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Catalyseurs de polymérisation, leur procédé de préparation, les précurseurs et procédé d’utilisation

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EP-A- 0 405 446
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The present invention relates to metal coordination complexes. The invention also relates to certain novel addition polymerization catalysts comprising such metal complexes. Furthermore, the invention relates to methods for the polymerization of addition polymerizable monomers and to the resulting polymers.

Because of the exposure of the active metal site of the metal coordination complexes of the invention, catalysts resulting therefrom have unique properties. Under certain conditions, the catalysts of the invention are capable of preparing novel olefin polymers having previously unknown properties due to their unique facile abilities to polymerize α-olefins, diolefins, hindered vinylidene aliphatic monomers, vinylidene aromatic monomers and mixtures thereof.

Numerous metal coordination complexes are known in the art including such complexes involving monocyclopentadienyl groups and substituted monocyclopentadienyl groups. The present metal coordination complexes differ from those previously known in the art due to the fact that the metal is bound to a cyclopentadienyl or substituted cyclopentadienyl or similar group by both a η⁵-bond and a bridging linkage including other ligands of the metal.

Also previously known in the art are transition metal coordination complexes known as tucked complexes. Such complexes are described in Organometallics 6, 232-241 (1987).

In US Serial No. 8,800, filed January 30, 1987 (published in equivalent form as EP-A-0277004) there are disclosed certain bis(cyclopentadienyl) metal compounds formed by reacting a bis(cyclopentadienyl) metal complex with salts of Bronsted acids containing a noncoordinating compatible anion. The reference discloses the fact that such complexes are usefully employed as catalysts in the polymerization of olefins. The foregoing catalysts are not considered to be particularly effective olefin polymerization catalysts.

Previous attempts to prepare copolymers of vinylidene aromatic monomers and α-olefins, in particular copolymers of styrene and ethylene, have either failed to obtain substantial incorporation of the vinylidene aromatic monomer or else have achieved polymers of low molecular weight. In Polymer Bulletin, 20, 237-241 (1988) there is disclosed a random copolymer of styrene and ethylene containing 1 mole percent styrene incorporated therein. The reported polymer yield was 8.3 x 10⁻⁴ grams of polymer per micromole titanium employed.

Thomas Kükenhöner disclosed, in a thesis entitled "Untersuchungen zur Darstellung Chiraler Organotitan (IV) Verbindung für Enantioselective Synthesen" submitted in August 1983 to Fachbereich Chemie der Philipps-Universität Marburg, 1-oxy-3-cyclopentadienyl-propane-1,3-diyl titanium (IV) complexes in which the propanediyl moiety is optionally substituted with alkyl. The exemplified complexes are 1-oxy-1-tert. butyl-3-dimethyl-3-cyclopentadienyl-propane-1,3-diyl titanium dihalides, dimethyl and halide methyl. No use is specified for the complexes.


\[
\begin{align*}
(C_5H_5-y-x R_x) & \quad (J R'_{z-1-y}) \\
B_y & \quad L_w \\
(M) & \quad Q \\
& \quad (Q)
\end{align*}
\]

wherein

M is titanium, zirconium or hafnium and is in its highest formal oxidation state (+4, d⁰ complex);

\((C_5H_5-y-x R_x)\) is (i) a cyclopentadienyl ring which is substituted from zero to five substituent groups R, x is 0, 1, 2, 3, 4 or 5 denoting the degree of substitution, and each substituent group R is, independently, a C₁-C₂₀ hydrocarbyl radical, a substituted C₁-C₂₀ hydrocarbyl radical wherein one or more hydrogen atoms is replaced by a halogen atom, C₁-C₂₀ hydrocarbyl-substituted metalloid radical wherein the metalloid is of Group 14 of the periodic Table of the Elements, or a halogen atom or (ii) a cyclopentadienyl ring in which two adjacent R-groups are joined forming a C₄-C₂₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

\((J R'_{z-1-y})\) is a heteroatom ligand in which J is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of the Elements, and each R' is,
independently a C₁-C₂₀ hydrocarbyl radical or a substituted C₁-C₂₀ hydrocarbyl radical wherein one or more hydrogen atoms is replaced by a halogen atom, and z is the coordination number of the element J;

each Q is independently a univalent anionic ligand, provided that where any Q is a hydrocarbyl such Q is different from \((\text{C}_5\text{H}_{5-y-x}\text{R}_x)\), or both Q together are a divalent anionic chelating agent;

B is a covalent bridging group containing an element of Group 14 or 15 of the Periodic Table of the Elements;

L is (i) a Lewis base or (ii) a second transition metal compound of the same type such that the two metal centers M and M' are bridged by Q and Q', wherein M' has the same meaning as M and Q' has the same meaning as Q;

w is a number from 0 to 1; and

y is 0 or 1 when w is greater than 0 and y is 1 when w is 0.


\[
\text{CpMX}_n^+\text{A}^- 
\]

wherein:

Cp is a single \(\eta^5\)-cyclopentadienyl or \(\eta^5\)-substituted cyclopentadienyl group optionally covalently bound to M through a substituent;

M is hafnium, titanium or zirconium bound in a \(\eta^5\) bonded mode to the cyclopentadienyl or substituted cyclopentadienyl group;

X is independently each occurrence hydride or a moiety selected from halo, alkyl, aryl, silyl, germyl, aryloxy, alkoxy, amide, siloxy and combinations thereof having of up to 20 non-hydrogen atoms, and neutral Lewis base ligands having up to 20 non-hydrogen atoms or optionally one X together with Cp forms a metallocycle with M of up to 20 non-hydrogen atoms;

R is alkyl or aryl of up to 10 carbons;

n is 1 or 2 depending on the valence of M; and

A is a noncoordinating, compatible anion of a Bronsted acid salt.

[S012] EP-A-0416815 from which the present application is divided claims a metal coordination complex corresponding to the Formula:
M is titanium bound in an \( \eta^5 \) bonding mode to the cyclopentadienyl group;

R' each occurrence is hydrogen or a moiety selected from silyl, alkyl, aryl, or combinations thereof having up to 10 carbon or silicon atoms;

X each occurrence is halo, alkyl, aryl, or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2 depending on the valence of M.

[0013] The present invention provides metal monocyclopentadienyl coordination complexes corresponding to the formula I:

![Diagram of Formula I]

wherein:

M is hafnium or zirconium bound in an \( \eta^5 \) bonding mode to the cyclopentadienyl group;

R' each occurrence is hydrogen or a moiety selected from silyl, alkyl, aryl, or combinations thereof having up to 20 non-hydrogen atoms;

X each occurrence is halo, alkyl, aryl, or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2 depending on the valence of M.

[0014] In one embodiment, the invention provides a metal coordination complex corresponding to the following Formula IA:

![Diagram of Formula IA]

wherein M, R', E, X and n are as defined above in connection with Formula I.

[0015] The metal coordination complexes corresponding to the foregoing Formula I can be prepared by contacting
a metal compound of the formula MX_{n+2} or a coordinated adduct thereof with a dianionic salt compound corresponding to the formula:

\[(L^{+})_{y}(\text{Cp}^{+}-(\text{SiR}_{2}^{+})_{m}^{+}\text{NR}^{+})^{2} \quad (\text{II})\]

or

\[((\text{LX}^{+})^{+})_{y}(\text{Cp}^{+}-(\text{SiR}_{2}^{+})_{m}^{+}\text{NR}^{+})^{2} \quad (\text{III})\]

wherein:

- Cp* is the cyclopentadienyl or substituted cyclopentadienyl group C_{5}R_{4} of Formula I;
- L is a metal of Group 1 or 2 of the Periodic Table of the elements,
- X is fluoro, chloro, bromo, or iodo,
- x and y are either 1 or 2 and the product of x and y equals 2, and
- m, n, M, and R' are as previously defined in an inert solvent.

**0016** The metal coordination complexes corresponding to the foregoing Formula I also can be prepared by the steps of:

A) contacting a metal compound of the formula MX_{n+1} or a coordinated adduct thereof with a dianionic salt compound corresponding to the formulas II or III in an inert solvent; and

B) oxidizing the metal to a higher oxidation state by contacting the reaction product of step A) with a noninterfering oxidizing agent.

**0017** The metal coordination complexes of the invention are used with an activating cocatalyst in addition polymerizations.

**0018** Use of the catalysts can provide EiPE polymers which are highly elastic, interpolymers of ethylene and one or more olefins other than ethylene.

**0019** Further, use of the catalysts can provide pseudo-random interpolymers of an α-olefin, particularly ethylene and a vinylidene aromatic monomer, a hindered aliphatic vinylidene monomer, or a mixture thereof.

**0020** The complexes of the invention are usefully employed as catalysts for addition polymerization processes to prepare polymers that are useful as molded articles, films for packaging applications, and foams for cushioning applications; and in the modification of synthetic and naturally occurring resins. The complexes may also be used as catalysts for hydrogenations, catalytic cracking processes, and in other industrial applications.

**0021** Illustrative atomic arrangements of complexes as determined from single crystal X-ray diffraction values are shown in Figures 1-4.

**0022** Figure 1 shows the single-crystal X-ray crystallographically determined structure of (t-butyl amido)-dimethyl (tetramethyl-η^{5}-cyclopentadienyl) silane-zirconium dimethyl. The angle formed by the centroid of the cyclopentadienyl ring (C2, C3, C3', C5, and C5'), the zirconium atom (ZR1), and the nitrogen atom (N9) was determined to be 102.0°.

**0023** Figure 2 shows the single-crystal X-ray crystallographically determined structure of (tert-butyl amido)dimethyl (η^{5}-cyclopentadienyl) silane-zirconium dichloride. The structure shows that this molecule crystallizes as a dimer with 2 bridging chlorides. The angle formed by the centroid of the cyclopentadienyl ring (C2, C3, C4, C5, and C6), the zirconium atom (ZR1), and the nitrogen atom (N10), or the angle formed by the centroid of the cyclopentadienyl ring (C102, C103, C104, C105, and C106), the zirconium atom (ZR101), and the nitrogen atom (N110) were determined to be 99.1°.

**0024** Figure 3 shows the single-crystal X-ray crystallographically determined structure of (t-butyl amido) -dimethyl (tetramethyl-η^{5}-cyclopentadienyl) silane-zirconium dichloride. The angle formed by the centroid of the cyclopentadienyl ring (C1, C2, C3, C4, and C5), the zirconium atom (ZR), and the nitrogen atom (N) was determined to be 102.0°.

**0025** Figure 4 shows the single-crystal X-ray crystallographically determined structure of (t-butyl amido)-tetramethyl
(tetramethyl-\(\eta^5\)-cyclopentadienyl)disilanezirconium dichloride. The relatively long disilyl linking group that connects the cyclopentadienyl ring to the nitrogen atom of the amide ligand allows the nitrogen atom to be less constrained. The angle formed by the centroid of the cyclopentadienyl ring (C2, C3, C5, C7, and C9), the zirconium atom (ZR1), and the nitrogen atom (N17) was determined to be 118.0°. The activity of this catalyst towards olefin polymerization is considerably diminished relative to the analogous monosilane linking group in (tert-butyl amido)dimethyl-(tetramethyl-\(\eta^5\)-cyclopentadienyl)zirconium dichloride (Figure 3).

[0026] The term "activating cocatalyst" as used herein refers to a secondary component of the catalyst able to cause the metal-containing complex to become effective as an addition polymerization catalyst or alternatively to balance the ionic charge of a catalytically activated species. Examples of the foregoing activating cocatalysts for use herein include aluminum compounds containing an Al-O bond such as the alkylation aluminum oxanes, especially methylaluminoxane; aluminum alkyls; aluminum halides; aluminum alkylhalides; Lewis acids; ammonium salts; noninterfering oxidizing agents, e.g., silver salts, and ferrocenium ions; and mixtures of the foregoing.

