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(54) **PROCEDE DE REGULATION DE L'ACTIVITE D'UNE
COMPOSITION CATALYSEUR DESTINEE A LA
POLYMERISATION DES OLEFINES**

(54) **METHOD OF CONTROLLING OLEFIN POLYMERIZATION
CATALYST COMPOSITION ACTIVITY**

(57) Cette invention concerne un procédé de régulation de l'activité de polymérisation d'oléfines d'une composition catalyseur non supportée et sous forme liquide que l'on prépare en mettant en contact un précurseur de catalyseur à site unique avec un cocatalyseur d'activation, en dehors d'un réacteur de polymérisation. Ledit procédé consiste à ajuster: soit a) la durée de contact entre le précurseur de catalyseur à site unique et le cocatalyseur d'activation; soit b) les concentrations du précurseur de catalyseur à site unique et du cocatalyseur d'activation au cours du contact; soit c) la proportion molaire du précurseur de catalyseur à site unique par rapport au cocatalyseur d'activation; soit d) la température au cours du contact; soit e) le degré de mélange du précurseur de catalyseur à site unique et du cocatalyseur d'activation.

(57) A method of controlling the olefin polymerization activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor with an activating cocatalyst outside of a polymerization reactor is provided. The method comprises adjusting at least one of: a) the period of time the single site catalyst precursor and the activating cocatalyst are contacted; b) the concentrations of the single site catalyst precursor and the activating cocatalyst during contacting; c) the mole ratio of the single site catalyst precursor to the activating cocatalyst during contacting; d) the temperature during contacting; and e) the degree of mixing of the single site catalyst precursor and the activating cocatalyst.

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(21) International Application Number: PCT/US98/00482 (22) International Filing Date: 8 January 1998 (08.01.98) (30) Priority Data: 08/782,499 10 January 1997 (10.01.97) US (71) Applicant: UNION CARBIDE CHEMICALS & PLASTICS TECHNOLOGY CORPORATION [US/US]; 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US). (72) Inventors: PETERSON, Thomas, Henry; 1311 Wychwood Road, Charleston, WV 25314 (US). SCHRECK, David, James; 5226 Sun Valley Drive, Cross Lanes, WV 25313 (US). WENZEL, Timothy, Todd; 888 Poplar Road, Charleston, WV 25302 (US). WILLIAMS, Clark, Curtis; 1105 Skytop Circle, Charleston, WV 25314 (US). (74) Agent: WIGGINS, Karen, Johnson; Union Carbide Chemicals & Plastics Technology Corporation, 39 Old Ridgebury Road, Danbury, CT 06817-0001 (US).		(81) Designated States: AU, BR, CA, CN, CZ, HU, JP, KP, KR, MX, PL, SG, TR, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: METHOD OF CONTROLLING OLEFIN POLYMERIZATION CATALYST COMPOSITION ACTIVITY (57) Abstract A method of controlling the olefin polymerization activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor with an activating cocatalyst outside of a polymerization reactor is provided. The method comprises adjusting at least one of: a) the period of time the single site catalyst precursor and the activating cocatalyst are contacted; b) the concentrations of the single site catalyst precursor and the activating cocatalyst during contacting; c) the mole ratio of the single site catalyst precursor to the activating cocatalyst during contacting; d) the temperature during contacting; and e) the degree of mixing of the single site catalyst precursor and the activating cocatalyst.		

METHOD OF CONTROLLING OLEFIN POLYMERIZATION CATALYST COMPOSITION ACTIVITY

The present invention provides a method for controlling the olefin polymerization activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor with an activating cocatalyst outside of a polymerization reactor.

BACKGROUND

A variety of catalyst compositions containing single site catalyst precursors have been shown to be highly useful in the preparation of polyolefins, producing relatively homogeneous copolymers at good polymerization rates and allowing one to tailor closely the final properties of the polymer produced. In contrast to traditional Ziegler-Natta catalyst precursors, single site catalyst precursors are catalytic compounds in which each catalyst molecule contains one or only a few polymerization sites. Metallocenes are the most well known type of single site catalyst precursor, and are organometallic coordination complexes containing one or more pi-bonded moieties (i.e., cycloalkadienyl groups) in association with a metal atom from Groups IIIB to VIII or the Lanthanide series of the Periodic Table of Elements.

U.S. Patent No. 5,317,036 to Brady, III, et al. relates to the use of unsupported, liquid form catalyst compositions, including those based on metallocenes. It discloses the gas phase polymerization of one or more monomers having 2 to 12 carbon atoms by: a) continuously introducing a gaseous stream comprising the monomers into a reaction zone; b) introducing a polymerization catalyst composition in liquid form into the reaction zone, and c) withdrawing polymeric product

from the reaction zone. The liquid form catalyst composition comprises a catalyst precursor such as a metallocene and, if required, a cocatalyst that are liquids in their neat form or dissolved or dispersed in a suitable solvent.

Unsupported, liquid form catalyst compositions have a number of practical benefits. Unsupported catalyst compositions avoid the costs associated with support material and its preparation, and they provide for the realization of a very high catalyst surface area to volume ratio. Furthermore, unsupported catalyst compositions produce polymers having a much lower residual ash content than polymers produced using supported catalyst compositions.

Although unsupported, liquid form catalyst compositions containing single site catalyst precursors have good activity, it is often necessary to adjust their activities to suit polymerization process conditions. To this end, applicants have discovered that the activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor with an activating cocatalyst outside of a polymerization reactor may be adjusted by varying one or more of: a) the period of time the single site catalyst precursor and the activating cocatalyst are contacted; b) the concentrations of the single site catalyst precursor and the activating cocatalyst during contacting; c) the mole ratio of the single site catalyst precursor to the activating cocatalyst during contacting; d) the temperature during contacting; and e) the degree of mixing of the single site catalyst precursor and the activating cocatalyst.

SUMMARY OF THE INVENTION

The invention provides a method of controlling the olefin polymerization activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor with an activating cocatalyst outside of a polymerization reactor for a period of time at concentrations, a mole ratio, and a temperature, which method comprises adjusting at least one of: a) the period of time the single site catalyst precursor and the activating cocatalyst are contacted; b) the concentrations of the single site catalyst precursor and the activating cocatalyst during contacting; c) the mole ratio of the single site catalyst precursor to the activating cocatalyst during contacting; d) the temperature during contacting; and e) the degree of mixing of the catalyst precursor and the activating cocatalyst.

The invention also provides a process for the production of an olefin polymer, which comprises contacting at least one olefin monomer under polymerization conditions with an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor with an activating cocatalyst outside of a polymerization reactor for a period of time at concentrations, a mole ratio, and a temperature wherein the activity of the catalyst composition is controlled by adjusting at least one of: a) the period of time the single site catalyst precursor and the activating cocatalyst are contacted; b) the concentrations of the single site catalyst precursor and the activating cocatalyst during contacting; c) the mole ratio of the single site catalyst precursor to the activating cocatalyst during contacting; d) the temperature during contacting; and e) the degree of mixing of the catalyst precursor and the activating cocatalyst.

DETAILED DESCRIPTION OF THE INVENTION

The invention is applicable to the polymerization of olefins by any polymerization mode that employs a solution catalyst. A variety of suspension, solution, slurry, and gas phase processes are known in the art, and the invention is not limited to any specific type of polymerization system. Generally, olefin polymerization temperatures range from about 0°C to about 200°C at atmospheric, subatmospheric, or superatmospheric pressures. Slurry or solution polymerization systems may utilize subatmospheric or superatmospheric pressures and temperatures in the range of about 40°C to about 110°C. A useful liquid phase polymerization system is described in U.S. Patent 3,324,095. Liquid phase polymerization systems generally comprise a reactor to which olefin monomer and catalyst composition are added, and which contains a liquid reaction medium for dissolving or suspending the polyolefin. The liquid reaction medium may consist of the bulk liquid monomer or an inert liquid hydrocarbon that is nonreactive under the polymerization conditions employed. Although such an inert liquid hydrocarbon need not function as a solvent for the catalyst composition or the polymer obtained by the process, it usually serves as solvent for the monomers employed in the polymerization. Among the inert liquid hydrocarbons suitable for this purpose are isopentane, hexane, cyclohexane, heptane, benzene, toluene, and the like. Reactive contact between the olefin monomer and the catalyst composition should be maintained by constant stirring or agitation. The reaction medium containing the olefin polymer product and unreacted olefin monomer is withdrawn from the reactor continuously. The olefin polymer product is separated, and the unreacted olefin monomer and liquid reaction medium are recycled into the reactor.

The invention is, however, especially useful with gas phase polymerization systems, with superatmospheric pressures in the range of 1 to 1000 psi, preferably 50 to 400 psi, most preferably 100 to 300 psi, and temperatures in the range of 30 to 130°C, preferably 65 to 110°C. Stirred or fluidized bed gas phase polymerization systems are particularly useful. Generally, a conventional gas phase, fluidized bed process is conducted by passing a stream containing one or more olefin monomers continuously through a fluidized bed reactor under reaction conditions and in the presence of the catalyst composition at a velocity sufficient to maintain a bed of solid particles in a suspended condition. A stream containing unreacted monomer is withdrawn from the reactor continuously, compressed, cooled, optionally partially or fully condensed, and recycled into the reactor. Product is withdrawn from the reactor and make-up monomer is added to the recycle stream. As desired for temperature control of the polymerization system, any gas inert to the catalyst composition and reactants may also be present in the gas stream. In addition, a fluidization aid such as carbon black, silica, clay, or talc may be used, as disclosed in U.S. Patent No. 4,994,534.

The polymerization system may comprise a single reactor or in two or more reactors in series, and is conducted substantially in the absence of catalyst poisons. Organometallic compounds may be employed as scavenging agents for poisons to increase the catalyst activity. Examples of scavenging agents are metal alkyls, preferably aluminum alkyls, most preferably triisobutylaluminum.

Conventional adjuvants may be used in the process, provided they do not interfere with the operation of the catalyst composition in forming the desired polyolefin. Hydrogen may be used as a chain

-6-

transfer agent in the process, in amounts up to about 10 moles of hydrogen per mole of total monomer feed.

Polyolefins that may be produced according to the invention include, but are not limited to, those made from olefin monomers such as ethylene and linear or branched higher alpha-olefin monomers containing 3 to about 20 carbon atoms. Homopolymers or interpolymers of ethylene and such higher alpha-olefin monomers, with densities ranging from about 0.86 to about 0.95 may be made. Suitable higher alpha-olefin monomers include, for example, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, and 3,5,5-trimethyl-1-hexene. Olefin polymers according to the invention may also be based on or contain conjugated or non-conjugated dienes, such as linear, branched, or cyclic hydrocarbon dienes having from about 4 to about 20, preferably 4 to 12, carbon atoms. Preferred dienes include 1,4-pentadiene, 1,5-hexadiene, 5-vinyl-2-norbornene, 1,7-octadiene, vinyl cyclohexene, dicyclopentadiene, butadiene, isobutylene, isoprene, ethylidene norbornene and the like. Aromatic compounds having vinyl unsaturation such as styrene and substituted styrenes, and polar vinyl monomers such as acrylonitrile, maleic acid esters, vinyl acetate, acrylate esters, methacrylate esters, vinyl trialkyl silanes and the like may be polymerized according to the invention as well. Specific polyolefins that may be made according to the invention include, for example, polyethylene, polypropylene, ethylene/propylene rubbers (EPR's), ethylene/propylene/diene terpolymers (EPDM's), polybutadiene, polyisoprene and the like.

