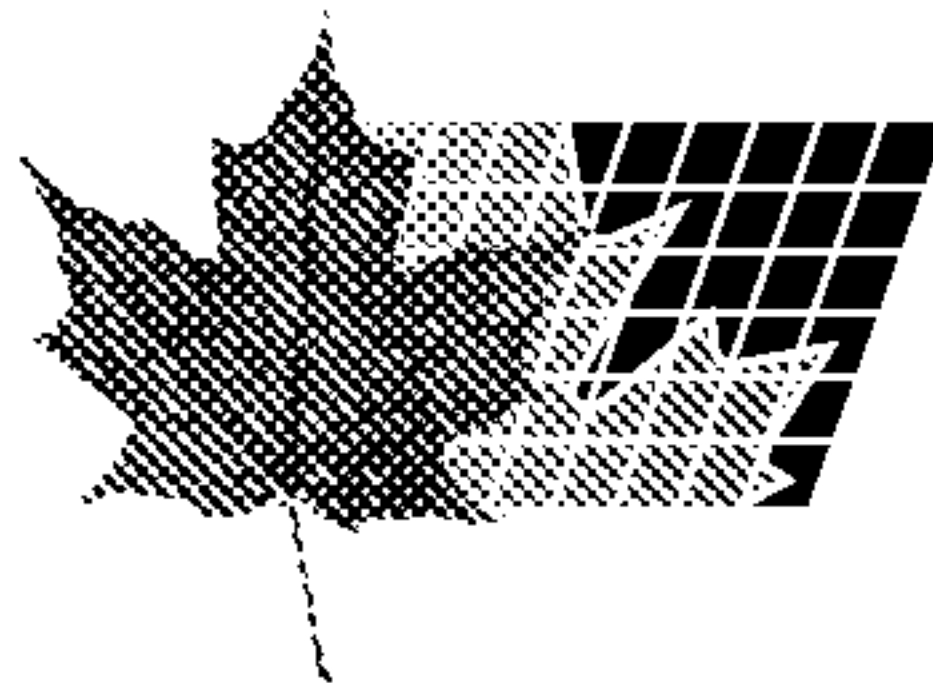




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(54) **CATALYSEUR A BASE D'ALUMOXANE, D'UN METAL DE
TRANSITION MONOCYCLOPENTADIENYLE ET D'UN
MODIFICATEUR POUR LA POLYMERISATION DES
OLEFINES**

(54) **A MODIFIED MONOCYCLOPENTADIENYL TRANSITION
METAL/ALUMOXANE CATALYST SYSTEM FOR
POLYMERIZATION OF OLEFINS**

(57) L'invention comprend un système catalyseur et un procédé utilisant ce système catalyseur pour la production de polyoléfines de masse moléculaire élevée, notamment de polyéthylène et de poly- α -oléfine supérieure, ainsi que de copolymères d'éthylène et/ou d' α -oléfines avec d'autres monomères insaturés, comprenant des dioléfines, des monomères insaturés acétyléniquement et des oléfines cycliques. Le système catalyseur comprend trois composants, un composé de métal de transition monocyclopentadiényle du Groupe IV B, un alumoxane, et un agent modifiant. Le système catalyseur est très actif, à de faibles rapports entre l'aluminium et le métal de transition du groupe IV B, et catalyse ainsi la production d'un produit de polyoléfine contenant de faibles niveaux de résidus métalliques du catalyseur.

(57) This invention comprises a catalyst system and a process using such catalyst system for the production of high molecular weight polyolefins, particularly polyethylene and higher poly- α -olefin, and copolymers of ethylene and/or α -olefins with other unsaturated monomers, including diolefins, acetylenically unsaturated monomers and cyclic olefins. The catalyst system comprises three components, a monocyclopentadienyl Group IV B transition metal compound, an alumoxane, and a modifier. The catalyst system is highly active, at low ratios of aluminum to the Group IV B transition metal, hence catalyzes the production of a polyolefin product containing low levels of catalyst metal residue.