[0027] Particular techniques for the preparation of aluminoxane type compounds by contacting an aluminum alkyl compound with an inorganic salt containing water of crystallization are disclosed in US-A-4,542,119. In a particularly preferred embodiment an aluminum alkyl compound is contacted with a regeneratable water-containing substance such as hydrated alumina, silica, or other substance. A process for preparing aluminoxane employing such regeneratable substance is disclosed in EP-A-0338,044.

[0028] Additional suitable activating cocatalysts include compounds corresponding to the formula:

\[
\text{AIR}_{n}X_{3-n}^{*}
\]

wherein:

R is each occurrence C\(_{1-10}\) alkyl or aralkyl;
X* is halogen; and
n is 1, 2 or 3.

[0029] Most preferably such cocatalysts are trialkyl aluminum compounds, particularly triethyl aluminum.

[0030] "Addition polymerizable monomers" include, for example, ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, and polyenes (e.g. C\(_{2-20}\) polyenes). Preferred monomers include the C\(_{2-10}\) α-olefins especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene. Other preferred monomers include styrene, halo- or alkyl substituted styrene, vinyl chloride, acrylonitrile, methyl acrylate, methacrylate, tetrafluoroethylene, methacrylonitrile, vinylidene chloride, vinylbenzocyclobutane, and 1,4-hexadiene.

[0031] By the term "hindered aliphatic vinylidene compounds" is meant addition polymerizable vinylidene monomers corresponding to the formula:

\[
\text{CG}_{2}=\text{CG}'\text{R}^{*}
\]

wherein \(\text{R}^{*}\) is an sterically bulky, aliphatic substituent of up to 20 carbons, \(\text{G}\) independently each occurrence is hydrogen or methyl, and \(\text{G}'\) independently each occurrence is hydrogen or methyl or alternatively \(\text{G}'\) and \(\text{R}^{*}\) together form a ring system. By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. Preferred hindered aliphatic vinylidene compounds are monomers in which one of the carbon atoms bearing ethynlic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexane, cycloheptene, cyclooctene, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, and norbornyl. Most preferred hindered aliphatic vinylidene compounds are the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylenide-2-norborn-ene. Especially suitable are 1-, 3-, and 4- vinylcyclo-hexene.

[0032] By the term "hindered vinylidene compound" is meant addition polymerizable vinylidene monomers corresponding to the formula:

\[
\text{CG}_{2}=\text{CG}'\text{R}^{**}
\]

wherein \(\text{R}^{**}\) is \(\text{R}^{*}\) or an aryl substituent of up to 20 carbons, and \(\text{G}\) and \(\text{G}'\) are as previously defined. For example, in
addition to hindered aliphatic vinylidene compounds, hindered vinylidene compounds also include the vinylidene aromatic monomers.

[0033] By the term "vinylidene aromatic monomers" is meant addition polymerizable compounds corresponding to the formula:

$$\text{CG}_{2}=\text{C}(\text{G}) \cdot \text{Ph}$$

wherein G independently each occurrence is hydrogen or methyl and Ph is phenyl, or a halo- or C<sub>1-4</sub> alkylsubstituted phenyl group. Preferred vinylidene aromatic monomers are monomers corresponding to the above formula wherein G each occurrence is hydrogen. A most preferred vinylidene aromatic monomer is styrene.

[0034] By the term "α-olefin" is meant ethylene and the C<sub>3-10</sub> olefins having ethylenic unsaturation in the α-position. Preferred α-olefins are ethylene, propylene, 1-butene, isobutylene, 4-methyl-1-pentene, 1-hexene, and 1-octene, and mixtures thereof.

[0035] As previously mentioned, the complexes according to the present invention preferably comprise structures having altered or enhanced catalytic activity at the metal site when the complex is combined with a cocatalyst. In this regard electron donating substituents have been found to improve the catalytic properties of the complexes.

[0036] It should be noted that whereas formulae herein indicate a cyclic structure for the catalysts, the bond between M and NR' is more accurately referred to as a coordinate-covalent bond. Also, it should be noted that the complex may exist as a dimer or higher oligomer.

[0037] Examples of the above most highly preferred metal coordination compounds include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; R' on the cyclopentadienyl group each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc.; and X is chloro, bromo, iodo, methyl, ethyl, propyl, butyl, pentyl, hexyl, (including isomers), norbornyl, benzyl, phenyl, etc. Specific compounds include (tert-butylamido) dimethyl (tetramethyl-η<sub>5</sub>-cyclopentadienyl) silanezirconium dibenzyl.

[0038] The complexes can be prepared by contacting the metal reactant and a group I metal derivative or Grignard derivative of the cyclopentadienyl compound in a solvent and separating the salt byproduct. Suitable solvents for use in preparing the metal complexes are aliphatic or aromatic liquids such as cyclohexane, methylcyclohexane, pentane, hexane, heptane, tetrahydrofuran, diethyl ether, C<sub>1-4</sub> alkyl ethers of mono- or diethylene glycol, C<sub>1-4</sub> alkyl ethers of mono- or dipropylene glycol, benzene, toluene, xylene, and ethylbenzene, or mixtures thereof.

[0039] In a preferred embodiment, the metal compound is MX<sub>n+1</sub>, i.e. M is in a lower oxidation state than in the corresponding compound, MX<sub>n+2</sub> and the oxidation state of M in the desired final complex. A noninterfering oxidizing agent may thereafter be employed to raise the oxidation state of the metal. The oxidation is accomplished merely by contacting the reactants utilizing solvents and reaction conditions used in the preparation of the complex itself. By the term "noninterfering oxidizing agent" is meant a compound having an oxidation potential sufficient to raise the metal oxidation state without interfering with the desired complex formation or subsequent polymerization processes. A particularly suitable noninterfering oxidizing agent is AgCl.

[0040] In order to assist in the handling of the metal complexes employed in the present process corresponding to the formula MX<sub>n+2</sub>, it may be beneficial first to form a solid adduct thereof by the use of a suitable coordinating agent according to well known techniques in the art. For example, whereas titanium tetrachloride is a fuming liquid which is difficult to handle, one may first form an adduct of TiCl<sub>4</sub> with an ether, tertiary amine, tertiary phosphine or other basic nonprotic compound. The resulting solids may be more easily handled. A preferred coordinating adduct is tetrahydrofuran.

[0041] The reactions employed in preparing the metal complex may be conducted either heterogeneously or homogeneously. That is, the various reactants or the resulting product need not be substantially soluble in the solvent mixture. Generally the reactants are contacted under an inert atmosphere for a time from several minutes to several days. Agitation may be employed if desired. The temperature of the reaction is generally from -90°C to 150°C, preferably from -20°C to 70°C.

[0042] Suitable catalysts for use according to the present invention are prepared by combining the metal coordination compound and activating cocatalyst compound in any order and in any suitable manner. Preferably the ratio of the coordination complex and cocatalyst on a molar basis is from 1:0.1 to 1:10,000. It will, of course, be appreciated that the catalyst system may also be formed in situ if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. Suitable solvents include toluene, ethylbenzene, alkanes and mixtures thereof. In certain cases the catalysts may be isolated from solution and retained under inert atmosphere prior to use. The catalysts’ components are sensitive to both moisture and oxygen and should be handled and transferred in an inert atmosphere such as nitrogen, argon or helium or under vacuum.
[0043] The polymerization is usually conducted according to known techniques for Ziegler-Natta or Kaminsky-Sinn type polymerizations. That is, the monomer(s) and catalyst are contacted at a temperature from -30°C to 250°C, at reduced, elevated or atmospheric pressures. The polymerization is conducted under an inert atmosphere which may be a blanketing gas such as nitrogen, argon, hydrogen, or ethylene, or under vacuum. Hydrogen may additionally be utilized in the control of molecular weight through chain termination as is previously known in the art. The catalyst may be used as is or supported on a suitable support such as alumina, MgCl₂ or silica to provide a heterogeneous supported catalyst. A solvent may be employed if desired. Suitable solvents include toluene, ethylbenzene, and excess vinylidene aromatic or olefin monomer. The reaction may also be conducted under solution or slurry conditions, in a suspension utilizing a perfluorinated hydrocarbon or similar liquid, in the gas phase, i.e., utilizing a fluidized bed reactor, or in a solid phase powder polymerization. A catalytically effective amount of the present catalyst and cocatalyst are any amounts that successfully result in formation of polymer. Such amounts may be readily determined by the routine experimentation by the skilled artisan. Preferred amounts of catalyst and cocatalyst are sufficient to provide an equivalent ratio of addition polymerizable monomer:catalyst of from 1 x 10¹⁰:1 to 100:1, preferably from 1 x 10⁸:1 to 500:1, most preferably from 1 x 10⁶:1 to 1000:1. The cocatalyst is generally utilized in an amount to provide an equivalent ratio of co- catalyst:catalyst from 10,000:1 to 0.1:1, preferably from 1,000:1 to 1:1.

[0044] It is to be understood that the metal complex may undergo various transformations or form intermediate species prior to and during the course of a polymerization. Thus other precursors could possibly be conceived to achieve the same catalytic species as are herein envisioned without departing from the scope of the present invention.

[0045] The resulting polymeric product is recovered by filtering or other suitable technique. Additives and adjuvants may be incorporated in the polymers of the present invention in order to provide desirable characteristics. Suitable additives include pigments, UV stabilizers, antioxidants, blowing agents, lubricants, plasticizers, photosensitizers, and mixtures thereof.

[0046] In the preparation of copolymers containing vinylidene aromatic or hindered aliphatic vinyl monomers it is desirable that a comonomer that is an α-olefin that is not particularly sterically hindered also be employed. Without wishing to be bound by any particular theory of operation, it is believed this is because the active site becomes crowded with the incorporation of the hindered vinyl compound making it unlikely that another hindered vinyl compound could enter into the polymerization as the next monomer in the sequence. After the incorporation of one or more olefins other than a hindered vinyl compound the active site once again becomes available for inclusion of a hindered vinyl monomer. On a limited basis however, the vinylidene aromatic monomer or sterically hindered vinyl monomer may insert into the polymer chain in reverse order, i.e. so as to result in two methylene groups between the substituted polymer backbone moiety.

[0047] Preferably such polymers possess a Mw of greater than 13,000, more preferably greater than 20,000 and most preferably greater than 30,000. Also preferably such polymers possess a melt index (I₂), ASTM D-1238 Procedure A, condition E, of less than 125, more preferably from 0.01 - 100 and most preferably from 0.1 to 10.

[0048] Due to the use of the previously mentioned catalyst system comprising a coordination complex of the invention, copolymers may be prepared that incorporate relatively bulky or hindered monomers in substantially random manner at low concentrations, and at higher concentrations according to an ordered insertion logic. The copolymers of α-olefins, especially ethylene and a hindered aliphatic vinylidene compound or vinylidene aromatic monomer can further be described as “pseudo-random”. That is, the copolymers lack well defined blocks of either monomer, however the respective monomers are limited to insertion according to certain rules.

[0049] These rules were deduced from certain experimental details resulting from an analysis of the polymers. The polymers were analyzed by ¹³C NMR spectroscopy at 130°C with a Varian VXR-300 spectrometer at 75.4 MHz. Samples of 200 to 250 mg polymer were dissolved in 15 mL of hot o-dichlorobenzene/1,1,2,2-tetrachloroethane-d₂ (approximately 70/30, v/v) which was approximately 0.05 M in chromium (III) tris(acetylacetonate) and a portion of the resulting solution was added to a 10 mm NMR tube. The following parameters and conditions were used: spectral width, 16,500 Hz; acquisition time 0.090 s; pulse width, 36°; delay, 1.0 s with the decoupler gated off during the delay.; FT size 32K; number of scans, >30,000; line broadening, 3Hz. Spectra, as recorded were referenced to tetrachloroethane-d₂ (δ 73.77 ppm, TMS scale).