The present invention is useful with unsupported, liquid form catalyst compositions comprising a single site catalyst precursor and

an activating cocatalyst. One or more than one single site catalyst precursor and activating cocatalyst may be employed in the catalyst composition.

As used herein, a single site catalyst precursor is a catalyst precursor that produces, when used with an appropriate activating cocatalyst in gas phase polymerization, a 0.950 density ethylene/1-hexene copolymer having a Crystallizable Chain Length Distribution Index (CCLDI) of less than 12. The Crystallizable Chain Length Distribution Index of a copolymer is determined using Temperature Rising Elution Fractionation (TREF). The analytical TREF method used is similar to that described in Wild et al., J. Polymer Sci., Poly. Phys. Ed., Vol. 20, p. 441 (1982). A dilute solution of the copolymer in a solvent such as 1,2,4-trichlorobenzene, at 1-4 mg/ml, is loaded at high temperature onto a packed column. The column is then allowed to slowly cool down at 0.1°C/min. to ambient temperature in a controlled manner so that the copolymer is crystallized onto the packing in the order of increasing branching (or decreasing crystallinity) with the decreasing temperature. The column is then heated in a controlled manner at 0.7°C/min to above 140°C with a constant solvent flow at 2ml/min through the column. The polymer fractions as they are eluted have decreasing branching (or increasing crystallinity) with the increasing temperature. An infrared concentration detector is used to monitor effluent concentrations. From the TREF temperature data, the branch frequency may be obtained for a given comonomer. Consequently, the main chain lengths between branches, expressed as L_w and L_n , may be calculated as follows. L_w is the weight average chain length between branches:

-8-

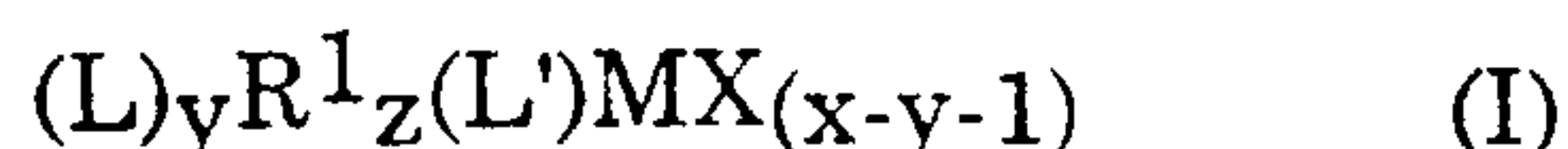
$$L_w = \sum_i w_i L_i$$

and L_n is the number average chain length between branches:

$$L_n = 1 / \sum_i (w_i / L_i),$$

wherein w_i is the weight fraction of the copolymer component i having an average backbone chain spacing L_i between two adjacent branch points.

The single site catalyst precursor may be a metallocene, i.e., an organometallic coordination complex of one or more π -bonded moieties in association with a metal atom from groups IIIB to VIII or the rare earth metals of the Periodic Table. Bridged and unbridged mono-, di-, and tri-cycloalkadienyl/metal compounds are the most common metallocenes, and generally are of the formula:



wherein M is a metal from groups IIIB to VIII or a rare earth metal of the Periodic Table; L and L' are the same or different and are π -bonded ligands coordinated to M , preferably cycloalkadienyl groups such as cyclopentadienyl, indenyl, or fluorenyl groups optionally substituted with one or more hydrocarbyl groups containing 1 to 20 carbon atoms; R^1 is selected from the group consisting of C_1 - C_4 substituted or unsubstituted alkylene radicals, dialkyl or diaryl germanium or silicon groups, and alkyl or aryl phosphine or amine radicals bridging L and L' ; each X is independently hydrogen, an aryl, alkyl, alkenyl, alkylaryl,

or arylalkyl radical having 1-20 carbon atoms, a hydrocarboxy radical having 1-20 carbon atoms, y is 0, 1, or 2; x is 1, 2, 3, or 4 depending upon the valence state of M; z is 0 or 1 and is 0 when y is 0; and $x-y \geq 1$.

Illustrative but non-limiting examples of metallocenes represented by formula I are dialkyl metallocenes such as bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diphenyl, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium methyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl, bis(cyclopentadienyl)zirconium di-neopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl)titanium phenyl chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)titanium methyl bromide; the trialkyl metallocenes such as cyclopentadienyl titanium trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium trineopentyl, cyclopentadienyl zirconium trimethyl, cyclopentadienyl hafnium triphenyl, cyclopentadienyl hafnium trineopentyl, and cyclopentadienyl hafnium trimethyl; monocyclopentadienyl titanocenes such as pentamethylcyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium trichloride, bis(pentamethylcyclopentadienyl)titanium diphenyl; the carbene

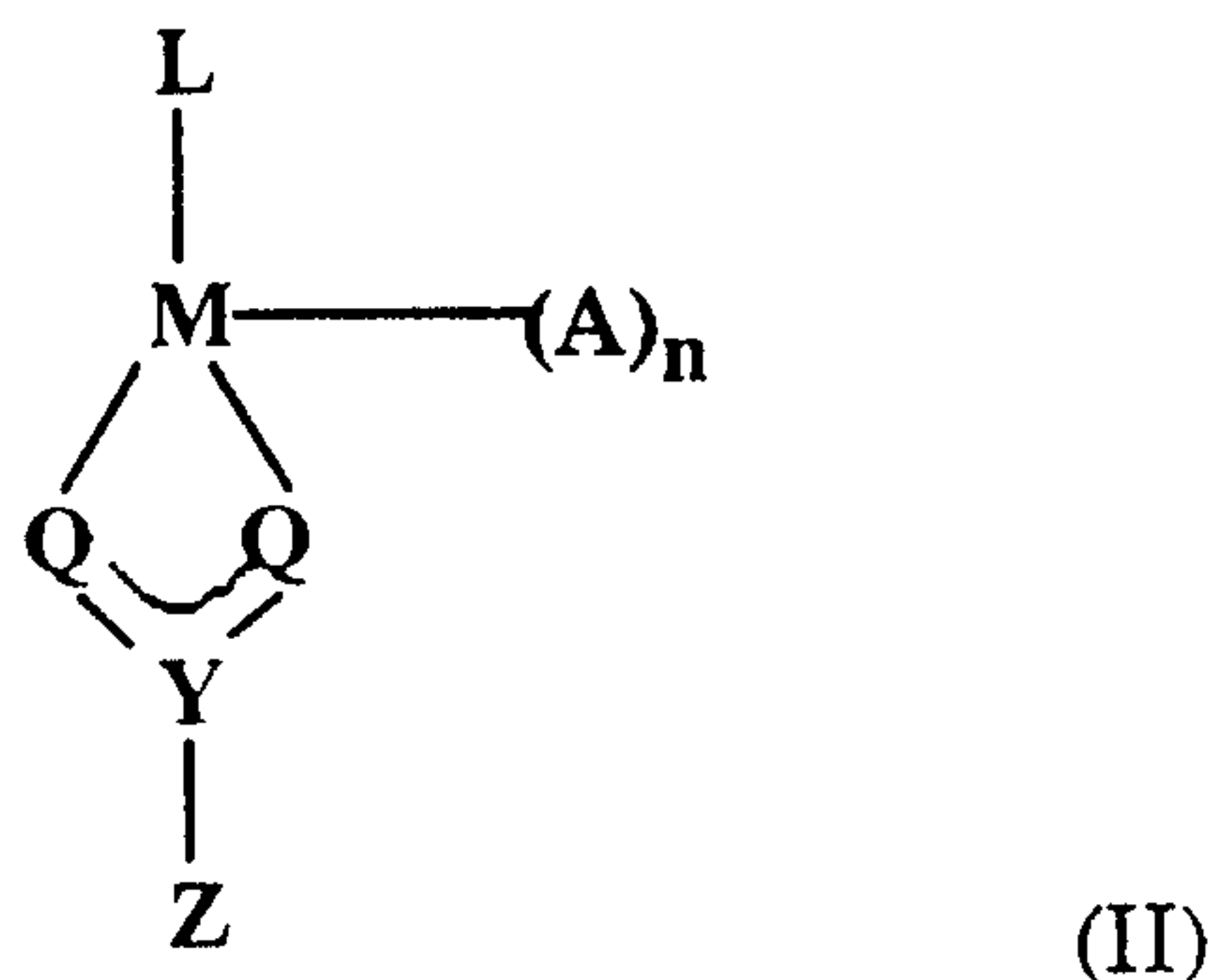
represented by the formula bis(cyclopentadienyl)titanium=CH₂ and derivatives of this reagent; substituted bis(cyclopentadienyl)titanium (IV) compounds such as bis(indenyl)titanium diphenyl or dichloride, bis(methylcyclopentadienyl)titanium diphenyl or dihalides; dialkyl, trialkyl, tetraalkyl and pentaalkyl cyclopentadienyl titanium compounds such as bis(1,2-dimethylcyclopentadienyl)titanium diphenyl or dichloride, bis(1,2-diethylcyclopentadienyl)titanium diphenyl or dichloride; silicon, phosphine, amine or carbon bridged cyclopentadiene complexes such as dimethyl silyldicyclopentadienyl titanium diphenyl or dichloride, methyl phosphine dicyclopentadienyl titanium diphenyl or dichloride, methylenedicyclopentadienyl titanium diphenyl or dichloride and other dihalide complexes, and the like, as well as isopropyl(cyclopentadienyl)(fluorenyl)zirconium dichloride, isopropyl(cyclopentadienyl) (octahydrofluorenyl)zirconium dichloride, diphenylmethylenecyclopentadienyl(fluorenyl)zirconium dichloride, diisopropylmethylenecyclopentadienyl(fluorenyl)zirconium dichloride, diisobutylmethylenecyclopentadienyl(fluorenyl)zirconium dichloride, ditertbutylmethylenecyclopentadienyl(fluorenyl)zirconium dichloride, cyclohexylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride, diisopropylmethylenecyclopentadienyl(2,5-dimethylcyclopentadienyl)(fluorenyl)-zirconium dichloride, isopropyl(cyclopentadienyl)(fluorenyl)-hafnium dichloride, diphenylmethylenecyclopentadienyl(fluorenyl)hafnium dichloride, diisopropylmethylenecyclopentadienyl(fluorenyl)hafnium dichloride, diisobutylmethylenecyclopentadienyl(fluorenyl)hafnium dichloride, ditertbutylmethylenecyclopentadienyl(fluorenyl)hafnium dichloride, cyclohexylidene(cyclopentadienyl)(fluorenyl)hafnium dichloride, diisopropylmethylenecyclopentadienyl(2,5-

dimethylcyclopentadienyl)(fluorenyl)hafnium dichloride,
isopropyl(cyclopentadienyl)(fluorenyl)titanium dichloride,
diphenylmethylenecyclopentadienyl)(fluorenyl)titanium dichloride,
diisopropylmethylenecyclopentadienyl)-(fluorenyl)titanium dichloride,
diisobutylmethylenecyclopentadienyl)(fluorenyl)titanium dichloride,
ditertbutylmethylenecyclopentadienyl)(fluorenyl)titanium dichloride,
cyclohexylidene(cyclopentadienyl)(fluorenyl)titanium dichloride,
diisopropylmethylenecyclopentadienyl)-
(fluorenyl)titanium dichloride, racemic-ethylene bis (1-indenyl)
zirconium (IV) dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-
indenyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (1-
indenyl) zirconium (IV) dichloride, racemic-dimethylsilyl bis (4,5,6,7-
tetrahydro-1-indenyl) zirconium (IV) dichloride, racemic-1,1,2,2-
tetramethylsilanylene bis (1-indenyl) zirconium (IV) dichloride,
racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-
indenyl) zirconium (IV), dichloride, ethylidene (1-indenyl
tetramethylcyclopentadienyl) zirconium (IV) dichloride, racemic-
dimethylsilyl bis (2-methyl-4-t-butyl-1-cyclopentadienyl) zirconium
(IV) dichloride, racemic-ethylene bis (1-indenyl) hafnium (IV)
dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium
(IV) dichloride, racemic-dimethylsilyl bis (1-indenyl) hafnium (IV)
dichloride, racemic-dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl)
hafnium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1-
indenyl) hafnium (IV) dichloride, racemic-1,1,2,2-
tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV),
dichloride, ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-
cyclopentadienyl) hafnium (IV) dichloride, racemic-ethylene bis (1-
indenyl) titanium (IV) dichloride, racemic-ethylene bis (4,5,6,7-

-12-

tetrahydro-1-indenyl) titanium (IV) dichloride, racemic- dimethylsilyl bis (1-indenyl) titanium (IV) dichloride, racemic- dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1-indenyl) titanium (IV) dichloride racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, and ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-cyclopentadienyl) titanium (IV) dichloride.