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(21) International Application Number: PCT/US92/11039 (22) International Filing Date: 21 December 1992 (21.12.92) (30) Priority data: 07/812,432 23 December 1991 (23.12.91) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 5200 Bayway Drive, Baytown, TX 77520-5200 (US). (72) Inventor: CANICH, Jo, Ann, Marie ; 900 Henderson Ave- nue, Apt. 808, Houston, TX 77058 (US). (74) Agents: BUTTS, Evan, K.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US) et al.		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, 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> 2125317
(54) Title: A MODIFIED MONOCYCLOPENTADIENYL TRANSITION METAL/ALUMOXANE CATALYST SYSTEM FOR POLYMERIZATION OF OLEFINS (57) Abstract This invention comprises a catalyst system and a process using such catalyst system for the production of high molecular weight polyolefins, particularly polyethylene and higher poly- α -olefin, and copolymers of ethylene and/or α -olefins with other unsaturated monomers, including diolefins, acetylenically unsaturated monomers and cyclic olefins. The catalyst system comprises three components, a monocyclopentadienyl Group IV B transition metal compound, an alumoxane, and a modifier. The catalyst system is highly active, at low ratios of aluminum to the Group IV B transition metal, hence catalyzes the production of a polyolefin product containing low levels of catalyst metal residue.		

A MODIFIED MONOCYCLOPENTADIENYL
TRANSITION METAL/ALUMOXANE CATALYST
SYSTEM FOR POLYMERIZATION OF OLEFINS

SPECIFICATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to catalyst systems, both supported and unsupported, and to a process using such catalyst systems for the production of high molecular weight polymers, particularly polyolefins. The catalyst systems comprise a monocyclopentadienyl transition metal compound, an alumoxane, and a modifier. The catalyst system is highly active, at low ratios of aluminum to the transition metal, hence catalyzes the production of a polyolefin product containing low levels of catalyst metal residue.

2. Description of the Related Art

As is well known, various processes and catalysts exist for the homopolymerization or copolymerization of olefins. For many applications it is of primary importance for a polyolefin to have a high weight average molecular weight while having a relatively narrow molecular weight distribution. A high weight average molecular weight, when accompanied by a narrow molecular weight distribution, provides a polyolefin or

2 1 2 6 3 1 7

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an ethylene- α -olefin copolymer with high strength properties.

Traditional Ziegler-Natta catalyst systems -- a transition metal compound cocatalyzed by an aluminum alkyl -- are capable of producing polyolefins having a high molecular weight but the polyolefins produced thereby are generally of a broad molecular weight distribution.

More recently a catalyst system has been developed wherein the transition metal compound has two or more cyclopentadienyl ring ligands -- such transition metal compound being referred to as a metallocene -- which catalyzes the production of olefin monomers to polyolefins. Accordingly, metallocene compounds of a Group IV B metal, particularly, titanocenes and zirconocenes, have been utilized as the transition metal component in such "metallocene" containing catalyst system for the production of polyolefins and ethylene- α -olefin copolymers. When such metallocenes are cocatalyzed with an aluminum alkyl -- as is the case with a traditional type Ziegler-Natta catalyst system -- the catalytic activity of such metallocene catalyst system is generally too low to be of any commercial interest.

It has since become known that such metallocenes may be cocatalyzed with an alumoxane -- rather than an aluminum alkyl -- to provide a metallocene catalyst system of high activity for the production of polyolefins. A metallocene-alumoxane catalyst system generally produces polyolefins of a narrow molecular weight distribution.

The zirconium metallocene species, as cocatalyzed or activated with an alumoxane, are commonly more active than their hafnium or titanium analogous for the polymerization of ethylene alone or together with an α -olefin comonomer. When employed in a non-supported form -- i.e., as a homogeneous or soluble catalyst

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system -- to obtain a satisfactory rate of productivity even with the most active zirconium species of metallocene typically requires the use of a quantity of alumoxane activator sufficient to provide an aluminum atom (Al) to transition metal atom (TM) ratio (Al:TM) of at least greater than 1000:1; often greater than 5000:1, and frequently on the order of 10,000:1. Such quantities of alumoxane impart to a polymer produced with such catalyst system an undesirable content of catalyst metal residue, i.e., an undesirable "ash" content (the nonvolatile metal content). In high pressure polymerization procedures using soluble catalyst systems wherein the reactor pressure exceeds about 500 bar only the zirconium or hafnium species of metallocenes may be used. Titanium species of metallocenes are generally unstable at such high pressure reactor conditions unless deposited upon a catalyst support.

A wide variety of Group IV B transition metal compounds have been named as possible candidates for an alumoxane cocatalyzed catalyst system. Although bis(cyclopentadienyl) Group IV B transition metal compounds have been the most preferred and heavily investigated for use in an alumoxane activated catalyst systems for polyolefin production, suggestions have appeared that mono and tris(cyclopentadienyl) transition metal compounds may also be useful. See, for example U.S. Patent Nos. 4,522,982; 4,530,914 and 4,701,431. Such mono(cyclopentadienyl) transition metal compounds as are suggested as candidates for an alumoxane activated catalyst system are mono(cyclopentadienyl) transition metal trihalides and trialalkyls.