[0050] Therefor, without wishing to be bound by any particular theory, the results of the foregoing experimental procedures indicate that a particular distinguishing feature of pseudo-random copolymers is the fact that all phenyl or bulky hindering groups substituted on the polymer backbone are separated by 2 or more methylene units. In other words, the polymers comprising a hindered monomer of the present invention can be described by the following general formula (using styrene as the hindered monomer for illustration):
where \( j, k, \text{and} l \geq 1 \)

[0051] In further explanation of the foregoing experimental and theoretical results, and without wishing to be bound
by any particular theory it can be concluded that during the addition polymerization reaction employing the present
catalysts, if a hindered monomer is inserted into the growing polymer chain, the next monomer inserted must be eth-
ylene or a hindered monomer which is inserted in an inverted or "tail-to-tail" fashion. This is illustrated below for a
hindered vinyl monomer where \( M \) is the catalyst metal center, HG is a hindering group, and P is the growing polymer
chain:

During the polymerization reaction, ethylene may be inserted at any time. After an inverted or "tail-to-tail"
hindered monomer insertion, the next monomer must be ethylene, as the insertion of another hindered monomer at
this point would place the hindering substituent closer together than the minimum separation as described above. A
consequence of these polymerization rules is the catalysts of this invention do not homopolymerize styrene to any
appreciable extent, while a mixture of ethylene and styrene is rapidly polymerized and may give high styrene content (up to 50 mole percent styrene) copolymers.

[0053] As a further illustration of the description of the α-olefin/hindered monomer copolymer of the present invention, a computer model of the polymerization reaction was used to calculate the expected $^{13}$C NMR spectrum of the polymer product. The computer program utilized a random number generator to select either α-olefin or hindered monomer to be inserted into a growing polymer chain, then calculated the number of each type of $^{13}$C NMR signals resulting from that insertion. Polymers were computer generated by repeating this process for 10,000 or more monomer insertions, and the resulting calculated $^{13}$C NMR spectrum was compared to actual experimental $^{13}$C NMR spectra for pseudo-random ethylene/styrene copolymers of the invention.

[0054] Computer simulations of the polymer and resulting $^{13}$C NMR spectra of the calculated pseudo-random ethylene/styrene copolymers were performed using the constraint that if styrene monomer were inserted into the growing polymer chain, the next monomer inserted must be ethylene or a styrene which is inserted in an inverted or “tail-to-tail” fashion. Optimum fits between experimental and calculated spectra were obtained if approximately 15 percent of the styrene insertions are in the “tail-to-tail” manner. The observed and calculated $^{13}$C NMR spectra for such pseudorandom ethylene/styrene copolymers containing 1.4, 4.8, 9.0, 13, 37, and 47 mole percent styrene are shown in Figures 5-10. In each case, the observed and calculated spectra are in excellent agreement.

[0055] Computer simulation of the polymer and resulting $^{13}$C NMR spectra of completely random α-olefin/hindered monomer copolymers were then performed using no constraints on hindered monomer insertion. In other words, the hindered monomer was allowed to insert into the growing polymer chain after a previous hindered monomer insertion if the random number generator selected hindered monomer as the next monomer to be inserted. The calculated spectra for these completely random copolymers do not agree with the observed $^{13}$C NMR spectra, as shown in Figure 11 for a 37 mole percent styrene containing ethylene/styrene copolymer.

[0056] Prior to polymerization according to the present process the monomers and solvents, if any, may be purified by vacuum distillation, and/or contacted with molecular sieves, silica, or alumina to remove impurities. In addition, reactive blanking agents, such as trialkylaluminum compounds, alkali metals and metal alloys, especially Na/K, may be used to remove impurities.

[0057] Suitable vinylidene aromatic monomers which may be employed according to the present invention include styrene as well as α-methyl styrene, the C$_1$-C$_4$ alkyl- or phenylring substituted derivatives of styrene, such as ortho-, meta-, and para-methylstyrene, or mixtures thereof, the ring halogenated styrenes, vinylbenzocyclobutanes, and divinylbenzene. A preferred vinylidene aromatic monomer is styrene.

[0058] In the polymerization of vinylidene aromatic monomers or hindered aliphatic vinylidene compounds and olefins the monomers are preferably combined in a proportion so as to achieve a vinylidene aromatic monomer (or hindered aliphatic vinylidene compound) content of at least 1.0 mole percent in the resulting polymer more preferably from 1.5 to less than 50 mole percent, highly preferably 5.0 to 48 mole percent, and most preferably from more than 8.0 up to 47 mole percent. Preferred operating conditions for such polymerization reactions are pressures from atmospheric to 1000 atmospheres (0.1 MPa to 100 MPa) and temperatures from 30°C to 200°C. Polymerizations at temperatures above the autopolymerization temperature of the respective monomers may contain small amounts of homopolymer polymerization products resulting from free radical polymerization.

[0059] Certain of the polymers prepared according to the present invention, especially copolymers of ethylene and an α-olefin other than ethylene, are characterized by unique rheological properties. In particular, it has been found that the polymers (hereinafter called Elastic Polyethylenes or EIPEs) are less Newtonian than conventionally prepared linear polyethylene resins of similar olefin content. The polymers also have higher elastic modulus particularly at high melt indices compared to such conventional polymers. This property makes the resin especially useful in the formation of films, foams and fabricated articles, for example by blow molding techniques. The above phenomenon is more particularly defined by reference to Figure 12 wherein complex viscosity, $\eta^*$ measured in poise at 190°C, is plotted as a function of shear rate, $\omega$, measured in radians per second for a typical EIPE copolymer of ethylene and 1-octene according to the invention. The slope of this curve indicates the melt is highly non-Newtonian. The actual values of $\eta^*$ and $\omega$ utilized in the graph are:

<table>
<thead>
<tr>
<th>$\eta^*$</th>
<th>$\omega$</th>
<th>$\eta^*$</th>
<th>$\omega$</th>
<th>$\eta^*$</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.962x10$^5$</td>
<td>0.01000</td>
<td>3.230x10$^4$</td>
<td>0.2512</td>
<td>1.088x10$^4$</td>
<td>6.310</td>
</tr>
<tr>
<td>1.511x10$^5$</td>
<td>0.01585</td>
<td>2.713x10$^4$</td>
<td>0.3981</td>
<td>9.336x10$^3$</td>
<td>10.000</td>
</tr>
<tr>
<td>1.115x10$^5$</td>
<td>0.02512</td>
<td>2.293x10$^4$</td>
<td>0.6310</td>
<td>7.964x10$^3$</td>
<td>15.850</td>
</tr>
<tr>
<td>8.292x10$^4$</td>
<td>0.03981</td>
<td>1.966x10$^4$</td>
<td>1.0000</td>
<td>6.752x10$^3$</td>
<td>25.120</td>
</tr>
<tr>
<td>6.322x10$^4$</td>
<td>0.06310</td>
<td>1.701x10$^4$</td>
<td>1.5850</td>
<td>5.677x10$^3$</td>
<td>39.810</td>
</tr>
<tr>
<td>4.920x10$^4$</td>
<td>0.10000</td>
<td>1.464x10$^4$</td>
<td>2.5120</td>
<td>4.721X10$^3$</td>
<td>63.100</td>
</tr>
</tbody>
</table>
Also plotted in Figure 12 is the tan $\delta$ value of the same ElPE polymer. This value is unitless and is calculated by dividing the viscous modulus value by the elastic modulus. The actual values of tan $\delta$ and $\omega$ utilized in the graph are:

<table>
<thead>
<tr>
<th>$\omega$</th>
<th>tan $\delta$</th>
<th>$\omega$</th>
<th>tan $\delta$</th>
<th>$\omega$</th>
<th>tan $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1585</td>
<td>0.5526</td>
<td>0.01000</td>
<td>1.243</td>
<td>0.2512</td>
<td>1.718</td>
</tr>
<tr>
<td>0.01585</td>
<td>0.5231</td>
<td>0.01585</td>
<td>1.381</td>
<td>0.3981</td>
<td>1.677</td>
</tr>
<tr>
<td>0.02512</td>
<td>0.5771</td>
<td>0.02512</td>
<td>1.543</td>
<td>0.6310</td>
<td>1.620</td>
</tr>
<tr>
<td>0.03981</td>
<td>0.6597</td>
<td>0.03981</td>
<td>1.615</td>
<td>1.0000</td>
<td>1.552</td>
</tr>
<tr>
<td>0.06310</td>
<td>0.7971</td>
<td>0.06310</td>
<td>1.690</td>
<td>1.5850</td>
<td>1.475</td>
</tr>
<tr>
<td>0.10000</td>
<td>0.9243</td>
<td>0.10000</td>
<td>1.729</td>
<td>2.5120</td>
<td>1.398</td>
</tr>
<tr>
<td>0.15850</td>
<td>1.0800</td>
<td>0.15850</td>
<td>1.737</td>
<td>3.9810</td>
<td>1.315</td>
</tr>
</tbody>
</table>

For improved performance in melt blowing applications preferably the tan $\delta$ value is from 0.1 to 3.0 for shear rates between 0.01-100 radian/sec.

EIPE resins are characterized by high elastic modulus in the melt. In particular, EIPE resins have a melt index (I2, ASTM D-1238 Procedure A, condition E), less than 200, preferably less than 125, most preferably less than 50 and an elastic modulus greater than 1000 dyne/cm², more preferably greater than 2000 dyne/cm². All of the foregoing rheological measurements are performed by standard techniques such as are disclosed in H. A. Barnes et al., Introduction to Rheology, Elsevier, publishing, Inc., 1989. Densities normally range from 0.85 to 0.97 g/ml, preferably from 0.89-0.97 g/ml. Molecular weight distributions (Mw/Mn) are greater than 2.0, preferably from 3.0-10.0. Typically melting points range from 50°C to 135°C.

Preferred polymers additionally demonstrate properties of homogeneous polymers as defined in US-A-3,645,992, i.e. ethylene copolymers having substantially random comonomer distribution within a given molecule and substantially the same ethylene/comonomer ratio between molecules. Polymers produced at elevated polymerization temperatures, especially temperatures greater than 130°C, may exhibit a heterogeneous melt curve. The polymers of the invention are further marked by high clarity. In particular the polymers have better optical properties, especially lower haze than typical ethylene polymers, making them especially well suited for film and injection molding applications.

In addition those polymers comprising an olefin and a vinylidene aromatic monomer, especially ethylene and styrene, have surprisingly been found to possess elastomeric properties. Thus, such polymers are uniquely suited for use in applications for thermoplastic elastomers such as impact modification of thermoplastic and thermosetting polymers including bitumens; adhesives; and elastomeric moldings.

The polymers of the invention may be modified by typical grafting, crosslinking, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. With particular regard to the polymers comprising vinylidene aromatic,vinylcyclohexene, or 1,4-hexadiene functionality, the same may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques. Additionally, the vinylcyclohexene based polymers are readily crosslinkable by reaction of the unsaturated ring functionality.

The polymers of the present invention, whether or not further modified, may be blended with synthetic or natural polymers to provide blends having desirable properties. In particular polyethylene, ethylene/\(\alpha\)-olefin copolymers, polypropylene, poly styrene, styrene/ acrylicitrile copolymers (including rubber modified derivatives thereof), syndiotactic polystyrene, polycarbonate, polyamide, aromatic polyester, polyisocyanate, polyurethane, polycrylonitrile, silicone, and polyphenyleneoxide polymers may be blended with the polymeric compositions of the present invention. The polymeric modifier is utilized in amounts from 0.1 to 99.0 preferably 0.5 to 50 weight percent.