A preferred class of single site catalyst precursors for use in the invention are complexes of transition metals, substituted or unsubstituted pi-bonded ligands, and heteroallyl moieties, such as those described in U.S. Patent No. 5,527,752. Preferably, such complexes have one of the following formulas:



wherein:

M is a transition metal, preferably Zr or Hf;

L is a substituted or unsubstituted, pi-bonded ligand coordinated to M, preferably a cycloalkadienyl ligand;

each Q is independently selected from the group consisting of -O-, -NR-, -CR₂- and -S-, preferably oxygen;

Y is either C or S, preferably carbon;

Z is selected from the group consisting of -OR, -NR₂, -CR₃, -SR, -SiR₃, -PR₂, -H, and substituted or unsubstituted aryl groups, with the proviso that when Q is -NR- then Z is selected from the group

-13-

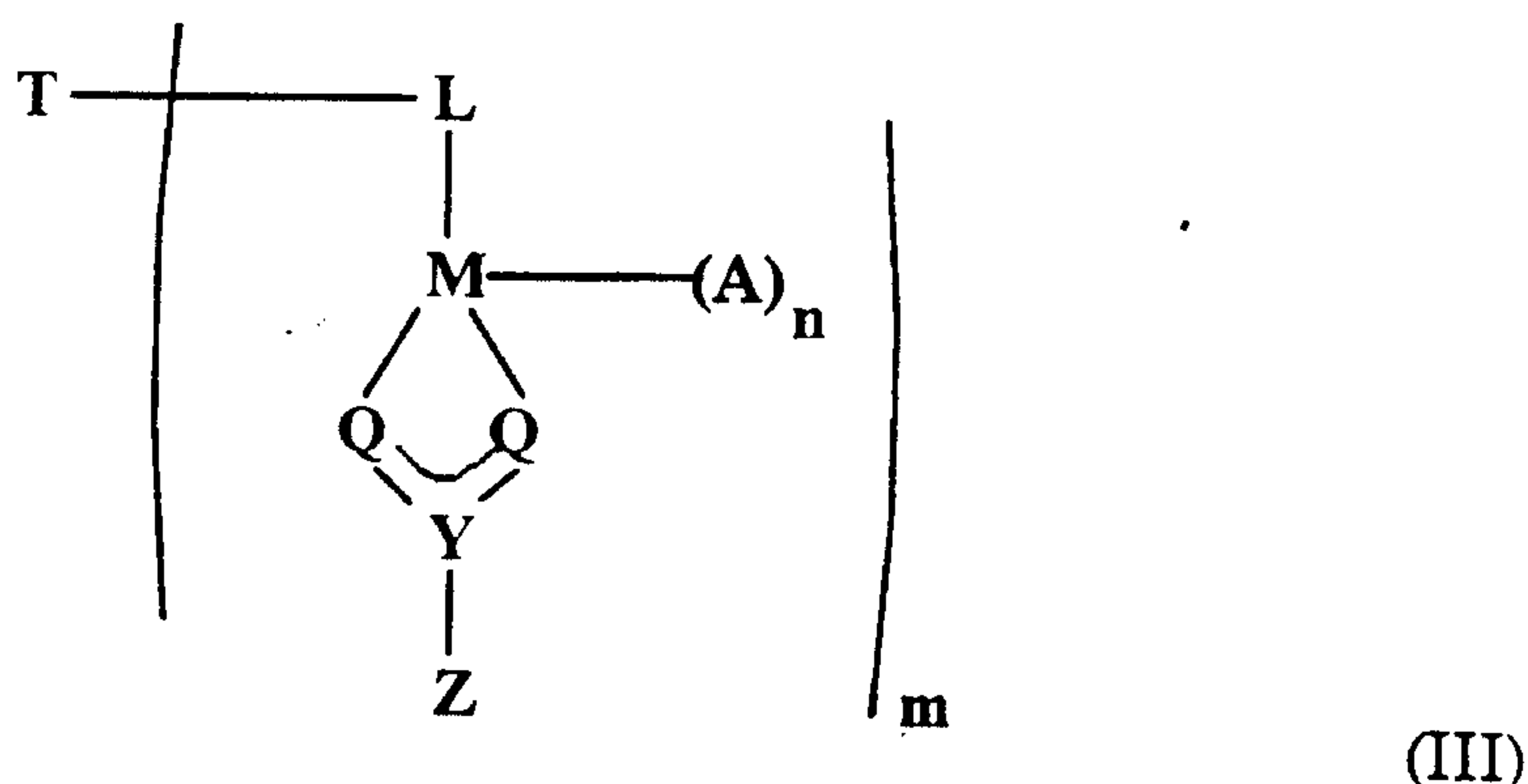
consisting of -OR, -NR₂, -SR, -SiR₃, -PR₂ and -H, preferably Z is selected from the group consisting of -OR, -CR₃ and -NR₂;

n is 1 or 2;

A is a univalent anionic group when n is 2 or A is a divalent anionic group when n is 1, preferably A is a carbamate, carboxylate, or other heteroallyl moiety described by the Q, Y and Z combination; and

each R is independently a group containing carbon, silicon, nitrogen, oxygen, and/or phosphorus where one or more R groups may be attached to the L substituent, preferably R is a hydrocarbon group containing from 1 to 20 carbon atoms, most preferably an alkyl, cycloalkyl, or an aryl group and one or more may be attached to the L substituent;

or



wherein:

M is a transition metal, preferably Zr or Hf;

L is a substituted or unsubstituted, pi-bonded ligand coordinated to M, preferably a cycloalkadienyl ligand;

each Q is independently selected from the group consisting of -O-, -NR-, -CR₂- and -S-, preferably oxygen;

-14-

Y is either C or S, preferably carbon;

Z is selected from the group consisting of -OR, -NR₂, -CR₃, -SR, -SiR₃, -PR₂, -H, and substituted or unsubstituted aryl groups, with the proviso that when Q is -NR- then Z is selected from the group consisting of -OR, -NR₂, -SR, -SiR₃, -PR₂ and -H, preferably Z is selected from the group consisting of -OR, -CR₃ and -NR₂;

n is 1 or 2;

A is a univalent anionic group when n is 2 or A is a divalent anionic group when n is 1, preferably A is a carbamate, carboxylate, or other heteroallyl moiety described by the Q, Y and Z combination;

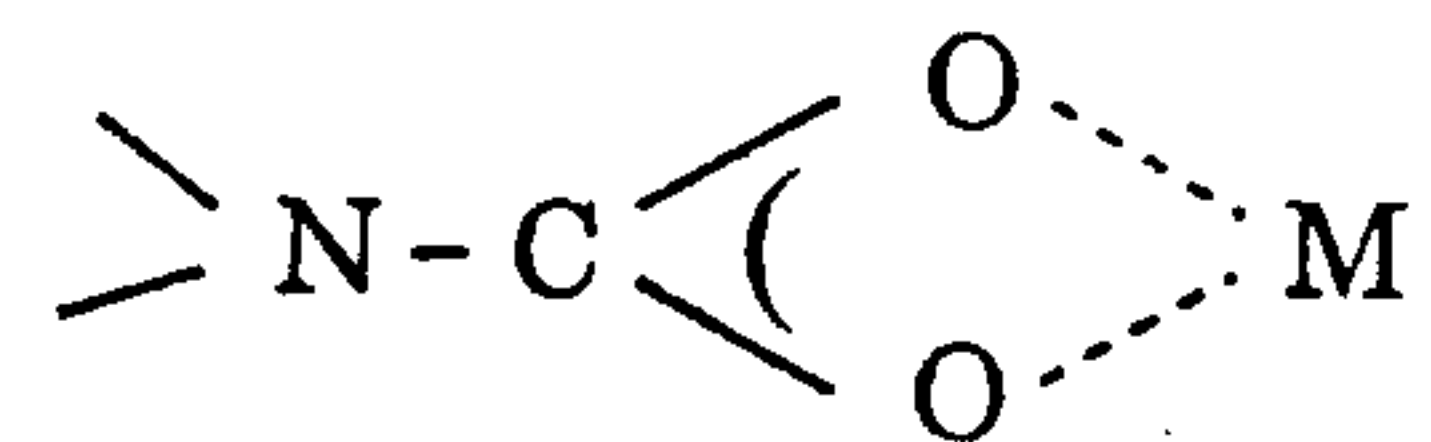
each R is independently a group containing carbon, silicon, nitrogen, oxygen, and/or phosphorus where one or more R groups may be attached to the L substituent, preferably R is a hydrocarbon group containing from 1 to 20 carbon atoms, most preferably an alkyl, cycloalkyl, or an aryl group and one or more may be attached to the L substituent;

T is a bridging group selected from the group consisting of alkylene and arylene groups containing from 1 to 10 carbon atoms optionally substituted with carbon or heteroatoms, germanium, silicone and alkyl phosphine; and

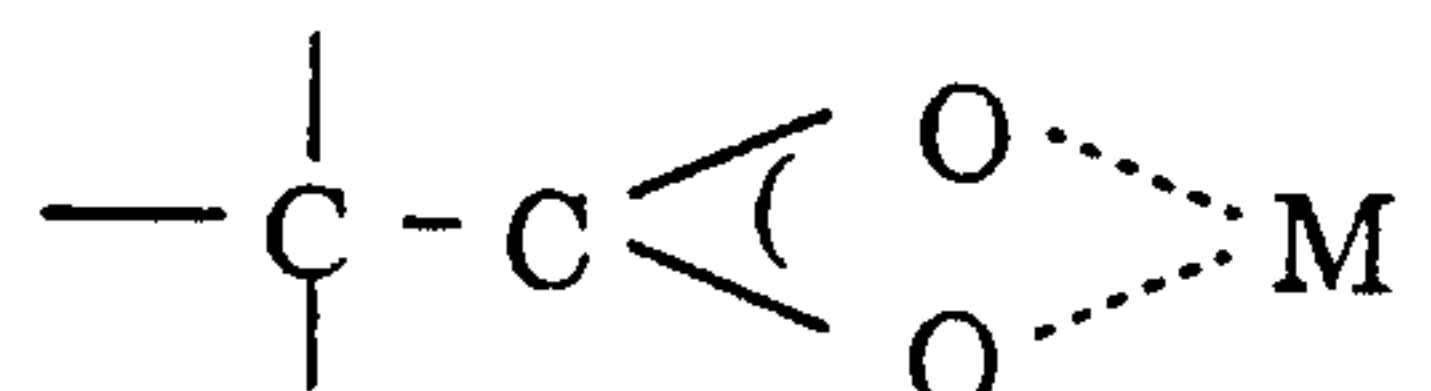
m is 2 to 7, preferably 2 to 6, most preferably 2 or 3.