More recently, International Publication No. WO 87/03887 described the use of a composition comprising a transition metal coordinated to at least one cyclopentadienyl and at least one heteroatom ligand

as a transition metal component for use in an alumoxane
5 activated catalyst system for α -olefin polymerization.
The composition is broadly defined as a transition metal,
preferably of Group IV B of the Periodic Table, which is
coordinated with at least one cyclopentadienyl ligand and
one to three heteroatom ligands, the balance of the
10 transition metal coordination requirement being satisfied
with cyclopentadienyl or hydrocarbyl ligands. Catalyst
systems described by this reference are illustrated
solely with reference to transition metal compounds which
are metallocenes, i.e., bis(cyclopentadienyl) Group IV B
15 transition metal compounds.

Even more recently, at the Third Chemical Congress
of North American held in Toronto, Canada in June 1988,
John Bercaw reported upon efforts to use a compound of a
Group III B transition metal coordinated to a single
20 cyclopentadienyl heteroatom bridged ligand as a catalyst
system for the polymerization of olefins. Although some
catalytic activity was observed under the conditions
employed, the degree of activity and the properties
observed in the resulting polymer product were
25 discouraging of a belief that such monocyclopentadienyl
transition metal compound could be usefully employed for
commercial polymerization processes.

U.S. Patent No. 4,931,517 (EP A 0303519) discloses a
process for the polymerization of ethylene which
30 comprises bringing ethylene, or ethylene and at least one
 α -olefin in contact with a catalyst comprising a
metallocene compound of a transition metal selected from
Groups IV B, V B and VI B, an alumoxane and a silicon
compound having a Si-O-C bond for polymerization. The
35 use of the silicon compound by the '517 patent results in
the production of ethylene polymers having a lower melt
flow rate due to the reduced content of the low-molecular
weight matters produced.

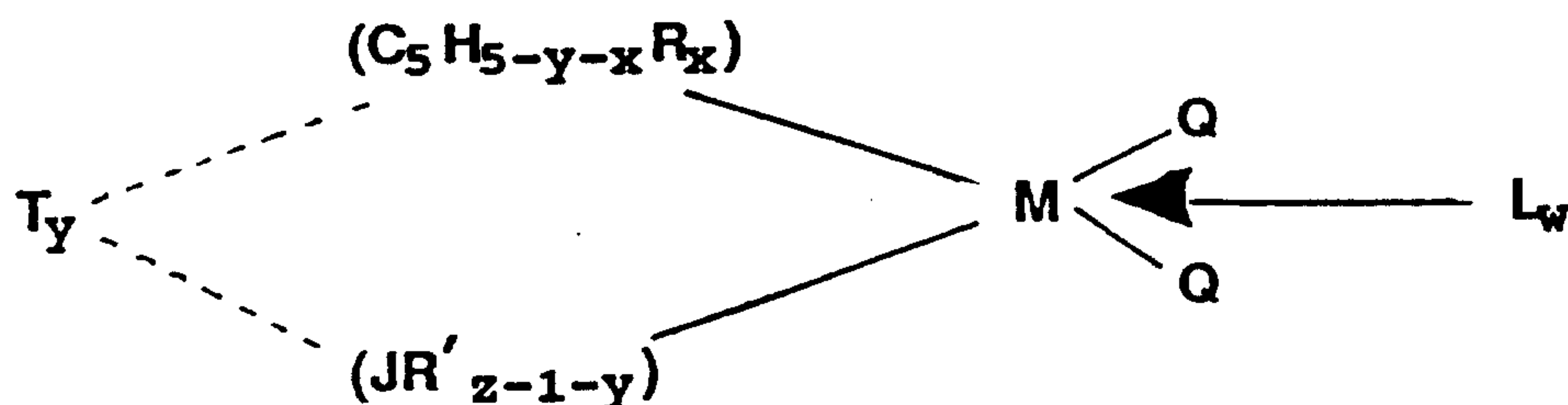
U.S. Patent No. 5,055,438 granted October 8, 1991; U.S. Patent No. 5,096,867 granted March 17, 1992; and EP A 0420436 (commonly owned) published April 3, 1991; and, more recently European Patent Application 416815A2 published March 13, 1991 describe an alumoxane activated catalyst system for olefin polymerization wherein the transition metal component comprises a Group IV B metal atom coordinated to a single cyclopentadienyl ligand, at least one heteroatom containing ligand wherein the heteroatom and cyclopentadienyl ligand may be (and in EPO 416815A2 must be) bridged together through a bridging group containing a Group IV A or V A element, and the balance of the valence of the transition metal atom comprises univalent anionic ligands.