In a highly preferred embodiment of the invention the polymers containing ethylene and styrene are elastomeric as defined in the definition of an elastomeric substance by ASTM Special Technical Bulletin No. 184 as a substance that can be stretched at room temperature to twice its length and will return to its original length upon release.

In addition to modification of synthetic thermoplastics the present polymers are also usefully employed as modifiers for asphalt or bitumen compositions. Desirably the polymers of styrene/ethylene are utilized in this manner.

The term "bitumen" can generally be defined as mixtures of hydrocarbons of natural or pyrogenous origin or combinations of both, frequently accompanied by their non-metallic derivatives, which may be gaseous, liquid, semi-solid or solid, and which are usually soluble in carbon disulfide. For the purposes of the present invention, bitumen of
a liquid, semi-solid or solid nature may be utilized. From a commercial standpoint, bitumen is generally restricted to asphalts and tars and pitches. A listing of various bituminous materials which can be utilized in the present invention include the following:

I. Asphalts

1. Petroleum Asphalts
   A. Straight-reduced asphalts
      1. Atmospheric or reduced-pressure reduction
      2. Solvent precipitated, as with propane
   B. Thermal asphalts, as residues from cracking operations on petroleum stocks
      1. Straight-blown
      2. "Catalytic"-blown
   C. Air-blown asphalts
      1. Straight-blown
      2. "Catalytic"-blown

2. Native Asphalts
   A. With mineral content below 5 percent
      1. Asphaltites such as gilsonite, graphamite, and glance pitch
      2. Bermudez and other natural deposits
   B. With mineral content over 5 percent
      1. Rock asphalts
      2. Trinidad and other natural deposits

II. Tars and Derivatives

1. Residua from coke-oven-dried coal tars
   A. Coal tars reduced to float grades, as RT (road tar) grades for paving purposes
   B. Coal-tar pitches, with reduction carried out to softening-point grades

2. Residua from other pyrogenous distillates as from water-gas, wood, peat, bone, shale, rosin, and fatty acid tars.

[0070] As can be readily appreciated by those skilled in the art, the weight average molecular weight of the various bitumens can vary over a very wide range, for example such as from 500 to 10,000. Additionally, the softening point of the various types of asphalt will also vary such as from 50°C to 400°C (10°F to 205°F).

[0071] Of the many types of asphalts which may be utilized, petroleum, and native are desired, with petroleum being preferred. Of the petroleum asphalts, the thermal asphalts are preferred.

[0072] The amount of bitumen utilized in the compositions of the invention preferably ranges from 65 to 99 parts by weight with preferred amounts ranging from 80 to 98 parts by weight.

Example 1

Preparation of (Tert-butyldiamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl) silane zirconium dichloride

[0074] To 0.443 g (1.90 mmol) ZrCl₄ in a flask was added 8 mL diethyl ether, then 15 mL tetrahydrofuran (THF). To the resulting slurry was slowly added a solution of 0.500 g (1.90 mmol) di lithium (tert-butyldiamido)dimethyl(tetramethylcyclopentadienyl)silane in 15 mL THF. The resulting yellow solution was stirred for several days. The solvent was
removed to give a gummy residue, which was extracted with 5/1 (volume) diethyl ether/pentane and filtered from a white solid. The solvent was removed from the yellow filtrate to give a light-yellow powder. Recrystallization from ether/pentane (5/1) yielded the product (C₅Me₄(Me₂Si-N-tert-Bu)ZrCl₂) as an off-white crystalline solid. The yield was 0.2207 g (28.2%). Identification was made by ¹³C and ¹H NMR.

Polymerization

[0075] A. Five mL of a 1.009 M solution of methyl aluminoxane (MAO) in toluene was added to a shot tank containing 25 mL of 4-methyl-1-pentene. The catalyst solution was prepared by adding 500 L of a 0.01172 M solution of C₅Me₄(Me₂-Si-N-tert-Bu)ZrCl₂ in toluene to 2 mL of toluene in a second shot tank. Both shot tanks were sealed, removed from the glove box, and attached to a 600 mL stainless steel pressure vessel. The pressure vessel was evacuated and purged with argon.

[0076] The 4-methyl-1-pentene/toluene/MAO solution was added to the pressure vessel and warmed to 89°C under 620 kPa (90 psig) ethylene with stirring. Upon addition of the catalyst solution to the 4-methyl-1-pentene/MAO/ethylene mixture, the ethylene pressure was increased to 1240-1275 kPa (180-185 psig). After 2 hours the solution was cooled to 30°C and vented. The yield of polymer obtained after drying under reduced pressure at 100°C overnight was 10.0 g. ¹³C NMR analysis of the polymer showed it to be a random copolymer of ethylene with 4-methyl-1-pentene.

[0077] B. The polymerization procedure of Polymerization A was essentially repeated except that 50 mL of 1-hexene was used instead of 4-methyl-1-pentene and the catalyst concentration was 0.01012 M in toluene. The catalyst solution was added to the 1-hexene/MAO/ethylene mixture and the ethylene pressure was increased to 1240-1275 kPa (180-185 psig). When the catalyst solution was added the temperature of the reaction climbed to 139°C. After 30 minutes the solution had cooled to 100°C. Heating and ethylene feed were discontinued and the reactor was cooled and vented. The yield of polymer obtained after drying under reduced pressure at 100°C overnight was 36.8 g. ¹³C NMR analysis of the polymer showed it to be a random copolymer of ethylene with 1-hexene (8 percent on a mole basis).

[0078] C. The polymerization procedure of Polymerization A was essentially repeated except that 213 L of the catalyst solution (0.01172 M in toluene) was used, and 143 mg of solid MAO was used. No additional olefin was added. When the catalyst solution was added to the reactor the temperature increased to 109°C due to the exothermic polymerization reaction. The reaction was halted after 1 hour by cooling and venting the reactor. The yield of polyethylene obtained after drying under reduced pressure at 100°C overnight was 11.0 g.

[0079] D. 150 mL of toluene was added to the pressure vessel employed in Polymerization A, followed by 100 g of propylene. A solution of 0.828 g of MAO in 8 mL of toluene was added, followed by 2130 L of the catalyst solution. The mixture was allowed to react for 3.0 h at 8°C. The reaction mixture was quenched with acidic methanol, and ¹³C NMR analysis of the polymer showed it to be atactic polypropylene.

Example 2 (Olefin Copolymer Polymerization)

[0081] In a glove box under argon atmosphere, 5.0 mL of 1.0 M solution of methylaluminoxane (MAO) in toluene was combined with 50 mL of 1-octene in a stainless steel (SS) shot tank fitted with ball valves on both ends. In another SS shot tank 500 L (5.06 mol) of a 0.0101 M solution of (tert-butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silazirconium dichloride in toluene was added to 2 mL toluene.

[0082] The shot tanks were sealed, removed from the glove box and attached to a 600 mL SS pressure vessel. The pressure vessel was evacuated and purged with argon. The solution of 1-octene and MAO was added to the pressure vessel. The solution was warmed to 89°C under 620 kPa (90 psig) ethylene with stirring. At this time the catalyst solution was added. An exothermic reaction occurred which raised the temperature to 142°C. The ethylene pressure was maintained between 1310-1345 kPa (190-195 psig).

[0083] After 0.5 hour the ethylene feed was discontinued. The reactor was cooled to 30°C, vented to the atmosphere, and the reaction was quenched with methanol. The product was collected on a fritted filter and washed with methanol. Residual solvents were removed under reduced pressure at 110°C which resulted in 35 g of material. ¹³C NMR analysis indicated that 1-octene was incorporated into the polymer in an amount of 7.8 mole percent. Differential Scanning Calorimetry (DSC) indicated a Tm of 100°C. Density 0.895 g/mL, Mw=44,000, Mw/Mn= 6.8

Example 3 (Olefin Copolymer Polymerization)

[0084] The procedure of Example 2 was substantially repeated excepting that 50 mL of 1-hexene was used instead of 1-octene. The temperature of the reaction was maintained at 133-140°C. Polymer yield was 37 g. Incorporation of 1-hexene was 8 percent on a molar basis, 21 percent by weight.
Example 4 (α-Olefin Homopolymerization)

[0085] A. 4-Methyl-1-pentene (6.0 mL, 4.0 g) was added to 1.0 mL of a 1.0 M MAO solution in toluene in a 20 mL crimp-top vial. To this was added 100 L of a 0.01172 M toluene solution of the zirconium complex catalyst of Example 2. The vial was sealed, shaken, and allowed to stand at room temperature (ca. 20°C) for 16 hours, then heated to 48°C for an additional 24 hours. The viscous polymer solution was precipitated by the addition of methanol. The resulting polymer was collected and the volatile components removed under reduced pressure for four hours at 100°C to give 3.8 g of a clear polymer (95 percent yield). 13C NMR analysis indicated that the polymer was atactic poly-4-methyl-1-pentene.

[0086] B. The procedure of Polymerization A was essentially repeated. 3.4 g of 1-hexene, 1.0 mL of MAO solution, and 100 L of the catalyst solution were added to a 20 mL crimp-top vial in an argon-filled drybox. The vial was sealed and heated at 50°C overnight. After quenching with acidified ethanol and drying there was obtained 3.0 g of poly(1-hexene).

Example 5 (Hindered Vinyl Aliphatic Monomer Polymerization)

[0087] 4-vinylcyclohexene was purified by vacuum distillation from Na/K alloy. The procedure of Example 2 was substantially repeated using, 50 mL of 4-vinylcyclohexene with 5.0 mL of a solution of 1.0 M methylaluminoxane (MAO) cocatalyst in toluene in one shot tank and 500 L of a 0.010 M solution of (tert-butylamido)dimethyl(tetramethyl-η5-cyclopentadienyl)silanezirconium dichloride in toluene added to 2 mL toluene in the other shot tank.

[0088] The exothermic reaction occurred which raised the temperature to 114°C. The ethylene feed was discontinued after 1h and the cooled and vented reaction was quenched with acidified methanol.

[0089] The product was 12.6 g of material. 13C NMR analysis indicated that vinylcyclohexene was incorporated into the polymer in an amount of 1.5 mole percent.

