally is from 5 minutes to 8 hours, and preferably from 10 minutes to 6 hours.

Alternatively, the foregoing polymerization may be carried out in a continuous loop reactor  
30 with or without a monomer, catalyst or shuttling agent gradient established between differing regions thereof, optionally accompanied by separated addition of catalysts and/or chain transfer agent, and operating under adiabatic or non-adiabatic solution polymerization conditions or combinations of the foregoing reactor conditions. Examples of suitable loop reactors and a variety

of suitable operating conditions for use therewith are found in U.S. Patents 5,977,251, 6,319,989 and 6,683,149.

Although not as desired, the catalyst composition may also be prepared and employed as a heterogeneous catalyst by adsorbing the requisite components on an inert inorganic or organic  
5 particulated solid, as previously disclosed. In an preferred embodiment, a heterogeneous catalyst is prepared by co-precipitating the metal complex and the reaction product of an inert inorganic compound and an active hydrogen containing activator, especially the reaction product of a tri (C<sub>1-4</sub> alkyl) aluminum compound and an ammonium salt of a hydroxyaryltris(pentafluorophenyl)borate, such as an ammonium salt of (4-hydroxy-3,5-ditertiarybutylphenyl)tris(pentafluorophenyl)borate.  
10 When prepared in heterogeneous or supported form, the catalyst composition may be employed in a slurry or a gas phase polymerization. As a practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization comprises one or more hydrocarbons or halogenated hydrocarbons with from 3 to 10 carbon atoms. As with a solution polymerization, the monomer or a mixture of different  
15 monomers may be used in whole or part as the diluent. Most preferably at least a major part of the diluent comprises the monomers to be polymerized.

As previously mentioned, functionalized derivatives of multi-block copolymers are also included within the present invention. Examples include metallated polymers wherein the metal is the remnant of the catalyst or chain shuttling agent employed, as well as further derivatives thereof,  
20 for example, the reaction product of a metallated polymer with an oxygen source and then with water to form a hydroxyl terminated polymer. In another embodiment, sufficient air or other quench agent is added to cleave some or all of the shuttling agent-polymer bonds thereby converting at least a portion of the polymer to a hydroxyl terminated polymer. Additional examples include olefin terminated polymers formed by  $\beta$ -hydride elimination and ethylenic unsaturation in the  
25 resulting polymer.

In one embodiment of the invention the multi-block copolymer may be functionalized by maleation (reaction with maleic anhydride or its equivalent), metallation (such as with an alkyl lithium reagent, optionally in the presence of a Lewis base, especially an amine, such as tetramethylethylenediamine), or by incorporation of a diene or masked olefin in a copolymerization  
30 process. After polymerization involving a masked olefin, the masking group, for example a trihydrocarbylsilane, may be removed thereby exposing a more readily functionalized remnant. Techniques for functionalization of polymers are well known, and disclosed for example in USP 5,543,458, and elsewhere.

Because a substantial fraction of the polymeric product exiting the reactor can be terminated with the chain shuttling agent, further functionalization is relatively easy. The metallated polymer species can be utilized in well known chemical reactions such as those suitable for other alkyl-aluminum, alkyl-gallium, alkyl-zinc, or alkyl-Group 1 compounds to form amine-, hydroxy-, epoxy-, ketone-, ester-, nitrile- and other functionalized terminated polymer products. Examples of suitable reaction techniques that are adaptable for use here in are described in Negishi, "Organometallics in Organic Synthesis", Vol. 1 and 2, (1980), and other standard texts in organometallic and organic synthesis.

Utilizing the present process, multi-block copolymers are readily prepared having a variety of desirable physical properties. Tacticity, if any, in the resulting interpolymers may be measured using any suitable technique, with techniques based on nuclear magnetic resonance (NMR) spectroscopy preferred. It is highly desirable that some of the polymer blocks comprise an isotactic polymer, preferably a highly isotactic polypropylene or poly-4-methyl-1-pentene, and any remaining polymer blocks predominantly comprise polymer containing regio-irregular 3,1-monomer insertions, essentially generating amorphous copolymer segments therein. Preferably the tactic segments or blocks are highly isotactic polypropylene or poly-4-methyl-1-pentene, especially homopolymers containing at least 99 mole percent propylene, 1-butene or 4-methyl-1-pentene therein. Further preferably, the amorphous polymer segments have Tg less than 25°C, preferably less than 0°C, more preferably less than -10°C, most preferably less than -25°C, and most highly preferably less than -30 °C.

Additionally, the interpolymers of the invention preferably comprise from 5 to 95 percent tactic, crystalline or other relatively hard segments, and 95 to 5 percent amorphous or relatively soft polymer segments, more preferably from 10 to 90 percent crystalline or relatively hard segments and 90 to 10 percent amorphous or relatively amorphous segments (soft segments).