In formulas II and III, the supportive substituent formed by Q, Y and Z is a uncharged polydentate ligand exerting electronic effects due to its high polarizability, similar to the cyclopentadienyl group. In the most preferred embodiments of this invention, the disubstituted carbamates,

-15-



and the carboxylates



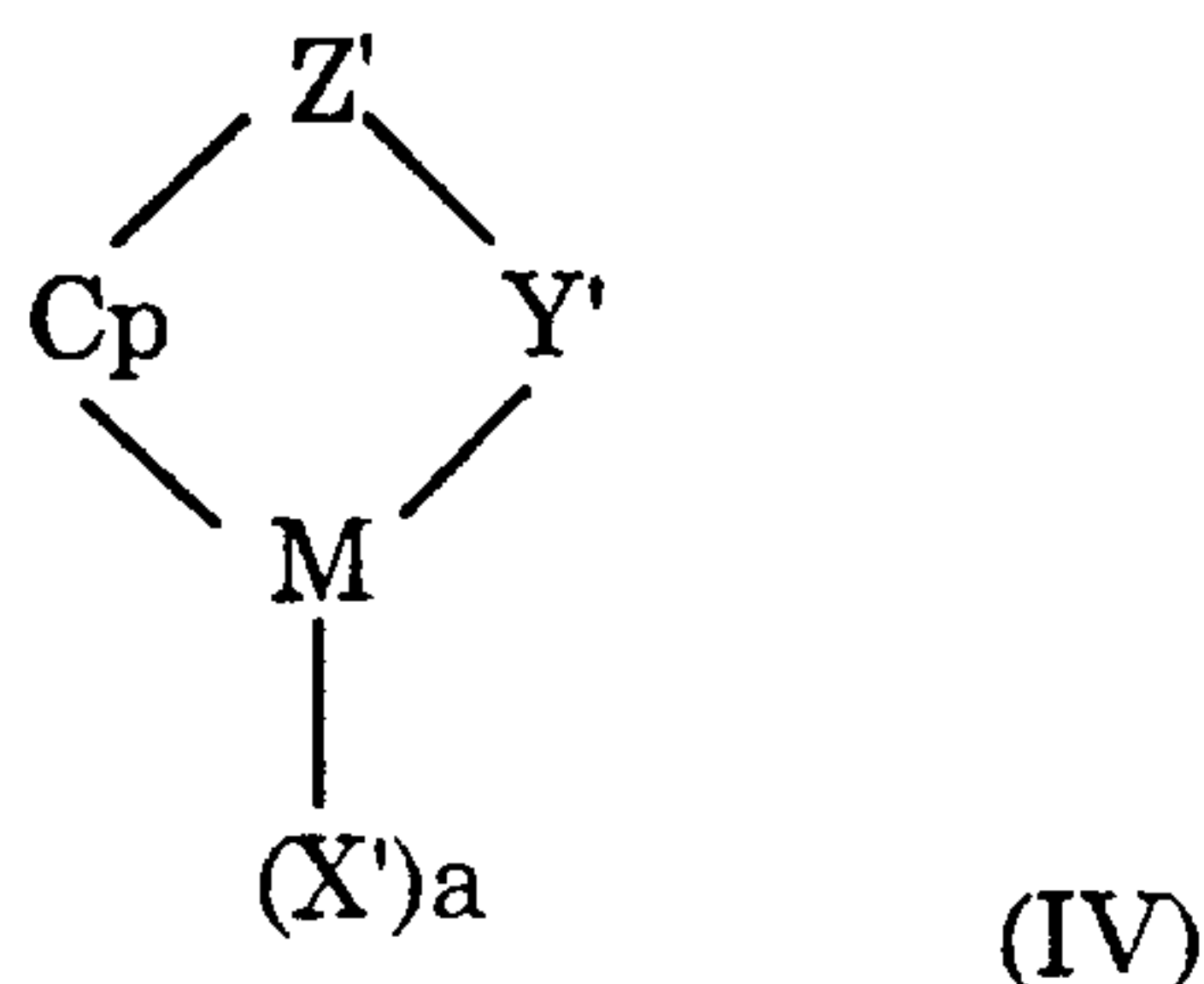
are employed.

Examples of complexes according to formulas II and III include indenyl zirconium tris(diethylcarbamate), indenyl zirconium tris(trimethylacetate), indenyl zirconium tris(p-toluate), indenyl zirconium tris(benzoate), (1-methylindenyl) zirconium tris(trimethylacetate), (2-methylindenyl) zirconium tris(diethylcarbamate), (methylcyclopentadienyl) zirconium tris(trimethylacetate), cyclopentadienyl tris(trimethylacetate), tetrahydroindenyl zirconium tris(trimethylacetate), and (pentamethylcyclopentadienyl) zirconium tris(benzoate). Preferred examples are indenyl zirconium tris(diethylcarbamate), indenyl zirconium tris(trimethylacetate), and (methylcyclopentadienyl) zirconium tris(trimethylacetate).

One method of manufacturing a preferred catalyst precursor, indenyl zirconium tris(diethylcarbamate), is to first react a source of cycloalkadienyl ligand with a metal compound of the formula $\text{M}(\text{NR}_2)_4$, in which M and R are defined above, to introduce the cycloalkadienyl ligand onto the metal compound. The resulting product is then dissolved in an inert solvent, such as toluene, and the heterocumulene CO_2 is contacted with the dissolved product to insert into one or more M-NR₂ bonds to form a carbamate.

-16-

Another type of single site catalyst precursor that can be used in accordance with the invention is a constrained geometry catalyst of the formula:



wherein:

M is a metal of groups IIIB to VIII of the Periodic Table;

Cp is a cyclopentadienyl or substituted cyclopentadienyl group bound in an η^5 mode to M;

Z' is a moiety comprising boron, or a member of group IVB of the Periodic Table and optionally sulfur or oxygen, the moiety having up to 20 non-hydrogen atoms, and optionally Cp and Z' together form a fused ring system;

X' is an anionic ligand group or a neutral Lewis base ligand group having up to 30 non-hydrogen atoms;

a is 0, 1, 2, 3 or 4 depending on the valence of M; and

Y' is an anionic or non-anionic ligand group bonded to Z' and M and is nitrogen, phosphorus, oxygen or sulfur having up to 20 non-hydrogen atoms, and optionally Y' and Z' together form a fused ring system.

Constrained geometry catalysts are well known to those skilled in the art and are disclosed in, for example, U.S. Patent Nos. 5,026,798 and 5,055,438 and published European Application No. 0 416 815 A2.

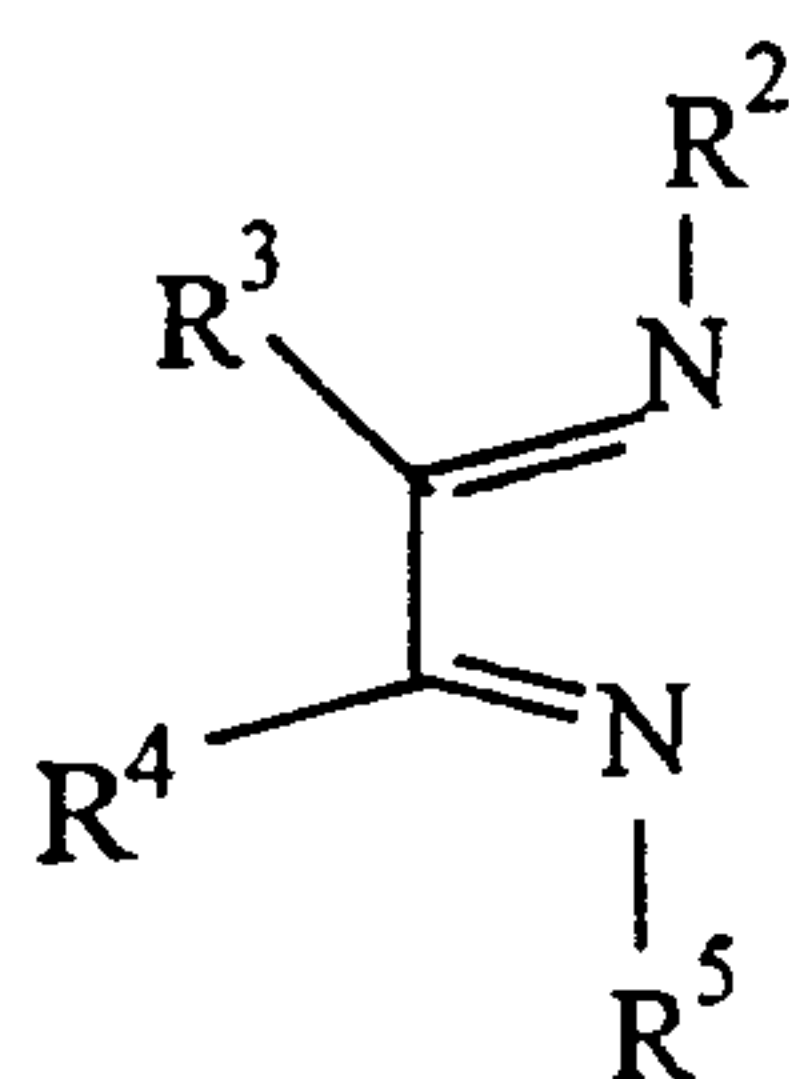
-17-

Illustrative but non-limiting examples of substituents Z', Cp, Y', X' and M in formula IV are:

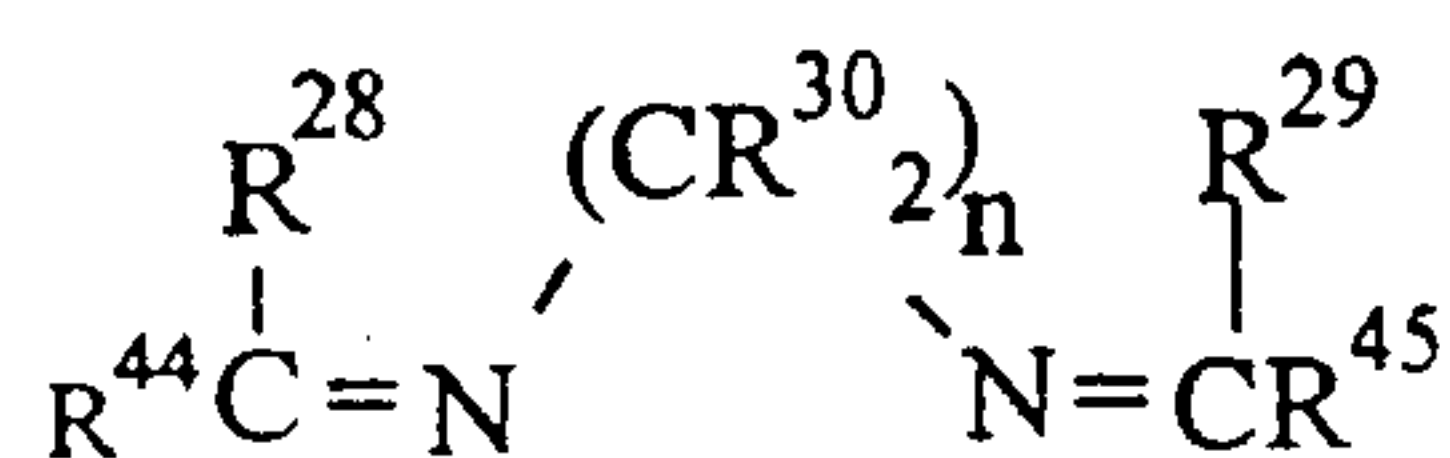
Z'	Cp	Y'	X'	M
dimethyl-silyl	cyclopentadienyl	t-butylamido	chloride	titanium
methyl-phenylsilyl	fluorenyl	phenylamido	methyl	zirconium
diphenyl-silyl	indenyl	cyclohexylamido		hafnium
tetramethyl-ethylene		oxo		
ethylene	tetramethyl-cyclopentadienyl			
diphenyl-methylene				

The invention is also useful with a third class of single site catalyst precursors, di(imine) metal complexes, as described in PCT Application No. WO 96/23010. Such di(imine) metal complexes are transition metal complexes of bidentate ligands selected from the group consisting of:

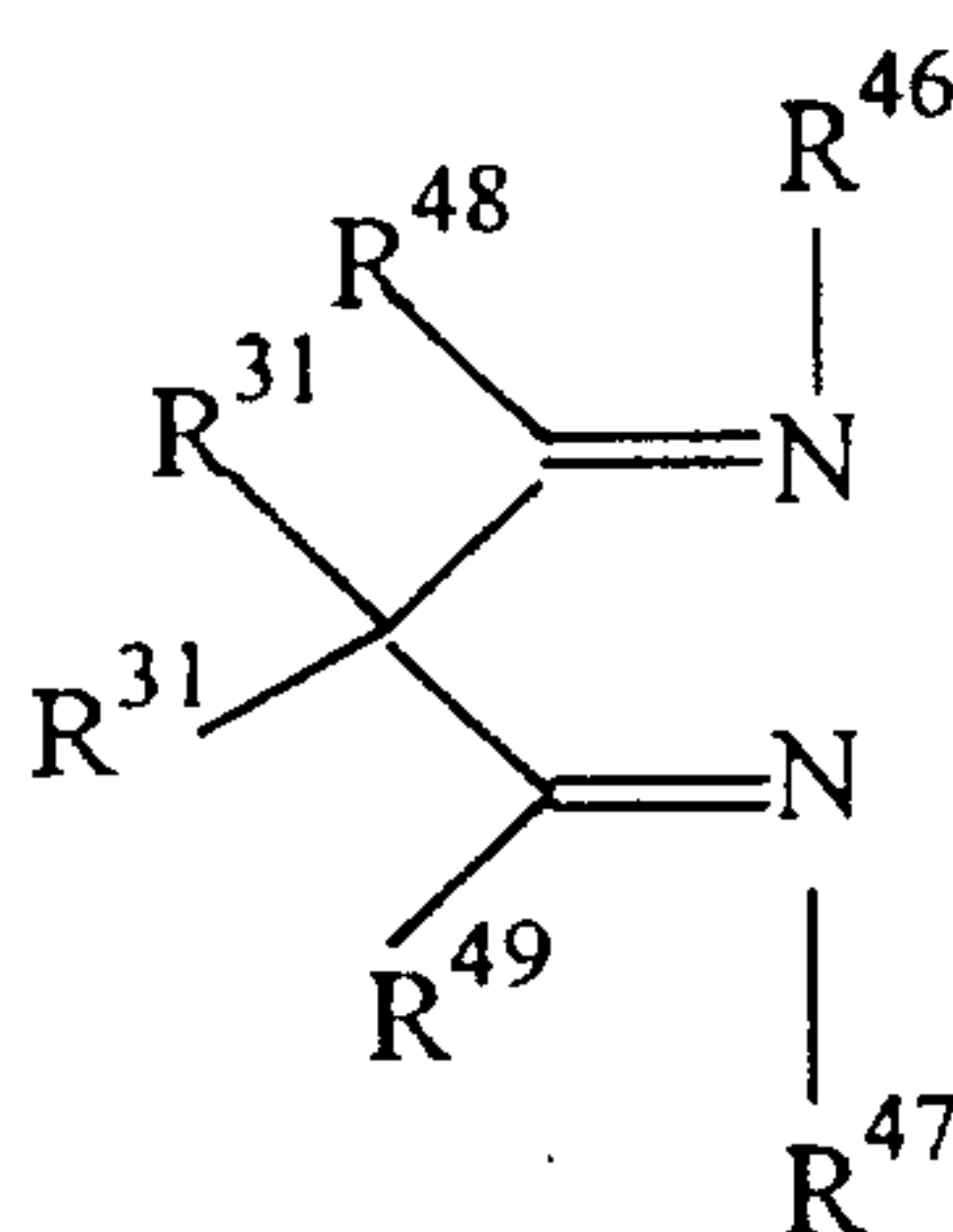
-18-



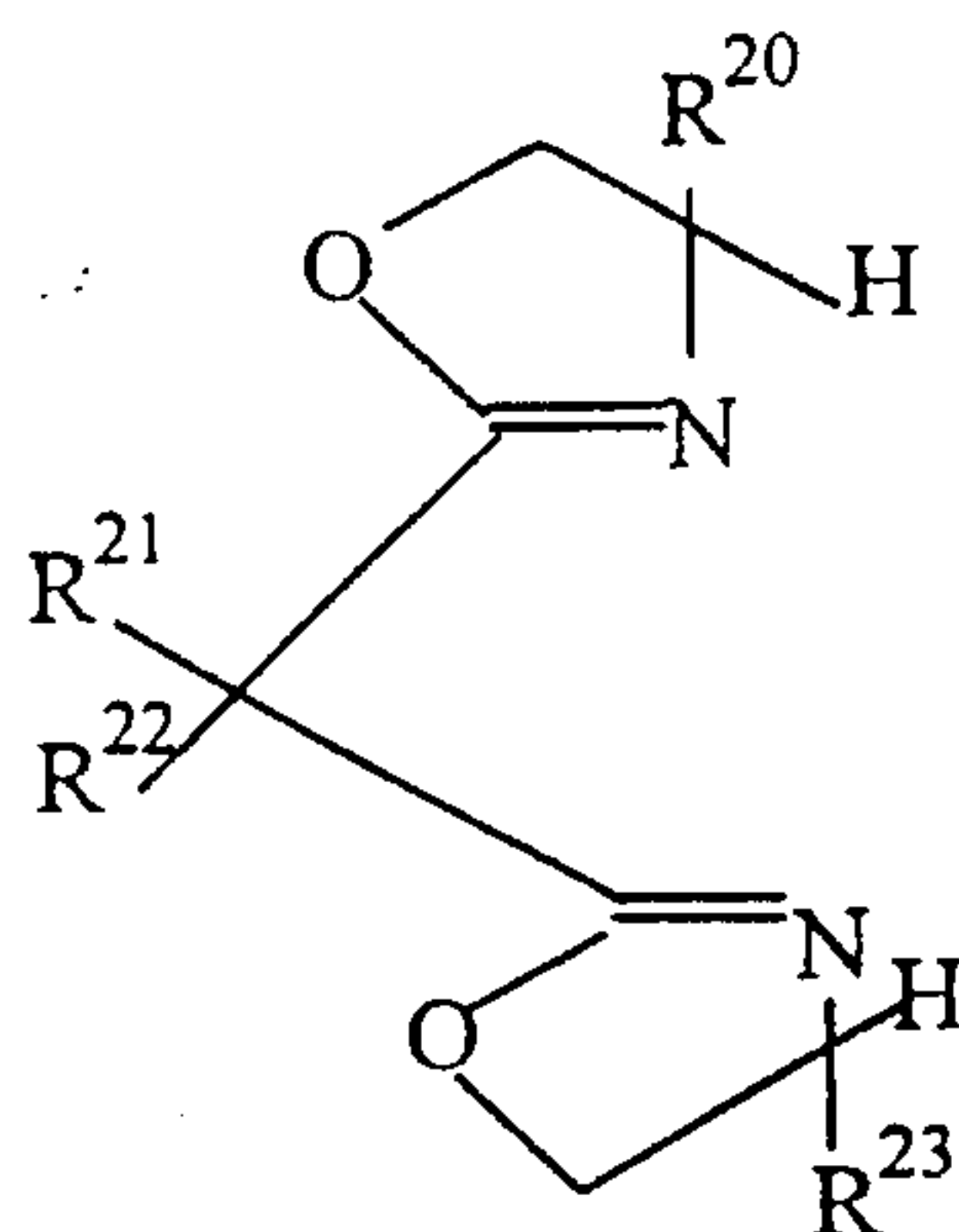
(V)



(VI)



(VII), and



(VIII)

wherein said transition metal is selected from the group consisting of Ti, Zr, Sc, V, Cr, a rare earth metal, Fe, Co, Ni, and Pd;

-19-

R² and R⁵ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R³ and R⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R³ and R⁴ taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring;

R⁴⁴ is hydrocarbyl or substituted hydrocarbyl, and R²⁸ is hydrogen, hydrocarbyl or substituted hydrocarbyl or R⁴⁴ and R²⁸ taken together form a ring;

R⁴⁵ is hydrocarbyl or substituted hydrocarbyl, and R²⁹ is hydrogen, substituted hydrocarbyl or hydrocarbyl, or R⁴⁵ and R²⁹ taken together form a ring;

each R³⁰ is independently hydrogen, substituted hydrocarbyl or hydrocarbyl, or two of R³⁰ taken together form a ring;

each R³¹ is independently hydrogen, hydrocarbyl or substituted hydrocarbyl;

R⁴⁶ and R⁴⁷ are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it;

R⁴⁸ and R⁴⁹ are each independently hydrogen, hydrocarbyl, or substituted hydrocarbyl;

R²⁰ and R²³ are independently hydrocarbyl or substituted hydrocarbyl;

R²¹ and R²² are independently hydrogen, hydrocarbyl or substituted hydrocarbyl; and

-20-

n is 2 or 3;

and provided that:

said transition metal also has bonded to it a ligand that may be displaced by or added to the olefin monomer being polymerized; and

when the transition metal is Pd, said bidentate ligand is (V), (VII) or (VIII).