Examples 6-15

[0090] In these examples, a 4 liter autoclave was charged with 2000 mL of mixed alkane solvent (Isopar-E) followed by various amounts of 1-octene. The catalyst was (tert-butylamido)dimethyl(tetramethyl-η5-cyclopentadienyl)-silanezirconium dichloride, dissolved in toluene. The cocatalyst was a 10 percent solution of MAO in toluene. Hydrogen, if desired, was added by expansion from a 100 mL vessel at a pressure indicated above the operating pressure of the reactor. The reactor was filled with solvent, 1-octene and MAO, heated to the reaction temperature, then pressurized to 3100 kPa (450 psig) with ethylene until the solution was saturated. The hydrogen (if any) was expanded into the reactor, followed by the addition of the catalyst solution. After 10 minutes, the solution was drained from the reactor into a container which had a small amount of antioxidant (Irganox 1010®, available from Ciba-Geigy). The polymer was dried under vacuum. Results are contained in Table I.
Table I

<table>
<thead>
<tr>
<th>Example</th>
<th>Temp °C</th>
<th>mL Octene</th>
<th>ΔH₂kPa (psiq)</th>
<th>Zr (mmole)</th>
<th>Al:Zr a</th>
<th>Zr eff x 10⁻³ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>150</td>
<td>300</td>
<td>345 (50)</td>
<td>0.02</td>
<td>500</td>
<td>50</td>
</tr>
<tr>
<td>7</td>
<td>140</td>
<td>300</td>
<td>&quot;</td>
<td>0.01</td>
<td>500</td>
<td>122</td>
</tr>
<tr>
<td>8</td>
<td>130</td>
<td>300</td>
<td>&quot;</td>
<td>0.005</td>
<td>500</td>
<td>285</td>
</tr>
<tr>
<td>9</td>
<td>130</td>
<td>450</td>
<td>&quot;</td>
<td>0.005</td>
<td>500</td>
<td>302</td>
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<td>10</td>
<td>130</td>
<td>150</td>
<td>&quot;</td>
<td>0.005</td>
<td>500</td>
<td>230</td>
</tr>
<tr>
<td>11</td>
<td>130</td>
<td>150</td>
<td>&quot;</td>
<td>0.01</td>
<td>250</td>
<td>158</td>
</tr>
<tr>
<td>12</td>
<td>130</td>
<td>150</td>
<td>&quot;</td>
<td>0.02</td>
<td>100</td>
<td>104</td>
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<tr>
<td>13</td>
<td>130</td>
<td>300</td>
<td>&quot;</td>
<td>0.01</td>
<td>100</td>
<td>154</td>
</tr>
<tr>
<td>14</td>
<td>140</td>
<td>450</td>
<td>0</td>
<td>0.015</td>
<td>200</td>
<td>84</td>
</tr>
<tr>
<td>15</td>
<td>140</td>
<td>450</td>
<td>690 (100)</td>
<td>0.02</td>
<td>200</td>
<td>101</td>
</tr>
</tbody>
</table>

a  equivalent ratio, assuming 58 Mw for MAO  
b  catalyst efficiency, g polymer/1 g metal
Examples 16-25 (Olefin polymerization)

[0091] Ethylene and/or ethylene/1-octene were respectively polymerized as a homopolymer or copolymer by adding a solution of the appropriate catalyst in combination with MAO or triethyl aluminum cocatalyst to a 3L SS pressure vessel containing mixed C₆ alkane solvent/1-octene (with varying ratios) under 3100 kPa (450 psig) of ethylene at 150°C (or 175°C where indicated) for 10 minutes. The ethylene pressure was held constant and a mass flow meter measured the uptake of ethylene. The consequent polymer was then removed from the pressure vessel and dried under reduced pressure at 90°C overnight. Results are contained in Table II.
<table>
<thead>
<tr>
<th>Example</th>
<th>Catalyst</th>
<th>Solvent/Octene</th>
<th>Wt. of polymer (g)</th>
<th>Melt Index (I₂)</th>
<th>Mw</th>
<th>Mn</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>Zr</td>
<td>1/1</td>
<td>55.2</td>
<td>1324.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>17</td>
<td>Zr</td>
<td>2/0.15</td>
<td>33.3</td>
<td>10.3</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>18</td>
<td>Zr</td>
<td>2/0</td>
<td>25.8</td>
<td>8.8</td>
<td>58,400</td>
<td>5310</td>
<td>10.90</td>
</tr>
<tr>
<td>19</td>
<td>Zr</td>
<td>0/2</td>
<td>102.9</td>
<td>168.1</td>
<td>30,900</td>
<td>8150</td>
<td>3.79</td>
</tr>
<tr>
<td>20&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Zr</td>
<td>2/0</td>
<td>17.8</td>
<td>147.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>21</td>
<td>Zr</td>
<td>2/0</td>
<td>25.3</td>
<td>240.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>22</td>
<td>Zr</td>
<td>2/0</td>
<td>20.6</td>
<td>2.8</td>
<td>101,000</td>
<td>7700</td>
<td>13.10</td>
</tr>
<tr>
<td>23</td>
<td>Zr</td>
<td>2/0.3</td>
<td>44.0</td>
<td>17.1</td>
<td>47,300</td>
<td>6550</td>
<td>7.22</td>
</tr>
<tr>
<td>24</td>
<td>Zr</td>
<td>0/2</td>
<td>96.6</td>
<td>149.2</td>
<td>43,500</td>
<td>4710</td>
<td>5.87</td>
</tr>
<tr>
<td>25</td>
<td>Zr</td>
<td>0/2</td>
<td>88.3</td>
<td>111.7</td>
<td>35,100</td>
<td>6440</td>
<td>5.45</td>
</tr>
</tbody>
</table>

<sup>a</sup> Zr = (tert-butyllamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)silanezirconium dichloride
<sup>b</sup> Metal/Al ratio = 1/1000 assuming 58 MW for MAO
<sup>c</sup> liters of each
<sup>d</sup> Run at 175°C
Example 26

Preparation of 1-(Tert-butylamido)-2-(tetramethyl-\(\eta^5\)-cyclopentadienyl)-1,1,2,2-tetramethyldisilane-zirconium dichloride

[0092] A slurry of 0.7500 g (2.333 mmol) dilithium 1-(tert-butylamido)-2-(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane (prepared according to the technique of Example 84 of EP-A-0416815) and 0.5436 g (2.333 mmol) \(\text{ZrCl}_4\) in 75 mL toluene was stirred for several days. The pale yellow reaction mixture was filtered and the solvent was removed. The residue was extracted with pentane and filtered. After concentration and cooling at -35°C in a freezer, the product as colorless crystals was collected on a frit. Yield: 0.6720 g, 61.3%. \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 2.14 (s, 6H), 1.94 (s, 6H), 1.49 (s, 9H), 0.36 (s, 6H), 0.34 (s, 6H). \(^{13}\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 134.1, 131.0, 119.1, 58.4, 34.2, 15.1, 11.8, 4.7, -2.1.

Example 27

Preparation of (Tert-butylamido)(dimethyl)(tetramethyl-\(\eta^5\)-cyclopentadienyl)silanezirconium dimethyl

[0093] A solution of 0.5000 g (1.215 mmol) (tert-butylamido)-(dimethyl)(tetramethylcyclopentadienyl)silanezirconium dichloride in 35 mL ether was cooled to -40°C. To this was slowly added 1.41 mL methyl lithium solution (1.72 M, 2.43 mmol). The reaction mixture was allowed to stir at room temperature for several hours. The solvent was removed and the residue was extracted with pentane and filtered. The filtrate was concentrated and chilled to -40°C. The colorless crystals which formed were isolated by decanting away the supernatant. Yield: 0.2215 g, 49.2 percent \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 1.97 (s, 6H), 1.91 (s, 6H), 1.40 (s, 9H), 0.46 (s, 6H), 0.00 (s, 6H). \(^{13}\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 130.2, 125.3, 95.7, 54.7, 35.4, 34.0, 13.9, 10.9, 6.2.

Example 28

Preparation of (Tert-butylamido)dimethyl(\(\eta^5\)-cyclopentadienyl)silanezirconium dichloride

[0094] To 0.6747 g (2.90 mmol) \(\text{ZrCl}_4\) in a flask was slowly added 4 mL diethyl ether, then 4 mL THF. The excess solvents were removed under vacuum to yield a solid which was broken up to a powder. The solid was combined with 0.6008 g (2.90 mmol) dilithium (tert-butylamido)(cyclopentadienyl)(dimethyl)silane (prepared according to the technique of Example 87 of EP-A-0415815 and 75 mL toluene. The resulting slurry was stirred for several days after which the colorless solution was filtered, the solvent removed under reduced pressure and the residue was slurried in pentane. The product was collected on a frit and dried under reduced pressure. Yield was 0.6186 g (60.0%). \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 6.43 (t, 2H), 6.08 (t, 2H), 4.17 (br s, 6H), 1.27 (s, 9H), 1.03 (br s, 6H), 0.22 (s, 6H). \(^{13}\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 122.0, 121.4, 109.5, 78, 57.2, 32.8, 25.2, 0.7. The structure was shown by x-ray crystallography to be dimeric (bridging chlorides) in the solid state.

Example 29

Preparation of (Anilido)(dimethyl)(tetramethyl-\(\eta^5\)-cyclopentadienyl)silanezirconium dichloride

[0095] To 0.6905 g (2.963 mmol) \(\text{ZrCl}_4\) in a flask was slowly added 3 mL diethyl ether, then 4 mL THF. The excess solvents were removed under vacuum to yield a solid which was broken up to a powder. The solid was combined with 0.8044 g (2.963 mmol) dilithium (anilido)(dimethyl)-(tetramethyl-\(\eta^5\)-cyclopentadienyl)silane and 70 mL toluene. Within minutes the slurry color became pale yellow-green. The slurry was stirred for several days after which time the solution was filtered, the solvent removed under reduced pressure and the residue was slurried in pentane. The very pale yellowish product was collected on a frit and dried under reduced pressure. \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 7.21 (t, 2H), 7.1 (t, 1H), 6.97 (m, 2H), 2.50 (s, 3H), 2.46 (s, 3H), 1.87 (s, 3H), 1.85 (s, 3H), 0.53 (s, 3H), 0.40 (s, 3H).

Example 30

Preparation of (p-Toluidino)(dimethyl)(tetramethyl-\(\eta^5\)-cyclopentadienyl)silanezirconium dichloride

(a) (p-Toluidino)(dimethyl)(tetramethylcyclopentadienyl) silane

[0096] To a solution of 2.000 g (9.302 mmol) (chloro)-(dimethyl)(2,3,4,5-tetramethylcyclopenta-diényl)silane in 70 mL THF was slowly added 1.259 g (9.302 mmol) lithium p-toluidide (0.3 ether adduct by \(^1\)H NMR). The reaction mixture
was stirred overnight. Monitoring by GC indicated the reaction was incomplete. Additional lithium p-toluidide was added
in small lots (0.725 g, 14.7 mmol total). The solvent was removed, the residue was extracted with pentane and filtered. The
pentane was removed under reduced pressure to give the product as a yellow oil. The yield was 2.456 g (92.5%).
Mass spec. m/e 285 (22%).

\[ \text{H NMR (C}_6\text{D}_6) \delta 6.96 (d, 2H), 6.57 (d, 2H), 3.07 (s, 1H), 3.01 (s, 1H), 2.17 (s, 3H), 1.91 (s, 6H), 1.80 (s, 6H), 0.08 (s, 6H). \]

\[ \text{C NMR (C}_6\text{D}_6) \delta 145.0, 136.2, 132.7, 130.2, 126.9, 116.9, 55.2, 20.5, 14.3, 11.3, -2.2. \]

(b) Dilitium (p-toluidino)(dimethyl)(tetramethylcyclopenta-dienyl)ilane

\[ \text{To a solution of 2.233 g (7.82 mmol) (p-toluidino)(dimethyl)(tetramethylcyclopentadienyl)silane in 65 mL ether was slowly added 6.17 mL of 2.60 M (16.0 mmol) butyllithium in mixed C}_6\text{ alkane solvent. The precipitate-free reaction mixture was stirred overnight. The solvent was removed under reduced pressure. The resulting white solid was slurried in pentane, collected on a frit, washed with pentane and dried under reduced pressure to give the product as a white powder. The yield was 2.34 g (100%).} \]

\[ \text{H NMR (THF-}\delta-8\text{) } \delta 6.42 (d, 2H), 6.18 (d, 2H), 2.09 (s, 6H), 2.01 (s, 3H), 1.94 (s, 6H), 0.36 (s, 6H). \]

\[ \text{C NMR (THF-}\delta-8\text{) } \delta 160.8, 129.1, 121.3, 115.9, 115.2, 112.2, 106.2, 20.8, 14.7, 11.7, 5.2. \]