Regio-irregular branching in the polymers of the invention may also arise as a result of chain walking or other branch forming process as previously disclosed. In the instance where chain walking in the polymerization of a C<sub>4-20</sub>  $\alpha$ -olefin occurs, the catalyst chain may "walk" to the terminal methyl unit of the monomer before inserting another monomer. Such insertions may include 1, $\omega$ - or 2, $\omega$ - insertions, and lead to either chain straightening or to differences in chain branching and/or lowered Tg in the segments containing the same. Specifically, 1, $\omega$ - insertions generally lead to a reduction in branching compared to a normal polymer. In addition, 2, $\omega$  insertions result in the formation of methyl branches. These insertions are included within the term "regio-irregular monomer insertion" or "regio-irregular branching" as used herein.

The polymers of the invention can have a melt index,  $I_2$ , from 0.01 to 2000 g/10 minutes, preferably from 0.01 to 1000 g/10 minutes, more preferably from 0.01 to 500 g/10 minutes, and especially from 0.01 to 100 g/10 minutes. Desirably, the invented polymers can have molecular weights,  $M_w$ , from 1,000 g/mole to 5,000,000 g/mole, preferably from 1000 g/mole to 1,000,000, more preferably from 10,000 g/mole to 500,000 g/mole, and especially from 10,000 g/mole to 300,000 g/mole. The density of the polymers desirably is from 0.80 to 0.99 g/cm<sup>3</sup> and preferably from 0.85 g/cm<sup>3</sup> to 0.97 g/cm<sup>3</sup>.

Additives and adjuvants may be included in any formulation comprising polymers of the present invention. Suitable additives include fillers, such as organic or inorganic particles, including clays, talc, titanium dioxide, zeolites, powdered metals, organic or inorganic fibers, including carbon fibers, silicon nitride fibers, steel wire or mesh, and nylon or polyester cording, nano-sized particles, clays, and so forth; tackifiers, oil extenders, including paraffinic or naphthenic oils; stabilizers, anti-oxidants, colorants, extrusion aids, slip additives, release additives, and other natural and synthetic polymers, including other polymers according to the invention.

15

### **Analytical Techniques**

#### DSC Standard Method

Differential Scanning Calorimetry results are determined using a model Q1000 DSC, available from TAI, Owings Mills, MD, equipped with an RCS cooling accessory and an autosampler, or equivalent instrument. A nitrogen purge gas flow of 50 ml/min. is used. 3-10 mg Of material is accurately weighed, placed in a light aluminum pan weighing approximately 50 mg, and then crimped shut. The thermal behavior of the sample is investigated with the following temperature profile. The sample is rapidly heated to 180 °C and held isothermally for 3 minutes in order to remove any previous thermal history. The sample is then cooled to -40 °C at a cooling rate of 10 °C/min. and held at -40 °C for 3 minutes. The sample is then heated to 150 °C at a heating rate of 10 °C/min. The cooling and second heating curves are recorded.

The DSC melting peak is measured as the maximum in heat flow rate (W/g) with respect to the linear baseline drawn between -30 °C and the end of melting. The heat of fusion is measured as the area under the melting curve between -30 °C and the end of melting using a linear baseline. If the melting point of the sample is > 150 °C, then the temperature of the isothermal first heat and second heat is increased accordingly.

#### GPC Method for Determining Polymer Mn, Mw

Gel permeation chromatograms are made using a Model PL-210 or Model PL-220 gel permeation instrument, available from Polymer Laboratories, or equivalent equipment. The column

35

and carousel compartments are operated at 140 °C. Three Polymer Laboratories 10-micron Mixed-B columns are used. The solvent is 1,2,4-trichlorobenzene. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent containing 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for 2 hours at 160 °C. The injection volume used is 100 microliters and the flow rate is 1.0 ml/minute.

Calibration of the GPC column set is performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, arranged in 6 "cocktail" mixtures with at least a decade of separation between individual molecular weights. The standards are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards are dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, *J. Polym. Sci., Polym. Let.*, 6, 621 (1968)):  $M_{\text{polyethylene}} = 0.431(M_{\text{polystyrene}})$ .

Polyethylene equivalent molecular weight calculations are performed using Viscotek TriSEC™ software Version 3.0, available from Viscotek Corporation, Houston, Texas.

## 20 Specific Embodiments

The following specific embodiments of the invention and combinations thereof are especially desirable and hereby delineated in order to provide detailed disclosure for the appended claims.

1. A process for forming a high molecular weight, multi-block copolymer comprising two or more chemically distinguishable segments or blocks, the process comprising polymerizing one or more olefin monomers in the presence of a chain shuttling agent and a catalyst composition comprising:

two or more olefin polymerization catalysts capable of preparing polymers having differing chemical or physical properties under equivalent polymerization conditions,

30 or

a catalyst composition comprising at least one olefin polymerization catalyst containing multiple active catalyst sites capable of preparing polymers having differing chemical or physical properties;

characterized in that the polymerization is conducted in the presence of a solvent comprising a polar, aprotic, organic liquid compound, having a dielectric constant greater than 2.4, preferably greater than or equal to 2.8, most preferably greater than or equal to 3.0.