The activating cocatalyst is capable of activating the catalyst precursor. Preferably, the activating cocatalyst is one of the following:

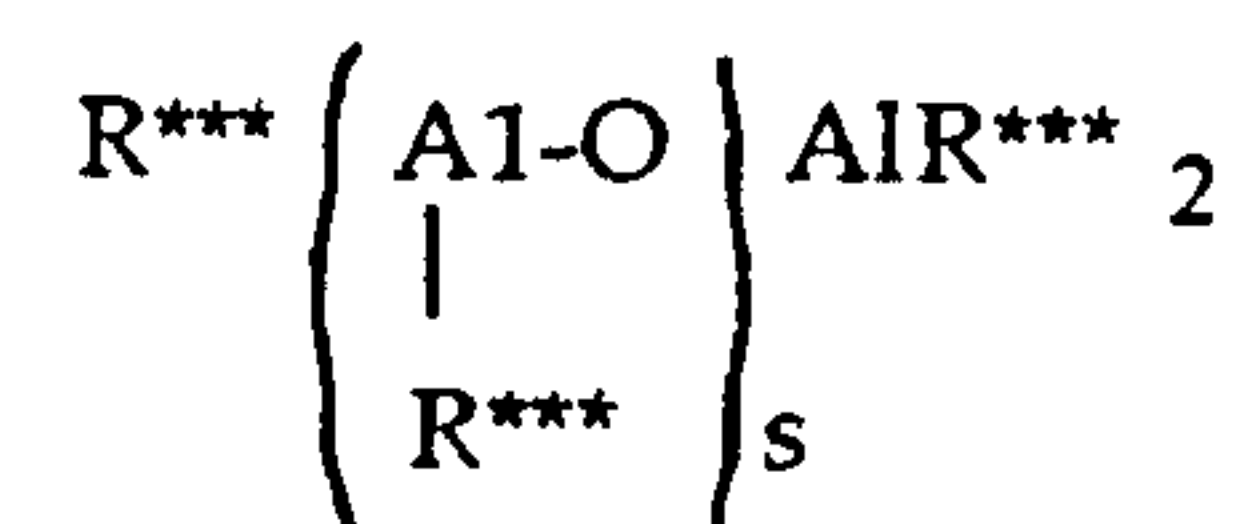
(a) branched or cyclic oligomeric poly(hydrocarbylaluminum oxide)s which contain repeating units of the general formula $-(Al(R^*)O)-$, where R^* is hydrogen, an alkyl radical containing from 1 to about 12 carbon atoms, or an aryl radical such as a substituted or unsubstituted phenyl or naphthyl group; (b) ionic salts of the general formula $[A^+][BR^{**}_4^-]$, where A^+ is a cationic Lewis or Bronsted acid capable of abstracting an alkyl, halogen, or hydrogen from the metallocene catalysts, B is boron, and R^{**} is a substituted aromatic hydrocarbon, preferably a perfluorophenyl radical; (c) boron alkyls of the general formula BR^{**}_3 , where R^{**} is as defined above; or mixtures thereof.

Ionic salts of the general formula $[A^+][BR^{**}_4^-]$ and boron alkyls can optionally be used with alkylating agents such as alkyl aluminum and alkyl lithium compounds.

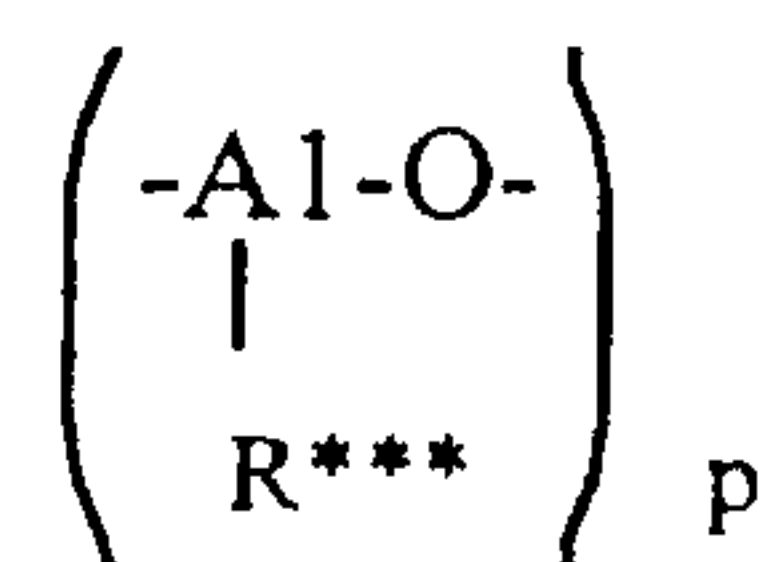
More preferably, the activating cocatalyst is a branched or cyclic oligomeric poly(hydrocarbylaluminum oxide) or a boron alkyl. Most preferably, the activating cocatalyst is an aluminoxane such as methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), or a boron alkyl.

-21-

Aluminoxanes are well known in the art and comprise oligomeric linear alkyl aluminoxanes represented by the formula:



and oligomeric cyclic alkyl aluminoxanes of the formula:



wherein s is 1-40, preferably 10-20; p is 3-40, preferably 3-20; and R^{***} is an alkyl group containing 1 to 12 carbon atoms, preferably methyl or an aryl radical such as a substituted or unsubstituted phenyl or naphthyl radical. Aluminoxanes may be prepared in a variety of ways well known in the art.

The catalyst composition is in unsupported, liquid form, for example as described in U.S. Patent 5,317,036. The catalyst composition is prepared by contacting outside of the polymerization reactor a single site catalyst precursor that is in the form of a neat liquid, a solution, or a dispersion, with an activating cocatalyst that is also in the form of a neat liquid, a solution, or a dispersion. The resulting unsupported, liquid form catalyst composition is then fed to the polymerization reactor.

The period of time the single site catalyst and the activating cocatalyst are contacted in general varies with the single site catalyst concentration and additive electrophonicity. Typically, contacting of the

-22-

single site catalyst precursor and activating cocatalyst takes place for a period of time ranging from about 0.001 to about 1000 minutes, preferably about 0.1 to 100 minutes, more preferably from about 1 to about 50 minutes.

When the cocatalyst is a branched or cyclic oligomeric poly(hydrocarbylaluminum oxide), the mole ratio of activating cocatalyst (based on aluminum) to single site catalyst precursor (based on the metal) is generally in the range of from about 2:1 to about 100,000:1, preferably in the range of from about 10:1 to about 10,000:1, and most preferably in the range of from about 50:1 to about 2,000:1. When the activating cocatalyst is an ionic salt of the formula $[A^+][BR^{**}_4^-]$ or a boron alkyl of the formula BR^{**}_3 , the mole ratio of activating cocatalyst (based on boron) to single site catalyst precursor (based on the metal) is generally in the range of from about 0.5:1 to about 10:1, preferably in the range of from about 1:1 to about 5:1.

The concentration of single site catalyst precursor in the mixture of single site catalyst precursor and activating cocatalyst (which mixture contains the single site catalyst precursor, the activating cocatalyst, and optionally one or more solvents) during contacting ranges from about 0.001 to about 30 weight percent, preferably about 0.01 to about 20 weight percent, more preferably about 0.10 to about 10 weight percent. When the cocatalyst is a branched or cyclic oligomeric poly(hydrocarbylaluminum oxide), the concentration of activating cocatalyst in the mixture of single site catalyst precursor and activating cocatalyst during contacting ranges from about 0.03 to about 50 weight percent, preferably about 0.10 to about 30 weight percent, more preferably from about 1 to about 25 weight percent. When the activating cocatalyst is an ionic salt of the

-23-

formula $[A^+][BR^{**}_4^-]$ or a boron alkyl of the formula BR^{**}_3 , the concentration of activating cocatalyst in the mixture of single site catalyst precursor and activating cocatalyst during contacting ranges from about 0.001 to about 30 weight percent, preferably about 0.01 to about 20 weight percent, more preferably from about 0.1 to about 10 weight percent.

The temperature during contacting of the single site catalyst precursor and the activating cocatalyst is typically from about -20 to about 80° C, preferably from about 0 to about 60° C. The pressure is typically up to about 300 psi, preferably up to about 20 psi.

According to the invention, the activity of the unsupported, liquid form catalyst composition may be controlled as desired by adjusting: a) the period of time the single site catalyst precursor and the activating cocatalyst are contacted; b) the concentrations of the single site catalyst precursor and the activating cocatalyst during contacting; c) the mole ratio of the single site catalyst precursor to the activating cocatalyst during contacting; d) the temperature during contacting; and e) the degree of mixing of the catalyst precursor and the activating cocatalyst. One of these factors may be adjusted alone to vary the activity of the catalyst composition. Alternatively, two or more of the factors may be adjusted simultaneously or successively to modify the activity of the catalyst composition. The activity of the catalyst composition may be increased or decreased by adjusting one or more of these factors.

The nature of both the single site catalyst precursor and the activating cocatalyst determine in part the magnitude and direction in which each of the factors should be adjusted in order to achieve a given activity for the catalyst composition. In addition, whether one desires

-24-

to increase or decrease the activity of the catalyst composition also determines the magnitude and direction in which each of the factors should be adjusted.

In a preferred embodiment of the invention, the activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor of formula II or III above with an aluminoxane activating cocatalyst outside a polymerization reactor is adjusted up or down by at least about 20% by performing one of the following during contacting of the single site catalyst precursor of formula II or III with aluminoxane: a) changing the period of time of contacting by at least about 50 %, b) changing the concentrations of the single site catalyst precursor and the aluminoxane by at least about 30% during contacting, c) changing the mole ratio of aluminoxane to single site catalyst precursor by at least about 20% during contacting, or d) changing the temperature 2-10° C during contacting.

In a highly preferred embodiment of the invention, the activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor of formula II or III above with an aluminoxane activating cocatalyst outside a polymerization reactor is changed by at least about 50% by changing the period of time of contacting the single site catalyst precursor with the aluminoxane by at least about 75%. Most preferably, the activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor of formula II or III above with an aluminoxane activating cocatalyst outside a polymerization reactor is changed by at least about 100% by changing the period of time of

-25-

contacting the single site catalyst precursor with the aluminoxane by at least about 100%.

In another embodiment of the invention, the activity of the unsupported, liquid form catalyst composition is increased by precontacting the single site catalyst precursor with a weakly coordinating electron donor prior to contacting it with the activating cocatalyst. This forms a reaction product between the single site catalyst precursor and the electron donor. Such precontacting typically takes place from about 0.01 to about 1000 minutes, preferably about 0.1 to about 100 minutes, more preferably about 1 to about 50 minutes. Precontacting takes place at temperatures of about -20 to about 80° C, preferably about 0 to about 60° C, and pressures of up to about 300 psi, preferably up to about 20 psi. Precontacting of the single site catalyst precursor with a weakly coordinating electron donor typically increases the overall activity of the unsupported, liquid form catalyst composition by at least about 50%.

Weakly coordinating electron donors are those capable of weakly binding to the metal atom in the single site catalyst precursor but readily displaced under the conditions of the olefin polymerization reaction. It is important that the weakly coordinating electron donor not substantially polymerize under the conditions of precontacting with the single site catalyst precursor or subsequent contacting with the activating cocatalyst. Preferably, the electron donor does not polymerize at all during precontacting or contacting. Examples of weakly coordinating electron donors are olefins and diolefins, such as 1,1-disubstituted olefins and alpha-olefins, including 1-hexene, butene, and isobutylene; amines such as tertiary amines including pyridines; ethers, especially hindered ethers such as methyl t-butyl ether, and

-26-

phosphines such as trimethylphosphine. Preferably, the electron donor is an olefin or diolefin, most preferably, the electron donor is selected from the group consisting of 1-hexene, butene and isobutylene.