(c) (p-Toluidino)(dimethyl)(tetramethyl-η^5-cyclopentadienyl)silanezirconium dichloride

\[ \text{To 0.7836 g (3.363 mmol) ZrCl}_4\text{ in a flask was slowly added 3 mL diethyl ether, then 4 mL THF. The excess solvents were removed under vacuum to yield a solid which was broken up to a powder. The solid was combined with 1.000 g (3.363 mmol) dilithium (p-toluidino)(dimethyl)-(tetramethyl-η^5-cyclopentadienyl)silane and 70 mL toluene. The slurry was stirred for several days. The initially yellowish slurry turned brownish. The yellow solution was filtered, the solvent removed under reduced pressure and the solid was slurried in pentane. The pale yellow product was collected on a frit and dried under reduced pressure. The yield was 0.8854 g (59.1%).} \]

\[ \text{H NMR (C}_6\text{D}_6\text{) } \delta 7.06 (d, 2H), 6.87 (d, 2H), 2.50 (s, 3H), 2.47 (s, 3H), 2.21 (s, 3H), 1.89 (s, 3H), 1.88 (s, 3H), 0.51 (s, 3H), 0.41 (s, 3H). \]

\[ \text{C NMR (C}_6\text{D}_6\text{) } \delta 145.2, 135.1, 132.2, 131.8, 129.4, 129.0, 128.9, 128.8, 127.0, 126.6, 126.3, 106.6, 57.2, 16.0, 15.6, 12.5, 11.8, 2.6. \]

Example 31

Preparation of (Benzylamido) dimethyl (tetramethyl-η^5-cyclopentadienyl)silanezirconium dichloride

\[ \text{In a flask were combined 0.3930 g (1.687 mmol) ZrCl}_4\text{, 0.5015 g (1.687 mmol) dilithium (benzylamido)dimethyl-(tetramethyl-η^5-cyclopentadienyl)silane and 40 mL toluene. The brownish yellow slurry was stirred for several days then filtered and the solvent was removed under reduced pressure. The moist tan residue was slurried in pentane and the product was collected on a frit and dried under reduced pressure. Yield of the off-white tan product: 0.2873 g (38.2%).} \]

\[ \text{H NMR (C}_6\text{D}_6\text{) } \delta 7.51 (d, 2H), 7.23 (t, 2H), 7.09 (t, 1H), 5.48 (d, 1H), 5.00 (d, 1H), 2.45 (s, 6H), 2.05 (s, 3), 2.01 (s, 3H), 0.34 (s, 3H), 0.20 (s, 3H). \]

\[ \text{C NMR (C}_6\text{D}_6\text{) } \delta 145.2, 135.1, 132.2, 131.8, 129.4, 129.0, 128.9, 128.8, 127.0, 126.6, 126.3, 106.6, 57.2, 16.0, 15.6, 12.5, 11.8, 2.6. \]

Example 32

Preparation of (Methylamido)dimethyl(tetramethyl-η^5-cyclopentadienyl)silanezirconium dichloride

\[ \text{In a flask 0.5705 g (2.448 mmol) ZrCl}_4\text{ and 0.6318 g (2.446 mmol) dilithium (methylamido)dimethyl(tetra-}
\text{methyl-η^5-cyclopentadienyl)silane were combined with 75 mL toluene. The slurry was stirred for several days after which time the resulting pale green solution was filtered, and the solvent was removed under reduced pressure. The residue was slurried in pentane, collected on a frit, washed with pentane and dried under reduced pressure. The yield of very pale powder blue product was 0.6162 g (68.2%).} \]

\[ \text{H NMR (C}_5\text{D}_5\text{) } \delta 3.50 (s, 3H), 2.49 (s, 3H) 2.36 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 0.46 (s, 3H), 0.43 (s, 3H). \]

Example 33 (Slurry Polymerization)

\[ \text{The following example demonstrates the use of a catalyst of the present invention under slurry conditions. The procedure of Examples 6-15 was substantially followed, excepting that the reaction was run under conditions where the polymer was insoluble in the reaction medium and precipitated from the reaction mixture as it formed. The temperature was 70°C, 10 mL of octene, 1190 mL of mixed alkane solvent, and 5 mL of 15 percent MAO in toluene were used. After 20 minutes, the reactor was drained to give 4.6 g of polymer. Additional solvent was added to the reactor and heated to 170°C to remove the polymer that had formed long filaments and wound around the stirrer. The} \]
melt index was 0.28.

Example 34

Preparation of (Tert-butlamido)dimethyl (tetramethylcyclopentadienyl) -silanehafnium dichloride

In the drybox, 0.50 g of HfCl₄ was suspended in 10 mL of toluene. 10 mL of THF was added, the slurry was stirred for 5 minutes, and 0.77 g of Me₄C₅SiMe₂N-t-BuMg₂Cl₂(THF)₂ was added. The solution was heated to reflux. After 30 minutes, the solution was cooled, and the volatile materials were removed under reduced pressure. Pentane (20 mL) was added, the solution was filtered, and the pentane was removed under reduced pressure to leave a white solid. This solid was washed with a small quantity of pentane to yield 0.077 g (10%) of a white solid, 1H NMR (C₆D₆): δ 2.08 (6H), 1.30 (9H), 0.44 (6H).

When ethylene was polymerized substantially according to the procedure of Example 7 of EP-A-0416815, a small amount of polyethylene was recovered.

Comparative 1

The polymerization procedure of Examples 6 - 15 was substantially followed using 1000 mL of mixed alkane solvent, 200 mL of 1-octene and 5 mL of 15 percent MAO in toluene and a reaction temperature of 130°C. Hydrogen was supplied from a 75 mL tank pressurized to 3450 kPa (500 psig) to give a delta pressure of 345 kPa (50 psi). 10 Micromoles of pentamethylcyclopentadienyltitanium trichloride was added to begin the polymerization. Ethylene was provided on demand at 3100 kPa (450 psig). The polymer yield was 4.6 g.

Comparative 2

The polymerization procedure of Comparative 1 was followed except that the catalyst was (tert-butylamino)-pentamethyl-η⁵-cyclopentadienyltitanium dichloride (1H NMR (C₆D₆) : δ 2.07 (s, 1H), 1.88 (s, 15H), 1.35 (s, 9H). 13C NMR (C₆D₆) : δ 61.0, 31.3, 12.6). The polymer yield was 2.0 g.

Comparative 3

The polymerization procedure of Comparative 1 was followed except that the catalyst was bis-(tert-butylamido)dimethylsilanetitanium dichloride. No polymer was observed after 10 minutes of reaction.

Comparative 4

The polymerization procedure of Comparative 1 was followed except that the catalyst was dicyclopentadienyl-zirconium dichloride. The polymer yield was 109.0 g, Mw = 16,300, Mw/Mn = 3.63, melt index ASTM D-1238 Procedure A, condition E, I₂, was greater than 1,000 indicating a very low molecular weight polymer.

Comparative 5

The polymerization procedure of Comparative 1 was followed except that the catalyst was dicyclopentadienyl-titanium dichloride. The polymer yield was 7.3 g, melt index, ASTM D-1238 Procedure A, condition E, I₂, was greater than 1,000 indicating a very low molecular weight polymer.

Claims

1. A metal coordination complex corresponding to the Formula I:
wherein:

M is zirconium or hafnium, bound in an $\eta^5$ bonding mode to the cyclopentadienyl group;

R' each occurrence is hydrogen or a moiety selected from silyl, alkyl, aryl, or combinations thereof having up to 10 carbon or silicon atoms;

X each occurrence is halo, alkyl, aryl, or alkoxy of up to 10 carbons;

m is 1 or 2; and

n is 1 or 2 depending on the valence of M.

2. A metal coordination complex as claimed in Claim 1 corresponding to the following Formula IA:

wherein M, R', X and n are as defined in Claim 1.

3. A metal coordination complex as claimed in Claim 1 or Claim 2, wherein each R' is hydrogen, C$_1$-$6$ alkyl, norbornyl, benzyl or phenyl; and X is chloro, bromo, iodo, C$_1$-$6$ alkyl, norbornyl, benzyl or phenyl.

4. A metal coordination complex as claimed in Claim 2, wherein X is methyl.

5. A metal coordination complex as claimed in Claim 3, wherein X is benzyl.

6. A metal coordination complex as claimed in any one of the preceding claims, wherein NR' is tert. butylamide.

7. A metal coordination complex as claimed in any one of Claims 1 to 5, wherein NR' is phenylamido.

8. A metal coordination complex as claimed in Claim 1 or Claim 2, wherein n is 1 or 2.

9. A metal coordination complex as claimed in Claim 1 or Claim 2, wherein n is 2.

10. A metal coordination complex as claimed in Claim 1, wherein m is 2.
11. 1-(Tert-butylamido)-2-(tetramethyl-η⁵-cyclopentadienyl)-1,1,2,2-tetramethyldisilane zirconium dichloride.

12. A metal coordination complex as claimed in Claim 1 or Claim 2, wherein M is zirconium.

13. A metal coordination complex selected from:
- (tert-butylamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)silane zirconium dibenzyl;
- (tert-butylamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)silane zirconium dichloride;
- (tert-butylamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)silane zirconium dimethyl;
- (tert-butylamido)dimethyl-(η⁵-cyclopentadienyl)silane zirconium dichloride;
- (anilido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)-silane zirconium dichloride;
- (p-toluidido) dimethyl-(tetramethyl-η⁵-cyclopentadienyl)silane zirconium dichloride;
- (benzylamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)silane zirconium dichloride; and
- (methylamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)silane zirconium dichloride.

14. A catalyst useful in addition polymerizations comprising
   a) a metal coordination complex as claimed in any one of Claims 1 to 13, and
   b) an activating cocatalyst.

15. A catalyst as claimed in Claim 14, wherein said activating cocatalyst comprises an aluminum compound.

16. A catalyst as claimed in Claim 15, wherein said aluminum compound is an alkylaluminoxane, aluminum alkyl, aluminum halide, or aluminum alkylhalide.

17. A catalyst as claimed in Claim 12, wherein the activating cocatalyst is selected from alkylaluminoxanes, and compounds corresponding to the formula:

   \[ \text{AlR}_nX^*_{3-n} \]

   wherein:
   - R is each occurrence \( \text{C}_{1-10} \) alkyl or aralkyl;
   - \( X^* \) is halogen; and
   - n is 1, 2 or 3.

18. A process for preparing a metal coordination complex corresponding to the Formula I as defined in Claim 1 comprising contacting a metal compound of the formula \( \text{MX}_{m+1} \) or a coordinated adduct thereof with a dianionic salt compound corresponding to the Formula II or III:

\[ (L^{x_1})_{y}(\text{Cp}^*(\text{SiR}_2'^m \cdot \text{NR})^2 \] (II)

or

\[ (LX^*)_{x_1}^y(\text{Cp}^*(\text{SiR}_2'^m \cdot \text{NR})^2 \] (III)

wherein:
- \( \text{Cp}^* \) is the cyclopentadienyl or substituted cyclopentadienyl group \( \text{C}_{5-8} \text{R}_4^* \) of Formula I;
- L is a metal of Group 1 or 2 of the Periodic Table of the Elements,
- \( x \) and \( y \) are either 1 or 2 and the product of \( x \) and \( y \) equals 2,
- \( X^* \) is fluoro, bromo, chloro or iodo, and
19. A process for preparing a metal coordination complex corresponding to the Formula I as defined in Claim 1 comprising

(a) contacting a metal compound of the formula \( \text{MX}_{n+1} \) or a coordinated adduct thereof with a dianionic salt compound corresponding to the Formula II or III:

\[
\left( L^{x+y} \right)^{y} (\text{Cp}^*-(\text{SiR'}_2)_m \cdot \text{NR'})^{-2}
\]  

or

\[
\left( L^{x+y} \right)^{y} (\text{Cp}^*-(\text{SiR'}_2)_m \cdot \text{NR'})^{-2}
\]  

wherein:

\( \text{Cp}^* \) is the cyclopentadienyl or substituted cyclopentadienyl group \( \text{C}_5 \text{R'}_4 \) of Formula I;
\( L \) is a metal of Group 1 or 2 of the Periodic Table of the Elements,
\( x \) and \( y \) are either 1 or 2 and the product of \( x \) and \( y \) equals 2,
\( X' \) is fluoro, bromo, chloro or iodo,
\( n, M, m, \text{ and } R' \) are as defined in Claim 1

in an inert solvent, and,

(b) contacting the product of (a) with a noninterfering oxidizing agent to raise the oxidation state of the metal.