2. A process according to embodiment 1 wherein the polar, aprotic compound is selected from the group consisting of: o-xylene, ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, isopropylbenzene, 1-methyl-2-ethylbenzene, 1,2-diethylbenzene, chlorobenzene, o-dichlorobenzene, chlorotoluene, 1-chloroethane, dichloromethane, 1,2-dichloroethane, 1-chloroethene, 1-chloropropane, 1,1-dichloroethane, 1-chlorobutane, 1-chloropentane, 1-chlorohexane, 1,1,1-trifluoroethane, difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoropropane, 1,1,1-trifluorobutane, 1,1,1-trifluoropentane, 1,1,1-trifluorohexane, 1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane, fluorocyclobutane, difluorocyclobutane, trifluorocyclobutane, pentafluorocyclobutane, fluorocyclohexane, 1,2-difluorocyclohexane, 1,3-difluorocyclohexane, fluorobenzene, o-difluorobenzene, m-difluorobenzene, p-difluorobenzene, fluorotoluene, difluorotoluene, 1-chloro-1-fluoroethane, 1,2-dichlorofluoroethane, dichlorofluoromethane, difluorochloromethane, 2-trifluoromethylpropane, tetrahydrofuran, methyl t-butyl ether, 2-butanone, diethylether, 1,2-dimethoxyethane, ethylene glycol dibutyl ether; diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, 1,4-dioxane, chloroform, sulfolane, dimethylformamide, and dimethylether

3. A process according to embodiment 2 wherein the solvent comprises a mixture of one or more polar, aprotic compounds with one or more aprotic compounds having a dielectric constant less than 2.4.

4. A process according to embodiment 2 wherein the polar, aprotic compound is o-xylene, chlorobenzene, dichlorobenzene, fluorobenzene, difluorobenzene, o-chlorotoluene or o-fluorotoluene.

5. A process according to embodiment 1 which is a continuous, solution polymerization.

6. A process according to embodiment 5 conducted at a temperature from 70 to 200 °C.

7. A process according to embodiment 1 wherein the shuttling agent is an organoaluminum- compound containing from 1 to 12 carbons in each organo group.

8. A process according to embodiment 7 wherein the shuttling agent is trimethyl aluminum.

9. A process according to any one of embodiments 1-6 wherein the shuttling agent is diethylzinc.

10. The process of claim 1 wherein the polar, aprotic organic liquid is noncoordinating.

11. A process for forming a high molecular weight, multi-block copolymer comprising two or more chemically distinguishable segments or blocks, the process comprising polymerizing one or more olefin monomers in the presence of a chain shuttling agent and a catalyst composition  
5 comprising:

two or more olefin polymerization catalysts capable of preparing polymers having differing chemical or physical properties under equivalent polymerization conditions,

or

a catalyst composition comprising at least one olefin polymerization catalyst containing  
10 multiple active catalyst sites capable of preparing polymers having differing chemical or physical properties;

characterized in that the polymerization is conducted in the presence of a solvent selected from the group consisting of: o-xylene, ethylbenzene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, isopropylbenzene, 1-methyl-2-ethylbenzene, 1,2-diethylbenzene, 1,2,4-trimethylbenzene, chlorobenzene, o-dichlorobenzene, chlorotoluene, 1-chloroethane, 1,2-dichloroethane, 1-chloropropane, 1,1-dichloroethane, 1-chlorobutane, 1-chloropentane, 1-chlorohexane, 1,1,1-trifluoroethane, difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoropropane, 1,1,1-trifluorobutane, 1,1,1-trifluoropentane, 1,1,1-trifluorohexane, 1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane,  
15 fluorocyclobutane, difluorocyclobutane, trifluorocyclobutane, pentafluorocyclobutane, fluorocyclohexane, 1,2-difluorocyclohexane, 1,3-difluorocyclohexane, fluorobenzene, o-difluorobenzene, m-difluorobenzene, p-difluorobenzene, fluorotoluene, difluorotoluene, 1-chloro-1-fluoroethane, 1,2-dichlorofluoroethane, dichlorofluoromethane, difluorochloromethane, 2-trifluoromethylpropane, tetrahydrofuran, methyl t-butyl ether, 2-butanone, diethylether, 1,2-dimethoxyethane, ethylene glycol dibutyl ether; diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, dichloromethane, chloroform, sulfolane, dimethylformamide, and dimethylether.  
20

The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component, step or ingredient which has not been specifically disclosed.