A need still exists for discovering catalyst systems and polymerization processes that permit the production of higher molecular weight polyolefins and desirably with a narrow molecular weight distribution. Desirably such catalyst systems should be of high activity and productivity. It is further desirable that a catalyst be discovered which, within reasonable ranges of ethylene to α -olefin monomer ratios, will catalyze the incorporation of higher contents of α -olefin comonomers in the production of ethylene- α -olefins copolymers.

SUMMARY OF THE INVENTION

A preferred catalyst system of this invention comprises a transition metal component of Group IV B metal of the Periodic Table of the Elements (the CAS version of CRC Handbook of Chemistry and Physics, 68th ed. 1987-1988), an alumoxane component, and a modifier. The catalyst of this invention may be employed in liquid solution, slurry, high pressure fluid, bulk, or gas phase polymerization reactors to produce a polyolefin of high weight average molecular weight and relatively narrow molecular weight distribution.

The "Group IV B transition metal component" of the catalyst system is represented by the formula:



wherein: M is Zr, Hf or Ti in its highest formal oxidation state (+4, d^0 complex);

$(\text{C}_5\text{H}_5\text{-y-xR}_x)$ is a cyclopentadienyl ring and may be substituted or unsubstituted; $(\text{JR}'_z\text{-1-y})$ is a heteroatom ligand in which J is an element selected from Groups V A and VI A of the Periodic Table of Elements; R' may be a substituted or unsubstituted $\text{C}_1\text{-C}_{20}$ hydrocarbyl radical and "z" is the coordination number of the element J; each Q may be independently a univalent anionic ligand such as a halide, hydride, or substituted $\text{C}_1\text{-C}_{20}$ hydrocarbyl, alkoxide, aryloxy, amide, arylamide, phosphide or arylphosphide, provided that where any Q is a hydrocarbyl such Q is different from $(\text{C}_5\text{H}_5\text{-4-xR}_x)$; "y" is 0 or 1 when "w" is greater than 0; y is 1 when w is 0; when "y" is 1, T is a covalent bridging group containing a Group III A, IV A, V A or VI A element; and L is a neutral Lewis base.

The alumoxane component of the catalyst may be represented by the formulas: $(\text{R}^3\text{-Al-O})_m$; $\text{R}^4(\text{R}^5\text{-Al-O})_m\text{-AlR}_2^6$ or mixtures thereof, wherein $\text{R}^3\text{-R}^6$ are, independently, a $\text{C}_1\text{-C}_5$ alkyl group or halide and "m" is an integer ranging from 1 to about 50 and preferably is from about 13 to about 25.

By themselves the transition metal and alumoxane components together form an active catalyst for olefin polymerization as described in commonly-owned U.S. Patent Nos. 5,055,438 and 5,096,867. In this invention a third component or

modifier is added to the transition metal and alumoxane
5 components to form a catalyst system of superior
properties compared to that of a two component catalyst.

The addition of the modifier is important in the
operation of the catalyst system of the present invention
for several reasons. First, the addition of the modifier
10 increases catalyst activity. Secondly, addition of the
modifier component typically increases comonomer
incorporation.

The modifier component can be represented by the
formula

15
$$R''_{a-c}E(G-R''_{b-1})_c \text{ or } R''(G-R''_{b-1})$$

wherein G is a Group V A or VI A element and "b" is equal
to the coordination number of G, E is a Group IV A or V A
element and "a" is equal to the coordination number of E,
20 "c" is an integer from 1 to 4, but not greater than "a",
and each R'' is independently a hydrogen, hydrocarbyl or
substituted hydrocarbyl radical.

A typical polymerization process of the invention
such as for the polymerization or copolymerization of
25 ethylene comprises the steps of contacting ethylene or
C₃-C₂₀ α-olefins alone, or with other unsaturated
monomers including C₃-C₂₀ α-olefins, C₄-C₂₀ diolefins,
and/or acetylenically unsaturated monomers either alone
or in combination with other olefins and/or other
30 unsaturated monomers, with a catalyst system comprising,
a Group IV B transition metal component; a modifier; and
a methylalumoxane (MAO) in an amount to provide a molar
aluminum to transition metal ratio of from about 1:1 to
about 20,000:1 or more; and reacting such monomer in the
35 presence of such catalyst system at a temperature of from
about -100°C to about 300°C for a time of from about 1
second to about 10 hours to produce a polyolefin having a
weight average molecular weight of from about 1,000 or