20. A process as claimed in Claim 18 or 19, wherein the solvent is selected from cyclohexane, tetrahydrofuran, methylcyclohexane, pentane, hexane, heptane, benzene, toluene, xylene and ethylbenzene.

21. A process as claimed in Claim 20, wherein the solvent is toluene or tetrahydrofuran.

22. A process for preparing a catalyst as claimed in Claim 14, comprising contacting a complex as defined in any one of Claims 1 to 13 with an activating cocatalyst.

23. A process for preparing a catalyst as claimed in Claim 22, wherein the activating cocatalyst is as defined in any one of Claims 15 to 17.

24. An addition polymerization process for preparing a polymer by contacting one or more addition polymerizable monomers with a catalyst under addition polymerization conditions characterized in that the catalyst is as defined in any one of Claims 14 to 17.

25. A process as claimed in Claim 24, wherein the addition polymerizable monomers are selected from ethylenically unsaturated monomers, acetylenic compounds, conjugated or nonconjugated dienes, and polyenes having from 2 to 20 carbons.

26. A process as claimed in Claim 25, wherein an alpha olefin is copolymerized with a vinlylidene aromatic or hindered aliphatic vinyl monomers.

27. A process as claimed in Claim 26, wherein ethylene is copolymerized with styrene or vinylcyclohexene.

28. A process for preparing a copolymer of a hindered aliphatic vinlylidene monomer and an alpha-olefin wherein the hindered aliphatic vinlylidene monomer is contacted with the alpha-olefin under polymerization conditions in the presence of a catalyst comprising
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A process as claimed in Claim 28, wherein the activating cocatalyst is as defined in any one of Claims 15 to 17.

A process as claimed in Claim 29, wherein the hindered aliphatic vinylidene monomer is one in which a carbon atom bearing ethylenic unsaturation is tertiary or quaternary substituted.

A process as claimed in Claim 30, wherein said carbon atom is substituted by a cyclic aliphatic group.

A process as claimed in Claim 31, wherein the hindered aliphatic vinylidene monomer is 1-, 3- or 4-vinylcyclohexene or 5-ethylidene-2-norbornene.

A process as claimed in any one of Claims 24 to 32, wherein the catalyst is formed in situ.

A process as claimed in Claim 24, wherein ethylene is copolymerized with propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene or 1-octene.

A heterogeneous supported catalyst comprising a metal coordination complex corresponding to the Formula I as defined in Claim 1 and an activating cocatalyst.

A heterogeneous supported catalyst as claimed in Claim 35, wherein the metal coordination complex corresponds to the Formula IA as defined in Claim 2.

A heterogeneous supported catalyst as claimed in Claim 35 or Claim 36, wherein the support is selected from alumina, MgCl₂ and silica.

A heterogeneous supported catalyst as claimed in Claim 35 or Claim 36, wherein the metal coordination complex is as defined in any one of Claims 3 to 9 or 12 and/or the activating cocatalyst is as defined in any one of Claims 15 to 17.

Patentansprüche

1. Metallkoordinationskomplex entsprechend der Formel I:

   \[
   M \text{gleich Zirkonium oder Hafnium ist, das in einem } \eta^5\text{-Bindungsmodus an die Cyclopentadienylgruppe gebunden ist;}
   \]

   \[
   R' \text{bei jedem Auftreten Wasserstoff oder eine Einheit, ausgewählt aus Silyl, Alkyl, Aryl oder Kombinationen daraus mit bis zu 10 Kohlenstoff- oder Siliciumatomen, ist;}
   \]

   \[
   X \text{bei jedem Auftreten Halogen, Alkyl, Aryl oder Alkoxy mit bis zu 10 Kohlenstoffatomen ist;}
   \]

   \[
   m \text{gleich 1 oder 2 ist und}
   \]

   \[
   n \text{in Abhängigkeit von der Valenz von } M \text{gleich 1 oder 2 ist.}
   \]
2. Metallkoordinationskomplex wie in Anspruch 1 beansprucht entsprechend der folgenden Formel IA:

![Diagram](image)

worin M, R', X und n wie in Anspruch 1 definiert sind.

3. Metallkoordinationskomplex wie in Anspruch 1 oder 2 beansprucht, worin jedes R' gleich Wasserstoff, C₁₋₆-Alkyl, Norbornyl, Benzyl oder Phenyl ist und X gleich Chlor, Brom, Jod, C₁₋₆-Alkyl, Norbornyl, Benzyl oder Phenyl ist.

4. Metallkoordinationskomplex wie in Anspruch 2 beansprucht, worin X gleich Methyl ist.

5. Metallkoordinationskomplex wie in Anspruch 3 beansprucht, worin X gleich Benzyl ist.

6. Metallkoordinationskomplex wie in einem der vorstehenden Ansprüche beansprucht, worin X gleich Benzyl ist.

7. Metallkoordinationskomplex wie in einem der Ansprüche 1 bis 5 beansprucht, worin NR' gleich Phenylamido ist.

8. Metallkoordinationskomplex wie in Anspruch 1 oder 2 beansprucht, worin n gleich 1 oder 2 ist.

9. Metallkoordinationskomplex wie in Anspruch 1 oder 2 beansprucht, worin n gleich 2 ist.

10. Metallkoordinationskomplex wie in Anspruch 1 beansprucht, worin m gleich 2 ist.

11. 1-(tert.-Butylamido)-2-(tetramethyl-η⁵-cyclopentadienyl)-1,1,2,2-tetramethyldisilanzirkonium-dichlorid.

12. Metallkoordinationskomplex wie in Anspruch 1 oder 2 beansprucht, worin M gleich Zirkonium ist.

13. Metallkoordinationskomplex ausgewählt aus:

   (tert.-Butylamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)disilanzirkonium dibenzyl; (tert.-Butylamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)disilanzirkonium dichlorid; (tert.-Butylamido)dimethyl-(tetramethyl-η⁵-cyclopentadienyl)disilanzirkonium dimethyl; (tert.-Butylamido)dimethyl-(η⁵-cyclopentadienyl)disilanzirkonium dichlorid; (tert.-Butylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)disilanzirkonium dichlorid; (Benzylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)disilanzirkonium dichlorid und (Methylamido)dimethyl(tetramethyl-η⁵-cyclopentadienyl)disilanzirkonium dichlorid.

14. Katalysator, der für Additionspolymerisationen geeignet ist, enthaltend:

   a) einen Metallkoordinationskomplex wie in einem der Ansprüche 1 bis 13 beansprucht und

   b) einen aktivierenden Cokatalysator.


16. Katalysator wie in Anspruch 15 beansprucht, worin diese Aluminiumverbindung ein Alkylaluminoxan, Aluminimumal-
kyl, Aluminiumhalogenid oder Aluminiumalkylhalogenid ist.

17. Katalysator wie in Anspruch 12 beansprucht, worin der aktivierende Cokatalysator ausgewählt ist aus Alkylaluminoxanen und Verbindungen entsprechend der Formel:

\[
\text{AlR}_n X^*_{3-n}
\]

worin:

R bei jedem Auftreten gleich C\textsubscript{1-10}-Alkyl oder -Aralkyl ist;
X* gleich Halogen ist und
n gleich 1, 2 oder 3 ist.

18. Verfahren zur Herstellung eines Metallkoordinationskomplexes entsprechend der Formel I wie in Anspruch 1 definiert, umfassend Inberührungsbringen einer Metallverbindung der Formel MX\textsubscript{n+1} oder einem koordinierten Addukt davon mit einer dianionischen Salzverbindung entsprechend der Formel II oder III:

\[
(L^{x})_y(Cp^*-(SiR')_m-NR')^{-2}
\]

oder

\[
(LX^*)^{x}y(Cp^*-(SiR')_m-NR')^{-2}
\]

worin:

Cp* die Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe C\textsubscript{5}R\textsubscript{4} der Formel I ist;
L ein Metall der Gruppe 1 oder 2 des Periodensystems der Elemente ist,
x und y entweder 1 oder 2 sind und das Produkt von x und y 2 entspricht,
X* gleich Fluor, Brom, Chlor oder Jod ist und
n, M, m und R' wie in Anspruch 1 definiert sind,
in einem inerten Lösungsmittel.

19. Verfahren zur Herstellung eines Metallkoordinationskomplexes entsprechend der Formel I wie in Anspruch 1 definiert, umfassend

(a) Inberührungsbringen einer Metallverbindung der Formel MX\textsubscript{n+1} oder einem koordinierten Addukt davon mit einer dianionischen Salzverbindung entsprechend der Formel II oder III:

\[
(L^{x})_y(Cp^*-(SiR')_m-NR')^{-2}
\]

oder

\[
(LX^*)^{x}y(Cp^*-(SiR')_m-NR')^{-2}
\]

worin:

Cp* die Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe C\textsubscript{5}R\textsubscript{4} der Formel I ist;
L ein Metall der Gruppe 1 oder 2 des Periodensystems der Elemente ist,
x und y entweder 1 oder 2 sind und das Produkt von x und y 2 entspricht,
X* gleich Fluor, Brom, Chlor oder Jod ist,
n, M, m und R' wie in Anspruch 1 definiert sind,

21. Verfahren wie in Anspruch 20 beansprucht, worin das Lösungsmittel Toluol oder Tetrahydrofuran ist.

22. Verfahren zur Herstellung eines Katalysators wie in Anspruch 14 beansprucht, umfassend Inberührungbringen eines Komplexes wie in einem der Ansprüche 1 bis 13 definiert mit einem aktivierenden Cokatalysator.

23. Verfahren zur Herstellung eines Katalysators wie in Anspruch 22 beansprucht, worin der aktivierende Cokatalysator wie in einem der Ansprüche 15 bis 17 definiert ist.


25. Verfahren wie in Anspruch 24 beansprucht, worin die additionspolymerisierbaren Monomere ausgewählt sind aus ethylenisch ungesättigten Monomeren, acetylenischen Verbindungen, konjugierten oder nichtkonjugierten Dienen und Polyenen mit 2 bis 20 Kohlenstoffatomen.


27. Verfahren wie in Anspruch 26 beansprucht, worin Ethylen mit Styrol oder Vinylcyclohexen copolymerisiert wird.

28. Verfahren zur Herstellung eines Copolymers eines sterisch gehinderten aliphatischen Vinylidenmonomers und eines α-Olefins, worin das sterisch gehinderte aliphatische Vinylidenmonomer mit dem α-Olefin unter Polymerisationsbedingungen in Gegenwart eines Katalysators, enthaltend

(a) einen Metallkoordinationskomplex wie in einem der Ansprüche 1 bis 13 definiert und
(b) einen aktivierenden Cokatalysator.

in Berührung gebracht wird.

29. Verfahren wie in Anspruch 28 beansprucht, worin der aktivierende Cokatalysator wie in einem der Ansprüche 15 bis 17 definiert ist.

30. Verfahren wie in Anspruch 28 oder 29 beansprucht, worin das sterisch gehinderte aliphatische Vinylidenmonomer eines ist, in welchem das Kohlenstoffatom, das ethylenische Unsättigung trägt, tertiär oder quartär substituiert ist.

31. Verfahren wie in Anspruch 30 beansprucht, worin dieses Kohlenstoffatom mit einer cyclischen aliphatischen Gruppe substituiert ist.

32. Verfahren wie in Anspruch 31 beansprucht, worin das sterisch gehinderte aliphatische Vinylidenmonomer 1-, 3- oder 4-Vinylcyclohexen oder 5-Ethyliden-2-norbornen ist.