#### Examples

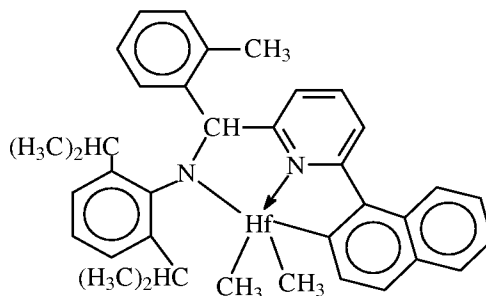
30 The following examples are provided as further illustration of the invention and are not to be construed as limiting. The term "overnight", if used, refers to a time of approximately 16-18 hours, the term "room temperature", refers to a temperature of 20-25 °C, and the term "mixed alkanes" refers to a commercially obtained mixture of C<sub>6-9</sub> aliphatic hydrocarbons available under the trade designation Isopar E<sup>®</sup>, from Exxon Mobil Chemicals Inc. In the event the name of a

compound herein does not conform to the structural representation thereof, the structural representation shall control. The synthesis of all metal complexes and the preparation of all screening experiments were carried out in a dry nitrogen atmosphere using dry box techniques. All solvents used were HPLC grade and were dried before their use.

5 Racemic Hafnium, [N-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -(2-methylphenyl)]-6-(1-naphthanlenyl- $\kappa$ -C<sup>2</sup>)-2-pyridine-methaneaminato(2-)- $\kappa$ N<sup>1</sup>,  $\kappa$ N<sup>2</sup>]dimethyl (*Rac-I*)

This complex is prepared according to the teachings of WO 2003/040195, WO/2004/024740, WO 2004/099268, and US-A-6,953,764.

10 (R)- Hafnium, [N-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -[2-(1-methyl)phenyl]]-6-(1-naphthanlenyl- $\kappa$ -C<sup>2</sup>)-2-pyridinemethanaminato(2-)- $\kappa$ N<sup>1</sup>,  $\kappa$ N<sup>2</sup>]dimethyl- (*R/I*)



In a 1000 mL round-bottomed flask equipped with a small magnetic stir-bar is placed 21.3 g (43.7 millimoles) of *rac*-2-pyridinemethanamine, *N*-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -[2-(1-methyl)phenyl]-6-(1-naphthanlenyl). 10.2 g (43.7 Millimoles) of (+)-(1*S*)-camphor-10-sulphonic acid are added along with 500 mL of THF. The mixture is stirred until all of the solids are dissolved, giving an amber-colored solution. This solution is reduced in volume by rotary evaporation. The resulting dry foam is dissolved in approximately 500 mL of boiling toluene and placed in a large, insulated, dewar flask to slowly cool. The resulting crystals are recovered by filtration after cooling overnight, and recrystallized twice using the same procedure. Following the final recrystallization, the crystals are dried under reduced pressure to yield 9.789 g (47 percent of theoretical) of (R)- pyridinemethanamine, *N*-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -[2-(1-methyl)phenyl]-6-(1-naphthanlenyl) [(*S*)-camphorsulfonate] salt as colorless crystals. Identity is confirmed by single crystal X-ray analysis.

25 To a glass jar equipped with a small magnetic stir-bar are added 7.17 g (7.56 millimoles) of the (R)- 2-pyridinemethanamine, *N*-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -[2-(1-methyl)phenyl]-6-(1-naphthanlenyl) [(*S*)-camphorsulfonate] salt and 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. A solution of 1.5 g (10 millimoles) of KOH in 25 mL of H<sub>2</sub>O is added. The mixture is stirred for 10 minutes, and then the layers are allowed to separate. The organic layer is washed with water 3 times, dried with



anhydrous MgSO<sub>4</sub>, and the solvent evaporated to give the desired product, (R)- 2-pyridinemethanamine, *N*-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -[2-(1-methyl)phenyl]-6-(1-naphthanlenyl). Yield, 3.403 g (93 percent of theoretical). The product is determined to be 98.4 percent e.e. by chiral HPLC chromatography.

5 In a dry box, to a jar containing a polytetrafluoroethylene coated magnetic stir-bar is added 3.0 g (6.2 mmoles) of (R)- 2-pyridinemethanamine, *N*-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -[2-(1-methyl)phenyl]-6-(1-naphthanlenyl) and 10 mL of dry hexanes. To this solution is added drop wise via syringe 4.0 mL of 1.6 M *n*-butyl lithium in hexanes (6.2 mmoles). The mixture is stirred for 1 hour, followed by removal of the solvent under reduced pressure. The product is collected on a frit  
10 and dried under reduced pressure. The product, (R)- 2-pyridinemethanamide, *N*-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -[2-(1-methyl)phenyl]-6-(1-naphthanlenyl) lithium, is recovered as a light yellow solid, washed with pentane, and dried under reduced pressure. Yield: 2.69 g (89 percent of theoretical)