The amount of electron donor required varies with the specific single site catalyst precursor and cocatalyst used. Typically, the mole ratio of electron donor to single site catalyst precursor is from about 1:10 to 10,000:1, preferably from about 1:2 to 5000:1, most preferably from about 1:1 to 1000:1. The electron donor may be neat or dissolved in an appropriate solvent such as isopentane, hexane, toluene, or the like.

The following examples further illustrate the invention.

Preparation of Indenyl Zirconium Tris(trimethylacetate) Solution

Catalyst precursor was prepared according to the general method described in U.S. Patent No. 5,527,752. A fresh stock catalyst solution (0.05 M) was prepared for each set of examples by dissolving 0.257 g of indenyl zirconium tris(trimethylacetate) in 10 mL of hexane.

Examples 1-8

In Examples 1-8, a series of unsupported, liquid form catalyst compositions were made by contacting indenyl zirconium tris(trimethylacetate) with modified methylaluminoxane (MMAO as a 1.91 M solution in heptane, 7.2 wt% aluminum, commercially available from Akzo Chemicals, Inc.) for periods of time varying from 2.5 to 30

-27-

minutes. The catalyst compositions were used for the copolymerization of ethylene and 1-hexene as follows.

In each Example, in a glove box containing prepurified nitrogen, 0.54 mL of the indenyl zirconium tris(trimethylacetate)solution (27 mmol) as prepared above was placed in a scintillation vial with a stir bar and 3.77 mL of hexane was then added via syringe. 0.69 mL of MMAO solution was then added to the catalyst precursor solution with vigorous stirring. The resulting solution was stirred between 2.5 and 30 minutes at ambient temperature.

During this time, a slurry phase, laboratory scale, stirred autoclave reactor was charged with 600 mL of dry hexane and 43 mL of 1-hexene and was heated to 55 °C under a nitrogen purge. Additional MMAO solution (0.5 mL, 0.95 mmol) was then added to the reactor via syringe to achieve a total reactor Al/ Zr mole ratio of 1000:1 for each polymerization run. After stirring for approximately 10 minutes, the reactor was charged with a 0.19 mL aliquot of the activated catalyst composition solution (1 mmol Zr), and was sealed, pressurized with ethylene (85 p.s.i.), and brought to 75 °C. Total polymerization time was 30 minutes.

The results in Table 1 below show that the activity of the unsupported, liquid phase, indenyl zirconium tris(trimethylacetate)/MMAO catalyst composition varied with the time of contact between the indenyl zirconium tris(trimethylacetate) and the MMAO. Activities are reported in (grams copolymer)/[(mmol Zr)(100 psi ethylene)(hour)].

TABLE 1

Example	Contact Time (min)	Activity
1	2.5	36941
2	3	66353
3	5	71059
4	10	66353
5	15	64706
6	20	32941
7	25	42353
8	30	10000

Examples 9-18

In Examples 9-18, a series of unsupported, liquid form catalyst compositions were made by precontacting indenyl zirconium tris(trimethylacetate) with 1-hexene and then contacting the resulting indenyl zirconium tris(trimethylacetate)/1-hexene reaction product with MMAO for periods of time varying from 3 to 1440 minutes.

Each of the catalyst compositions of Examples 9-18 were made in the same manner as Examples 1-8, except that in each case the indenyl zirconium tris(trimethylacetate) was precontacted with 0.5mL of 1-hexene prior to the addition of only 3.27mL of hexane. The resulting mixture was then contacted with 0.69 mL of the MMAO solution.

The catalyst compositions were used for the copolymerization of ethylene and 1-hexene as described in Examples 1-8. Activities are reported in (grams copolymer)/[(mmol Zr)(100 psi ethylene)(hour)].

TABLE 2

Example	Contact Time (min)	Activity
9	3	27765
10	5	51294
11	10	76235
12	15	85647
13	20	83059
14	25	67765
15	30	81176
16	60	69882
17	300	36706
18	1440	13647

The results in Table 2 show that the activity of the unsupported, liquid phase, indenyl zirconium tris(trimethylacetate)/MMAO catalyst composition, wherein the catalyst precursor has been precontacted with 1-hexene, varied with the time of contact between the indenyl zirconium tris(trimethylacetate) and the MMAO.

Example 19-24

In Examples 19-24, a series of unsupported, liquid form catalyst compositions were made by precontacting indenyl zirconium tris(trimethylacetate) with 1-hexene, and then contacting with MMAO at varying Al/Zr mole ratios. The catalyst compositions were used for the copolymerization of ethylene and 1-hexene as follows.

The catalyst compositions were prepared in a glove box containing prepurified nitrogen. In each Example, 0.38 mL of indenyl

-30-

zirconium tris(trimethylacetate) solution (19 mmol) was placed in a scintillation vial with a stir bar and 3.13 mL of hexene was added via syringe. Hexane and the desired amount of MMAO were then added to the stirred solution via syringe with vigorous stirring. The resulting solution was stirred for 30 minutes at ambient temperature.

During this time, a slurry phase, laboratory scale, stirred autoclave reactor was charged with 600 mL of dry hexane and 43 mL of 1-hexene and was heated to 55 °C under a nitrogen purge. Triisobutylaluminum (100 eq) was then added to the reactor via syringe to scavenge impurities. After stirring for approximately 10 minutes, the reactor was charged with a 1.33 mL aliquot of the activated catalyst composition solution (1 mmol Zr), and was sealed, pressurized with ethylene (85 p.s.i.), and brought to 75 °C. Total polymerization time was 30 minutes.

Activities are reported in (grams copolymer)/[(mmol Zr)(100 psi ethylene)(hour)]. MI is melt index (dg/min), measured using ASTM D-1238 Condition E at 190° C. FI is flow index (dg/min), measured using ASTM D-1238-Condition F. MFR is Melt Flow Ratio, FI/MI. M_w and M_n are Weight Average Molecular Weight and Number Average Molecular Weight, respectively, determined by size exclusion chromatography methods known in the art. PDI is Polydispersity Index, or Molecular Weight Distribution (M_w/M_n).

TABLE 3

Ex.	Al/Zr Mole Ratio	Activity
19	50	32941
20	200	39529

WO 98/30608

PCT/US98/00482

-31-

Ex.	Al/Zr Mole Ratio	Activity
21	300	56471
22	400	59059
23	500	95529
24	1000	141412

The results in Table 3 show that the activity of the unsupported, liquid phase, indenyl zirconium tris(trimethylacetate)/MMAO catalyst composition, wherein the catalyst precursor has been precontacted with 1-hexene, varied with the mole ratio of MMAO (based on Al) to indenyl zirconium tris(trimethylacetate) (based on Zr).

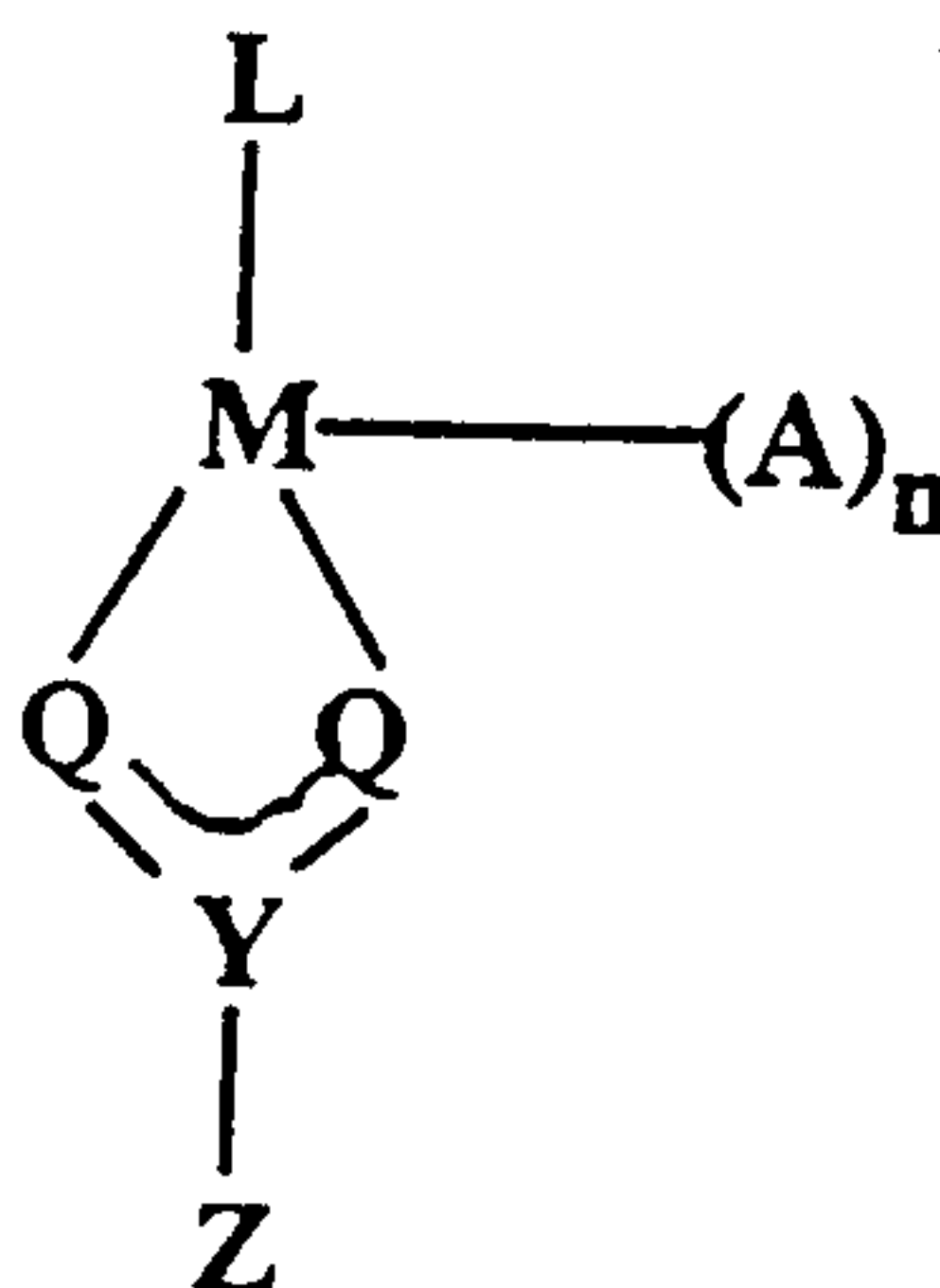
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- 32 -

We Claim:

1. A method of controlling the olefin polymerization activity of an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor with an activating cocatalyst outside of a polymerization reactor for a period of time at concentrations, a mole ratio, and a temperature, which method comprises simultaneously adjusting two or more of:
- a) the period of time the single site catalyst precursor and the activating cocatalyst are contacted;
 - b) the concentrations of the single site catalyst precursor and the activating cocatalyst during contacting;
 - c) the mole ratio of the activating cocatalyst to the single site catalyst precursor during contacting;
 - d) the temperature during contacting; and
 - e) the degree of mixing the single site catalysts precursor and the activating cocatalyst.