33. Verfahren wie in einem der Ansprüche 24 bis 32 beansprucht, worin der Katalysator in situ gebildet wird.

34. Verfahren wie in Anspruch 24 beansprucht, worin Ethylen mit Propylen, Isobutylen, 1-Buten, 1-Hexen, 4-Methyl-1-penten oder 1-Octen copolymerisiert wird.

35. Heterogener Katalysator auf einem Träger, enthaltend einen Metallkoordinationskomplex entsprechend der Formel I wie in Anspruch 1 definiert und einen aktivierenden Cokatalysator.

36. Heterogener Katalysator auf einem Träger wie in Anspruch 35 beansprucht, worin der Metallkoordinationskomplex
der Formel IA wie in Anspruch 2 definiert entspricht.

37. Heterogener Katalysator auf einem Träger wie in Anspruch 35 oder Anspruch 36 beansprucht, worin der Träger aus Aluminiumoxid, MgCl₂ und Siliciumdioxid ausgewählt ist.

38. Heterogener Katalysator auf einem Träger wie in Anspruch 35 oder Anspruch 36 beansprucht, worin der Metallkoordinationskomplex wie in einem der Ansprüche 3 bis 9 oder 12 definiert ist und/oder der aktivierende Cokatalysator wie in einem der Ansprüche 15 bis 17 definiert ist.

**Revendications**

1. Complexe de coordination métallique correspondant à la formule I :

   ![Image](image1.png)

   où

   M est du zirconium ou de l'hafnium, lié par une liaison de type η⁵ au groupe cyclopentadiényle ; chaque R' est l'hydrogène ou un fragment choisi parmi un silyle, alkyle aryle ou des combinaisons de ceux-ci ayant jusqu'à 10 atomes de carbone ou de silicium ; chaque X est un radical halogéno, alkyle, aryle, ou alcoxy ayant jusqu'à 10 atomes de carbone ; m est égal à 1 ou 2 ; et n est égal à 1 ou 2 en fonction de la valence de M.

2. Complexe de coordination métallique selon la revendication 1 correspondant à la formule IA suivante :

   ![Image](image2.png)

   où M, R', X et n sont comme définis dans la revendication 1.

3. Complexe de coordination métallique selon la revendication 1 ou 2, dans lequel chaque R' est l'hydrogène, un alkyle en C₁₋₆, norbornyle, benzyle ou phényle, et X est un radical chloro, bromo, iodo, alkyle en C₁₋₆, norbornyle, benzyle ou phényle.

4. Complexe de coordination métallique selon la revendication 2 dans lequel X est un méthyle.

5. Complexe de coordination métallique selon la revendication 3 dans lequel X est un benzyle.
6. Complexe de coordination métallique selon l'une quelconque des revendications précédentes, dans lequel NR' est un tert-butylamide.

7. Complexe de coordination métallique selon l'une quelconque des revendications 1 à 5, dans lequel NR' est un phénylamido.

8. Complexe de coordination métallique selon la revendication 1 ou 2, dans lequel n est égal à 1 ou 2.

9. Complexe de coordination métallique selon la revendication 1 ou 2, dans lequel n est égal à 2.

10. Dichlorure de 1-(tert-butylamido)-2-(tétraméthyl-η⁵-cyclopentadiényle)-1,1,2,2-tétraméthylidisilanezirconium.

12. Complexe de coordination métallique selon la revendication 1 ou 2, dans lequel M est le zirconium.

13. Complexe de coordination métallique choisi parmi :

   - le (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium dibenzyle ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium diméthyle ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium ;
   - le dichlorure de (tert-butylamido)diméthyl-(tétraméthyl-η⁵-cyclopentadiényle)diméthylsilane zirconium.

14. Catalyseur utile dans les polymérisations par addition comprenant :

   a) un complexe de coordination métallique selon l'une quelconque des revendications 1 à 13 et
   b) un cocatalyseur d'activation.

15. Catalyseur selon la revendication 14, dans lequel ledit co-catalyseur d'activation comprend un composé d'aluminium.

16. Catalyseur selon la revendication 15, dans lequel ledit composé d'aluminium est un alkylaluminoxane, un alkyle d'aluminium, un halogénure d'aluminium, ou un alkyl-halogénure d'aluminium.

17. Catalyseur selon la revendication 12, dans lequel le co-catalyseur d'activation est choisi parmi les alkylaluminoxanes, et les composés correspondant à la formule :

   \[ \text{AIR}_nX^*_{3-n} \]

   où

   - chaque R est un aralkyle ou alkyle en C₁₋₁₀
   - X⁺ est un halogène ; et
   - n est égal à 1, 2 ou 3.

18. Procédé pour la préparation d'un complexe de coordination métallique correspondant à la formule I comme définie dans la revendication 1, comprenant la mise en contact d'un composé métallique de formule MXₙ₊₁ ou d'un produit d'addition de coordonnation de celui-ci avec un composé de sel dianionique correspondant à la formule II ou III :

   \[ (\text{L}^{*x})_y(C\text{p}^*\text{-(SiR'}^2_{m-N}\text{R'})^{-2} \]

   (II)
ou

\[(LX^*)^{x}y(Cp^*-(SiR'_2)^m-NR')^{-2}\]  \hspace{1cm} \text{(III)}

ou

\[\text{Cp}^* \text{ est un groupe cyclopentadiényle ou cyclopentadiényle substitué C}_5\text{R'}_4 \text{ de formule I ;} \]
\[\text{L est un métal du groupe 1 ou 2 du Tableau périodique des éléments ;} \]
\[x \text{ et } y \text{ valent soit 1 soit 2 et le produit de } x \text{ par } y \text{ est égal à 2 ;} \]
\[X^* \text{ est un radical fluoro, bromo, chloro ou iodo, et} \]
\[n, M, m \text{ et } R' \text{ sont comme définis dans la revendication 1.} \]

19. Procédé pour la préparation d'un complexe de coordination métallique correspondant à la formule I comme définie dans la revendication 1 comprenant

(a) la mise en contact d'un composé métallique de formule MX_{n+1} ou d'un produit d'addition coordonné de celui-ci avec un composé sel dianionique correspondant à la formule II ou III :

\[\text{ou} \]
\[\text{(L}^{x}y(Cp^*-(SiR'_2)^m-NR')^{-2}\]  \hspace{1cm} \text{(II)}

\[\text{ou}\]
\[\text{(LX}^{*})^{x}y(Cp^*-(SiR'_2)^m-NR')^{-2}\]  \hspace{1cm} \text{(III)}

\[\text{où} \]
\[\text{Cp}^* \text{ est un groupe cyclopentadiényle ou cyclopentadiényle substitué C}_5\text{R'}_4 \text{ de formule I ;} \]
\[\text{L est un métal du groupe 1 ou 2 du Tableau périodique des éléments ;} \]
\[x \text{ et } y \text{ valent soit 1 soit 2 et le produit de } x \text{ par } y \text{ est égal à 2 ;} \]
\[X^* \text{ est un radical fluoro, bromo, chloro ou iodo ;} \]
\[n, M, m \text{ et } R' \text{ sont comme définis dans la revendication 1} \]

(dans un solvant inerte, et,

(b) la mise en contact du produit de (a) avec un agent oxydant non-interférant pour augmenter l'état d'oxydation du métal.

20. Procédé selon la revendication 18 ou 19, dans lequel le solvant est choisi parmi le cyclohexane, le tétrahydrofurane, le méthylcyclohexane, le pentane, l'hexane, l'heptane, le benzène, le toluène, le xylène et l'éthylbenzène.

21. Procédé selon la revendication 20, dans lequel le solvant est le toluène ou le tétrahydrofurane.

22. Procédé pour la préparation d'un catalyseur selon la revendication 14 comprenant la mise en contact d'un complexe comme défini dans l'une quelconque des revendications 1 à 13 avec un co-catalyseur d'activation.

23. Procédé pour la préparation d'un catalyseur selon la revendication 22, dans lequel le co-catalyseur d'activation est comme défini dans l'une quelconque des revendications 15 à 17.

24. Procédé de polymérisation par addition pour préparer un polymère en faisant entrer en contact un ou plusieurs monomères polymérisables par addition avec un catalyseur dans des conditions de polymérisation par addition, caractérisé en ce que le catalyseur est comme défini dans l'une quelconque des revendications 14 à 17.

25. Procédé selon la revendication 24, dans lequel les monomères polymérisables par addition sont choisis parmi les monomères éthyléniquement insaturés, les composés acényléniques, les diènes conjugués ou non conjugués, et les polyènes ayant de 2 à 20 atomes de carbone.
26. Procédé selon la revendication 25, dans lequel une alpha-oléfine est copolymérisée avec un monomère de vinyle aliphatique encombré ou un monomère aromatique de vinylidène.

27. Procédé selon la revendication 36, dans lequel l'éthylène est copolymérisé avec du styrène ou du vinylcyclohexène.

28. Procédé pour préparer un copolymère d'un monomère de vinylidène aliphatique encombré et une alpha-oléfine dans lequel le monomère de vinylidène aliphatique encombré est mis en contact avec l'alpha-oléfine dans des conditions de polymérisation en présence d'un catalyseur comprenant :
   a) un complexe de coordination métallique comme défini dans l'une quelconque des revendications 1 à 13,
   b) un cocatalyseur d'activation

29. Procédé selon la revendication 28, dans lequel le cocatalyseur d'activation est comme défini dans l'une quelconque des revendications 15 à 17.

30. Procédé selon la revendication 28 ou 29, dans lequel le monomère de vinylidène aliphatique encombré est un monomère où un atome de carbone portant l'insaturation éthénique est substitué de manière tertiaire ou quaternaire.

31. Procédé selon la revendication 30, dans lequel l'atome de carbone est substitué par un groupe aliphatique cyclique.

32. Procédé selon la revendication 31, dans lequel le monomère de vinylidène aliphatique encombré est du 1-, 3- ou 4-vinylcyclohexène ou du 5-éthylidène-2-norbornène.

33. Procédé selon l'une quelconque des revendications 24 à 32, dans lequel le catalyseur est formé in situ.

34. Procédé selon la revendication 24, dans lequel l'éthylène est copolymérisé avec du propylène, de l'isobutyle, de l'1-butène, de l'1-hexène, du 4-méthyl-1-pentène ou de l'1-octène.

35. Catalyseur supporté hétérogène comprenant un complexe de coordination métallique correspondant à la formule I comme définie dans la revendication 1 et un cocatalyseur d'activation.

36. Catalyseur supporté hétérogène selon la revendication 35, dans lequel le complexe de coordination métallique correspond à la formule 1A comme définie dans la revendication 2.

37. Catalyseur supporté hétérogène selon la revendication 35 ou 36, dans lequel le support est choisi entre l'alumine, le MgCl₂ et la silice.

38. Catalyseur supporté hétérogène selon la revendication 35 ou 36, dans lequel le complexe de coordination métallique est comme défini dans l'une quelconque des revendications 3 à 9 ou 12 et/ou le co-catalyseur d'activation est comme défini dans l'une quelconque des revendications 15 à 17.
FIG. 5
Ethylene/Styrene Pseudo-random Copolymer 1.4 Mole % Styrene, 15% Tail-to-Tail

Chemical Shift, ppm
FIG. 7

Ethylene/Styrene Pseudo-random Copolymer 9.0 Mole % Styrene, 15% Tail-to-Tail

Chemical Shift, ppm
FIG. 10
Ethylene / Styrene Pseudo-random Copolymer 47 Mole % Styrene, 15% Tail-to-Tail

Chemical Shift, ppm

Calc. Obs.
FIG. 11
Ethylene / Styrene Random Copolymer 37 Mole % Styrene, 15% Tail-to-Tail

Chemical Shift, ppm