To a 100 mL round-bottomed flask containing a magnetic stir bar 2.69 g (5.48 mmoles) of  
15 (R)- 2-pyridinemethanamide, *N*-[2,6-bis(1-methylethyl)phenyl]- $\alpha$ -[2-(1-methyl)phenyl]-6-(1-naphthanlenyl) lithium and 50 mL of toluene are combined and stirred until dissolved. To this solution is added 2.069 g (5.48 mmoles) of HfCl<sub>4</sub>(DME) and the mixture is heated to reflux. After 3 hours of reflux, the solution is cooled, 5.9 mL of 3.0 M MeMgBr in Et<sub>2</sub>O (19.19 mmoles) are added, and the mixture allowed to stir for 3 hours. The solvent is removed, and the solid extracted  
20 with toluene, filtered through diatomaceous earth filter aid, and the toluene removed under reduced pressure to give the desired product as a light yellow solid. Yield: 2.70 g (71 percent of theoretical)

**Cocatalyst** - methylalumoxane (MAO) (EURECEN™ AL 5100-10T, available commercially from Crompton Corporation).

**Shuttling agent** – trimethylaluminum (TMA) present in MAO in an amount of  
25 approximately 33 percent based on aluminum as determined by <sup>1</sup>H NMR.

#### Propylene Polymerization Conditions

Propylene is polymerized in a batch reactor at 70 °C in either toluene ( $\epsilon$ =2.4) or  
difluorobenzene ( $\epsilon$ =14.3) solvents. Propylene is supplied on demand to maintain the indicated concentration in the reactor. The reaction is terminated by addition of methanol at low yield to  
30 avoid mass transfer effects in viscous solutions and maintain concentration of shuttling agent nearly constant.

Runs 1-7 employ a racemic mixture (Rac-1) of the foregoing metal complex. Run 8 employs the substantially pure R-enantiomer, R1. Results are contained in Table 1.

Table 1

Ex.	Solvent	Hf ( $\mu\text{mol}$ )	[C <sub>3</sub> H <sub>6</sub> ] M	MAO (mmol)	Al(CH <sub>3</sub> ) <sub>3</sub> (mmol)	Time, (min.)	Yield (g)	Mw/ Mn	Mn ( $\times 10^3$ )
A*	toluene	5.0	0.24	0.60	0.30	130	0.4	3.8**	2.8
1	C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	5.0	“	“	“	3.5	0.7	1.2	2.0
B*	toluene	5.0	“	1.20	0.60	38	1.0	3.8**	2.2
2	C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	5.0	“	“	“	11	1.0	1.1	1.5
C*	toluene	5.0	“	2.40	1.20	56	1.0	1.4	1.8
3	C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	5.0	“	2.40	“	20	1.5	1.1	1.0
4	C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	2.5	“	1.20	0.60	17	1.2	1.5	2.3
5	C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	10.0	“	“	“	6.5	0.8	1.1	1.2
6	C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	5.0	0.42	“	“	3.1	0.9	1.2	1.5
7	C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	5.0	0.62	“	“	2.0	1.5	1.4	2.1
8	C <sub>6</sub> F <sub>2</sub> H <sub>4</sub>	5.0	0.24	“	“	9.0	1.1	1.2	1.7

\* comparative, not an example of the invention

\*\* bimodal molecular weight distribution

The experiment is designed to determine whether chain transfer to the aluminum (catalyzed  
 5 chain growth, as explained in *J. Am. Chem. Soc.* 2005, 127, 9913-9923) occurs under the conditions  
 tested. Such chain growth is necessary for obtaining chain shuttling in the presence of two catalysts  
 (the two enantiomeric forms of the metal complex). In experiment 8, the use of the polar solvent  
 results in extremely narrow molecular weight distribution polymer having few inversions or regio-  
 errors. Enhanced levels of catalyzed chain growth on aluminum is evidenced by narrowing  
 10 polydispersity and reduction in average polymer molecular weight of the resulting polymer species  
 for the examples of the invention. Direct evidence of the occurrence of multiblock polymer  
 formation (shuttling) is shown by <sup>13</sup>C NMR spectroscopic analysis of the resulting polymer. The  
 occurrence of inversions in the polymer produced in Example 4 (Figure 1) is apparent based on the  
 presence of several peaks in the <sup>13</sup>C NMR, especially at 20.85 ppm, that are absent in the spectrum  
 15 of the corresponding product made using R-1 catalyst (Figure 2). The results indicate that  
 organoaluminum compounds, specifically tri(C<sub>1-4</sub> alkyl) aluminum compounds, represented by  
 trimethylaluminum, are rendered more effective as chain shuttling agents, at least with respect to  
 the R- and S- enantiomers of the tested metal complex if a more polar solvent such as  
 difluorobenzene, rather than a less polar solvent, such as toluene, is used. Based on this result, it  
 20 may be predicted that shuttling agents are much more effective if used in combination with a  
 solvent comprising a polar aprotic compound having a dielectric constant,  $\epsilon$ , greater than 2.4.