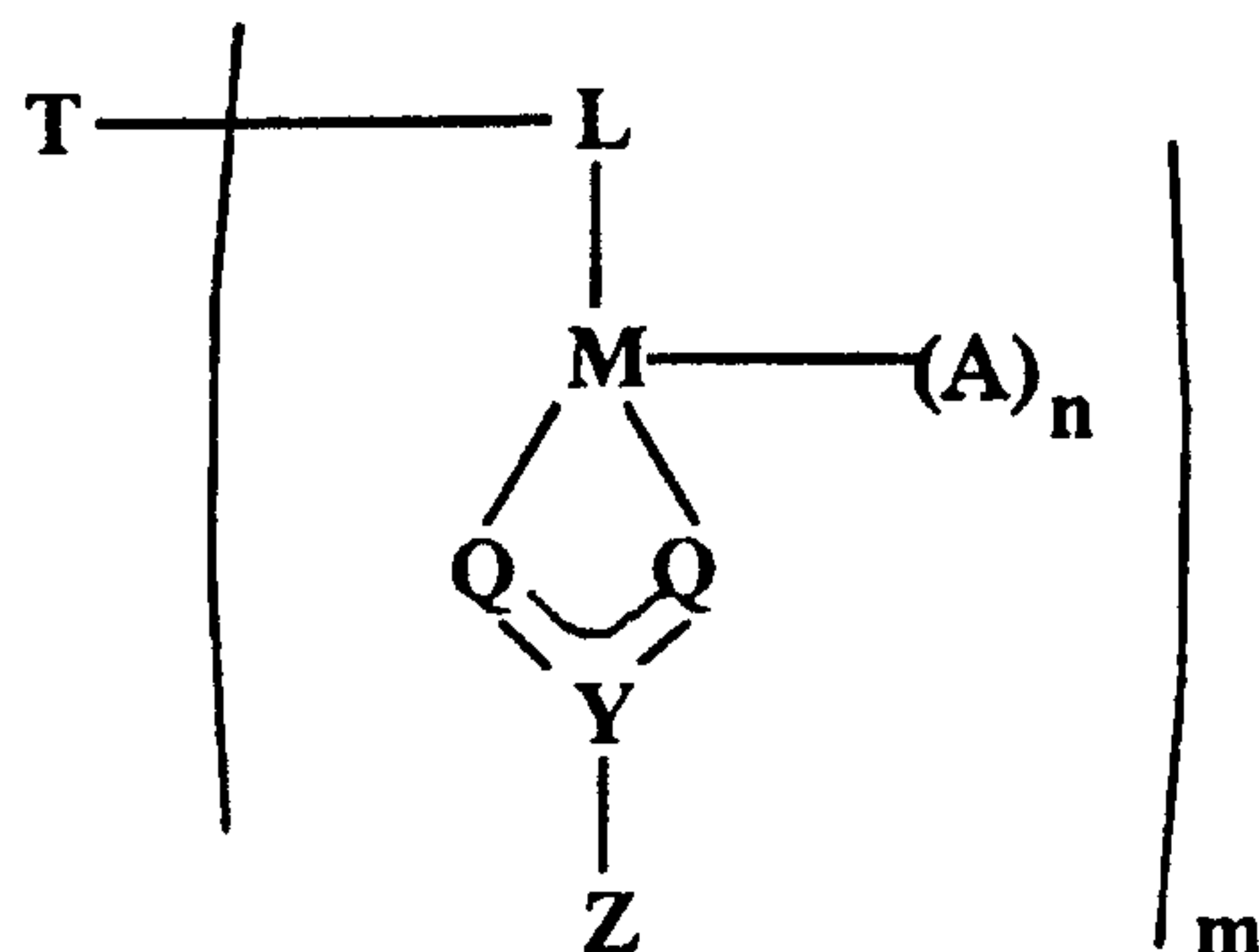
2. The method of claim 1, wherein the single site catalyst precursor has the formula:



AMENDED SHEET

-33-

or



wherein:

M is a transition metal;

L is a substituted or unsubstituted, pi-bonded ligand coordinated to *M*;

each *Q* is independently selected from the group consisting of -O-, -NR-, -CR₂- and -S-;

Y is C or S;

Z is selected from the group consisting of -OR, -NR₂, -CR₃, -SR, -SiR₃, -PR₂, -H, and substituted or unsubstituted aryl groups, with the proviso that when *Q* is -NR- then *Z* is selected from the group consisting of -OR, -NR₂, -SR, -SiR₃, -PR₂ and -H;

n is 1 or 2;

A is a univalent anionic group when *n* is 2 or *A* is a divalent anionic group when *n* is 1;

each *R* is independently a group containing carbon, silicon, nitrogen, oxygen, and/or phosphorus where one or more *R* groups may be attached to the *L* substituent;

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- 34 -

T is a bridging group selected from the group consisting of alkylene and arylene groups containing from 1 to 10 carbon atoms optionally substituted with carbon or heteroatoms, germanium, silicone and alkyl phosphine; and

m is 2 to 7.

3. The method of claim 2, wherein the single site catalyst is selected from the group consisting of indenyl zirconium tris(diethylcarbamate), indenyl zirconium tris(trimethylacetate), and (methylcyclopentadienyl) zirconium tris(trimethylacetate).

4. A process for the production of an olefin polymer, which comprises contacting at least one olefin monomer under polymerization conditions with an unsupported, liquid form catalyst composition prepared by contacting a single site catalyst precursor with an activating cocatalyst outside of a polymerization reactor for a period of time at concentrations, a mole ratio, and a temperature, wherein the activity of the catalyst composition is controlled by simultaneously adjusting two or more of:

- a) the period of time the single site catalyst precursor and the activating cocatalyst are contacted;
- b) the concentrations of the single site catalyst precursor and the activating cocatalyst during contacting;
- c) the mole ratio of the single site catalyst precursor to the activating cocatalyst during contacting;
- d) the temperature during contacting; and

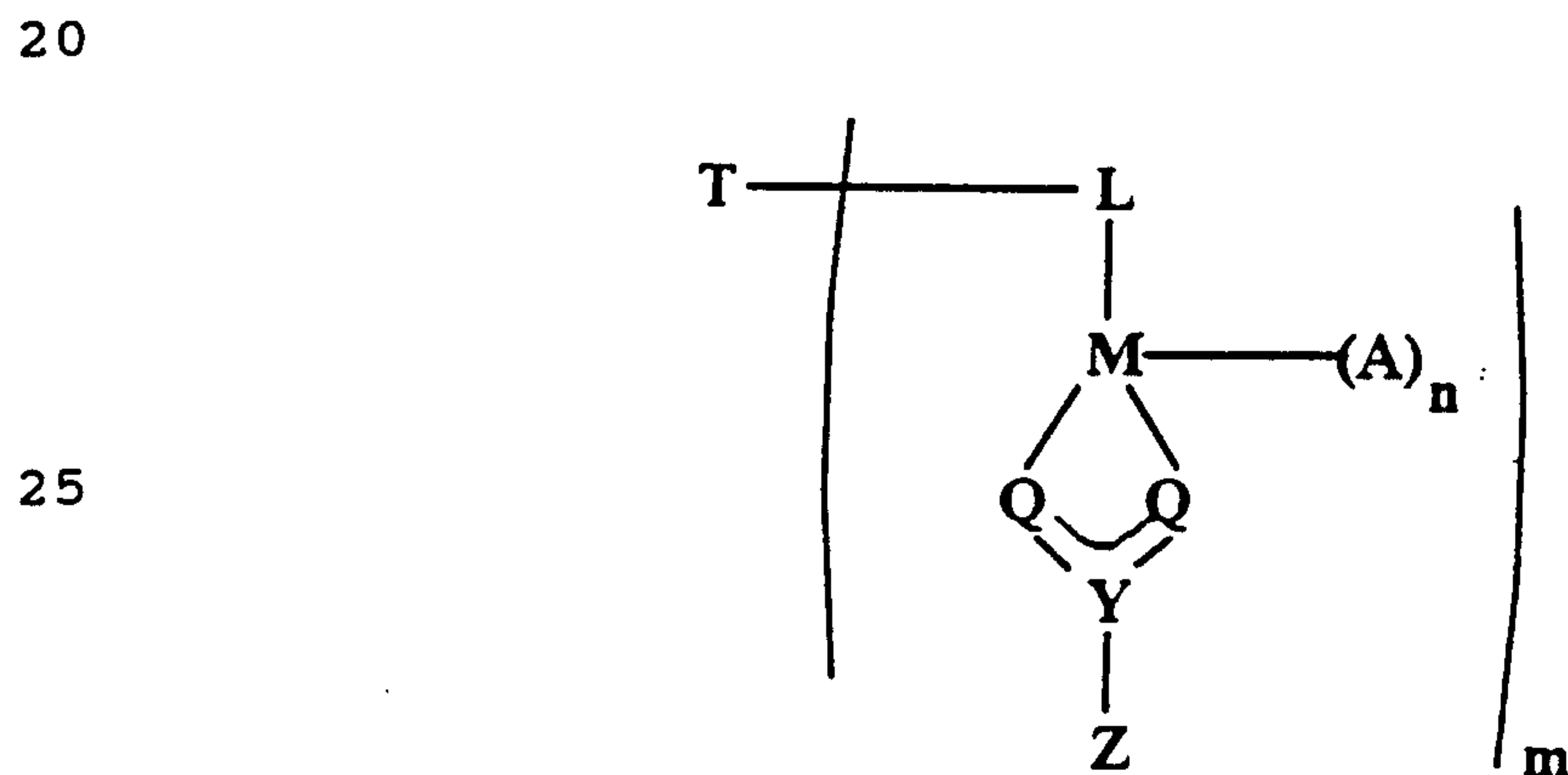
- 35 -

e) the degree of mixing of the single site catalyst precursor and the activating cocatalyst.

5. The process of claim 4, wherein the single site catalyst has the formula:



or



wherein:

M is a transition metal;

L is a substituted or unsubstituted, pi-bonded ligand coordinated to M;

35 each Q is independently selected from the group

AMENDED SHEET

- 36 -

consisting of -O-, -NR-, CR₂- and -S-;

Y is C or S;

5 Z is selected from the group consisting of -OR, -NR₂, -CR₃, -SR, -SiR₃, -PR₂, -H, and substituted or unsubstituted aryl groups, with the proviso that when Q is -NR- then Z is selected from the group consisting of -OR, -NR₂, -SR, -SiR₃, -PR₂ and -H;

n is 1 or 2;

10 A is a univalent anionic group when n is 2 or A is a divalent anionic group when n is 1;

each R is independently a group containing carbon, silicon, nitrogen, oxygen, and/or phosphorus where one or more R groups may be attached to the L substituent;

15 T is a bridging group selected from the group consisting of alkylene and arylene groups containing from 1 to 10 carbon atoms optionally substituted with carbon or heteroatoms, germanium, silicone and alkyl phosphine; and

20 m is 2 to 7.

6. The process of claim 5, wherein the single site catalyst is selected from the group consisting of indenyl zirconium tris(diethylcarbamate), indenyl
25 zirconium tris(trimethylacetate), and (methylcyclopentadienyl) zirconium tris(trimethylacetate).

7. The process of claim 4, wherein the olefin
30 polymer is an ethylene polymer.

8. The process of claim 4, wherein polymerization is conducted in the gas phase.

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