CLAIMS:

1. A process for forming a high molecular weight, multi-block copolymer comprising two or more chemically distinguishable segments or blocks, the process comprising polymerizing one or more olefin monomers in the presence of a chain shuttling agent and a catalyst composition  
5 comprising:

two or more olefin polymerization catalysts capable of preparing polymers having differing chemical or physical properties under equivalent polymerization conditions,

or

a catalyst composition comprising at least one olefin polymerization catalyst containing  
10 multiple active catalyst sites capable of preparing polymers having differing chemical or physical properties;

characterized in that the polymerization is conducted in the presence of a solvent comprising a polar, aprotic, organic liquid compound, having a dielectric constant greater than 2.4.

2. A process according to claim 1 wherein the polar, aprotic compound is selected  
15 from the group consisting of: o-xylene, ethylbenzene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, isopropylbenzene, 1-methyl-2-ethylbenzene, 1,2-diethylbenzene, chlorobenzene, o-dichlorobenzene, chlorotoluene, 1-chloroethane, dichloromethane, 1,2-dichloroethane, 1-chloroethene, 1-chloropropane, 1,1-dichloroethane, 1-chlorobutane, 1-chloropentane, 1-chlorohexane, 1,1,1-trifluoroethane, difluoromethane,  
20 trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoropropane, 1,1,1-trifluorobutane, 1,1,1-trifluoropentane, 1,1,1-trifluorohexane, 1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane, fluorocyclobutane, difluorocyclobutane, trifluorocyclobutane, pentafluorocyclobutane, fluorocyclohexane, 1,2-difluorocyclohexane, 1,3-difluorocyclohexane, fluorobenzene, o-difluorobenzene, m-difluorobenzene, p-difluorobenzene,  
25 fluorotoluene, difluorotoluene, 1-chloro-1-fluoroethane, 1,2-dichlorofluoroethane, dichlorofluoromethane, difluorochloromethane, 2-trifluoromethylpropane, tetrahydrofuran, methyl t-butyl ether, 2-butanone, diethylether, 1,2-dimethoxyethane, ethylene glycol dibutyl ether; diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, 1,4-dioxane, chloroform, sulfolane, dimethylformamide, and dimethylether.

3. A process according to claim 2 wherein the solvent comprises a mixture of one or more polar, aprotic compounds with one or more aprotic compounds having a dielectric constant less than 2.4.

4. A process according to claim 2 wherein the polar, aprotic compound is o-xylene, chlorobenzene, dichlorobenzene, fluorobenzene, difluorobenzene, o-chlorotoluene, methylene  
35 chloride, diethyl ether, dibutyl ether, tetrahydrofuran, 1,4-dioxane, or o-fluorotoluene.

5. A process according to claim 1 which is a continuous, solution polymerization.
6. A process according to claim 5 conducted at a temperature from 70 to 200 °C.
7. A process according to claim 1 wherein the shuttling agent is an organoaluminum-compound containing from 1 to 12 carbons in each organo group.
- 5 8. A process according to any one of claims 1-6 wherein the shuttling agent is trimethyl aluminum.
9. A process according to any one of claims 1-6 wherein the shuttling agent is diethylzinc.
- 10 10. The process of any one of claims 1-7 wherein the polar, aprotic, organic liquid has a dielectric constant from 2.4 to 50.
11. The process of claim 1 wherein the polar, aprotic organic liquid is noncoordinating.
12. A process for forming a high molecular weight, multi-block copolymer comprising two or more chemically distinguishable segments or blocks, the process comprising polymerizing one or more olefin monomers in the presence of a chain shuttling agent and a catalyst composition  
15 comprising:
  - two or more olefin polymerization catalysts capable of preparing polymers having differing chemical or physical properties under equivalent polymerization conditions,
  - or
  - a catalyst composition comprising at least one olefin polymerization catalyst containing  
20 multiple active catalyst sites capable of preparing polymers having differing chemical or physical properties;characterized in that the polymerization is conducted in the presence of a polar aprotic compound selected from the group consisting of: o-xylene, ethylbenzene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, isopropylbenzene, 1-methyl-2-ethylbenzene, 1,2-diethylbenzene, 1,2,4-  
25 trimethylbenzene, chlorobenzene, o-dichlorobenzene, chlorotoluene, 1-chloroethane, 1,2-dichloroethane, 1-chloropropane, 1,1-dichloroethane, 1-chlorobutane, 1-chloropentane, 1-chlorohexane, 1,1,1-trifluoroethane, difluoromethane, trifluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,1-trifluoropropane, 1,1,1-trifluorobutane, 1,1,1-trifluoropentane, 1,1,1-trifluorohexane, 1,1,1,3,3-pentafluoropropane, 1,1,1,3,3-pentafluorobutane,  
30 fluorocyclobutane, difluorocyclobutane, trifluorocyclobutane, pentafluorocyclobutane, fluorocyclohexane, 1,2-difluorocyclohexane, 1,3-difluorocyclohexane, fluorobenzene, o-difluorobenzene, m-difluorobenzene, p-difluorobenzene, fluorotoluene, difluorotoluene, 1-chloro-1-fluoroethane, 1,2-dichlorofluoroethane, dichlorofluoromethane, difluorochloromethane, 2-trifluoromethylpropane, tetrahydrofuran, methyl t-butyl ether, 2-butanone, diethylether, 1,2-

dimethoxyethane, ethylene glycol dibutyl ether; diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, dichloromethane, chloroform, sulfolane, dimethylformamide, and dimethylether.

Fig. 1

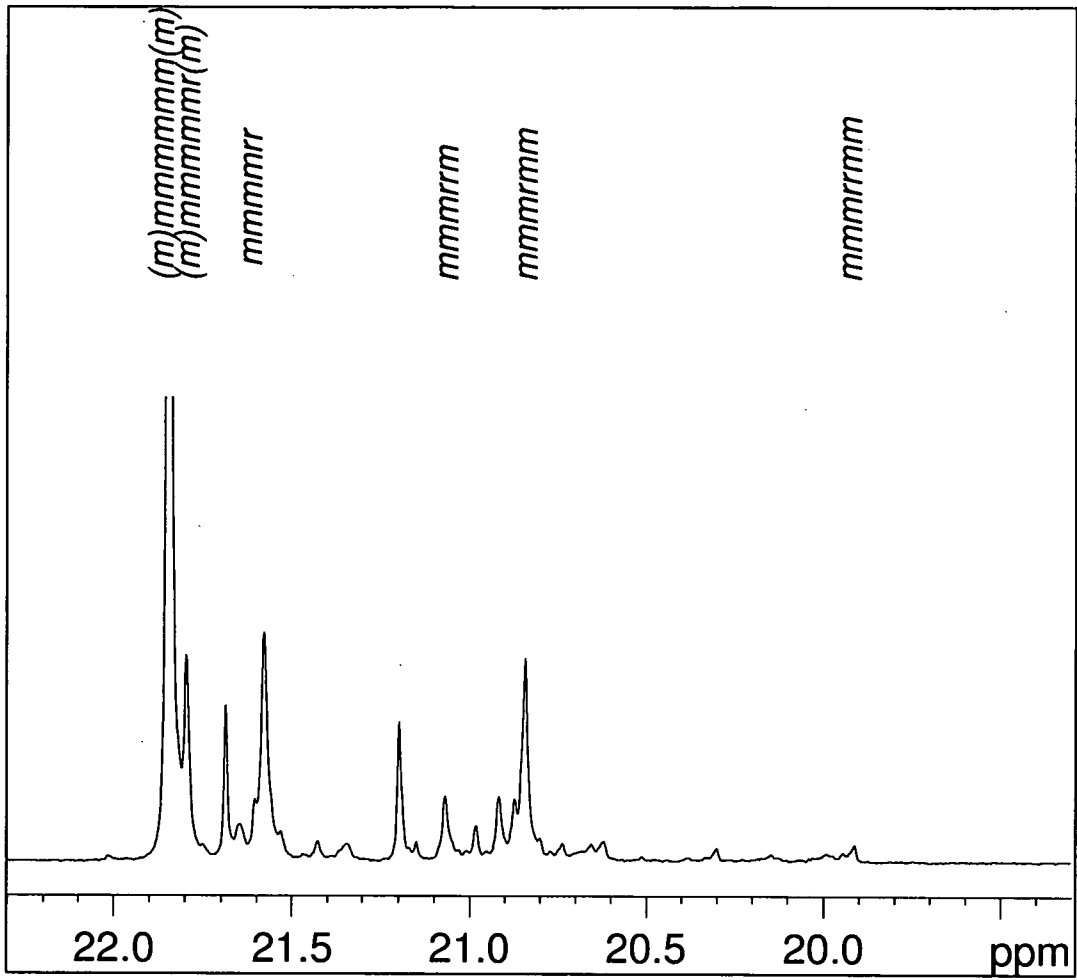
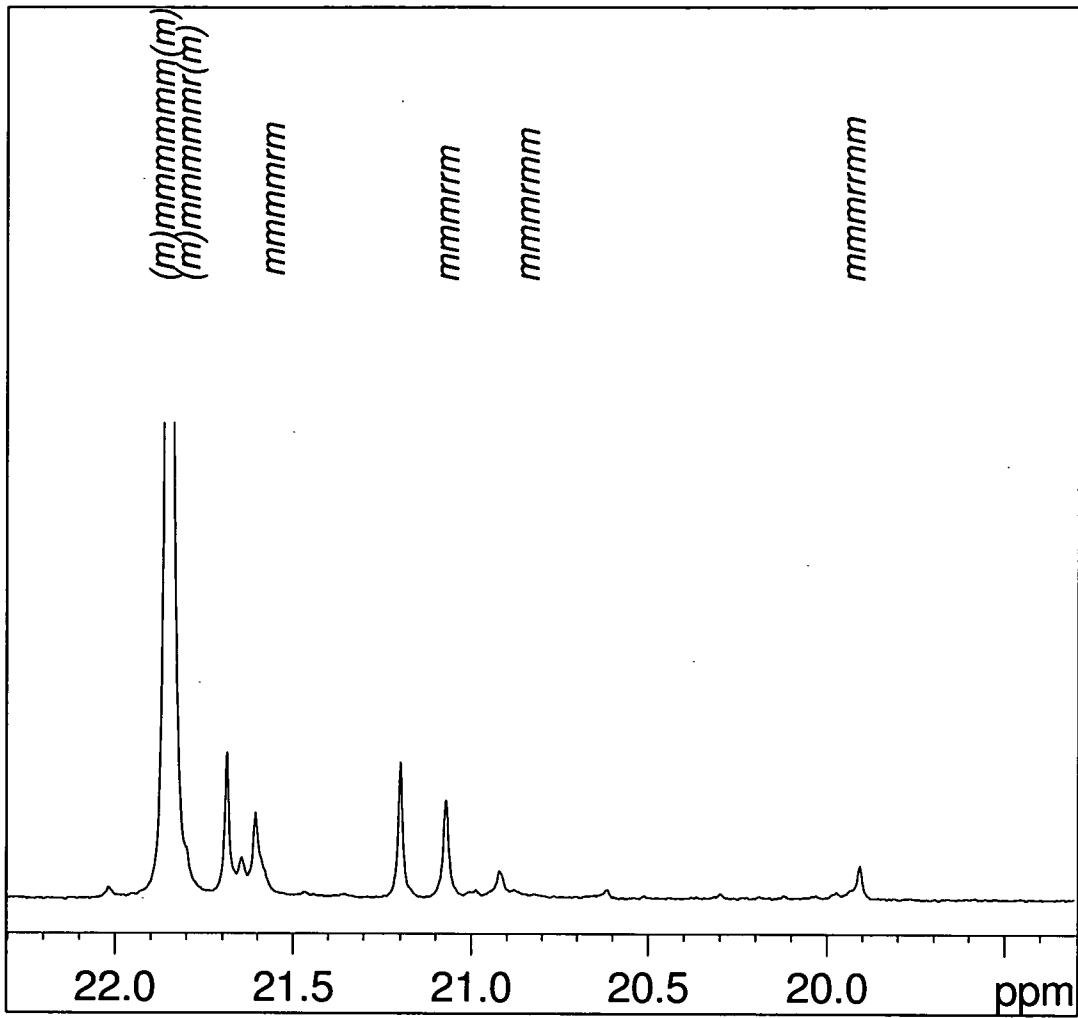


Fig. 2



**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US 08/62183

<p><b>A. CLASSIFICATION OF SUBJECT MATTER</b>                  IPC(8) - A61K 8/73 (2008.04)                  USPC - 524/27                  According to International Patent Classification (IPC) or to both national classification and IPC</p>												
<p><b>B. FIELDS SEARCHED</b></p> <p>Minimum documentation searched (classification system followed by classification symbols)                  USPC: 524/27</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)                  Electronic Databases Searched: USPTO WEST (PGPUB, EPAB, JPAB, USPT), Google patent, Google Scholar. Search Terms Used: aprotic, multiple site, solvent, polymerization or catalyst, copolymer and olefin, copolymers\$, multiple adj active adj site, polar or aprotic</p>												
<p><b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b></p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>2003/0055179 A1 (Ota et al.) 20 March 2003 (20.03.2003) entire document especially abstract: para [0385]; [0420]; [0423]; [0817]-[0818]; [0826]</td> <td>1-12</td> </tr> <tr> <td>A</td> <td>US 2003/0050411 A1 (Gaynor et al.) 13 March 2003 (13.03.2003) entire document</td> <td>1-12</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	2003/0055179 A1 (Ota et al.) 20 March 2003 (20.03.2003) entire document especially abstract: para [0385]; [0420]; [0423]; [0817]-[0818]; [0826]	1-12	A	US 2003/0050411 A1 (Gaynor et al.) 13 March 2003 (13.03.2003) entire document	1-12	
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A	US 2003/0050411 A1 (Gaynor et al.) 13 March 2003 (13.03.2003) entire document	1-12										
<p><input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/></p>												
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"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)</td> <td>"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</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td>"&amp;" document member of the same patent family</td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance	"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	"E" earlier application or patent but published on or after the international filing date	"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	"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)	"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	"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	"P" document published prior to the international filing date but later than the priority date claimed	
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<p>Date of the actual completion of the international search                  30 July 2008 (30.07.2008)</p>		<p>Date of mailing of the international search report  <b>04 AUG 2008</b></p>										
<p>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</p>		<p>Authorized officer:                  Lee W. Young                  PCT Helpdesk: 571-272-4300                  PCT OSP: 571-272-7774</p>										