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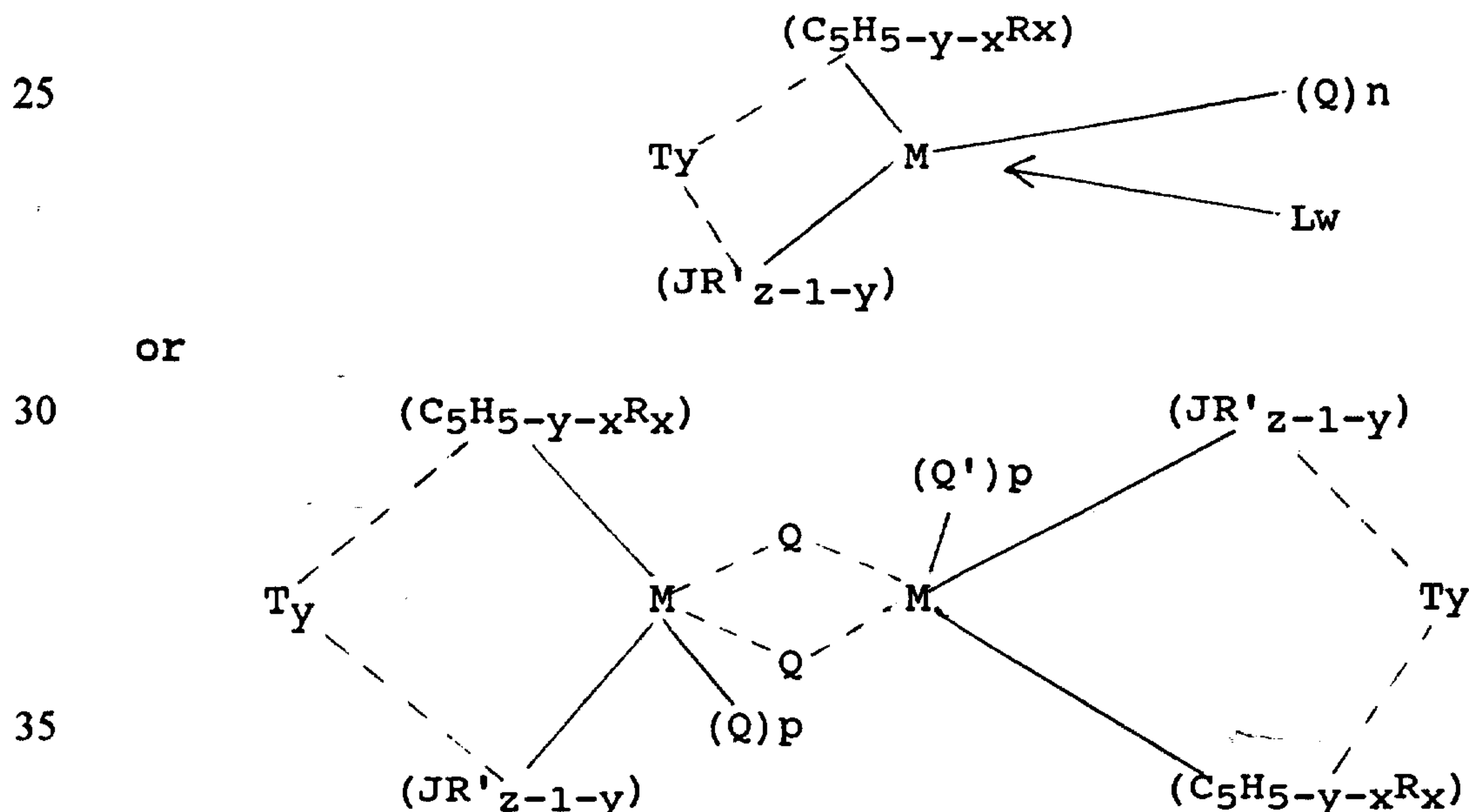
less to about 5,000,000 or more and a molecular weight
 5 distribution of from about 1.5 to about 15.0.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Catalyst Component

This invention relates to a catalyst system which
 may be prepared in supported or unsupported form,
 10 comprising, a monocyclopentadienyl transition metal
 compound, an alumoxane, and a modifier. This invention
 further relates to a process using such catalyst systems
 for the production of high molecular weight polyolefins,
 particularly polyethylene and higher poly- α -olefins, and
 15 copolymers of ethylene and/or α -olefins with other
 unsaturated monomers, including diolefins, acetylenically
 unsaturated monomers and cyclic olefins. The catalyst
 system is highly active at low ratios of aluminum to the
 transition metal, hence catalyzes the production of a
 20 polyolefin product containing low levels of catalyst
 metal residue.

The transition metal compound is of the general
 formula

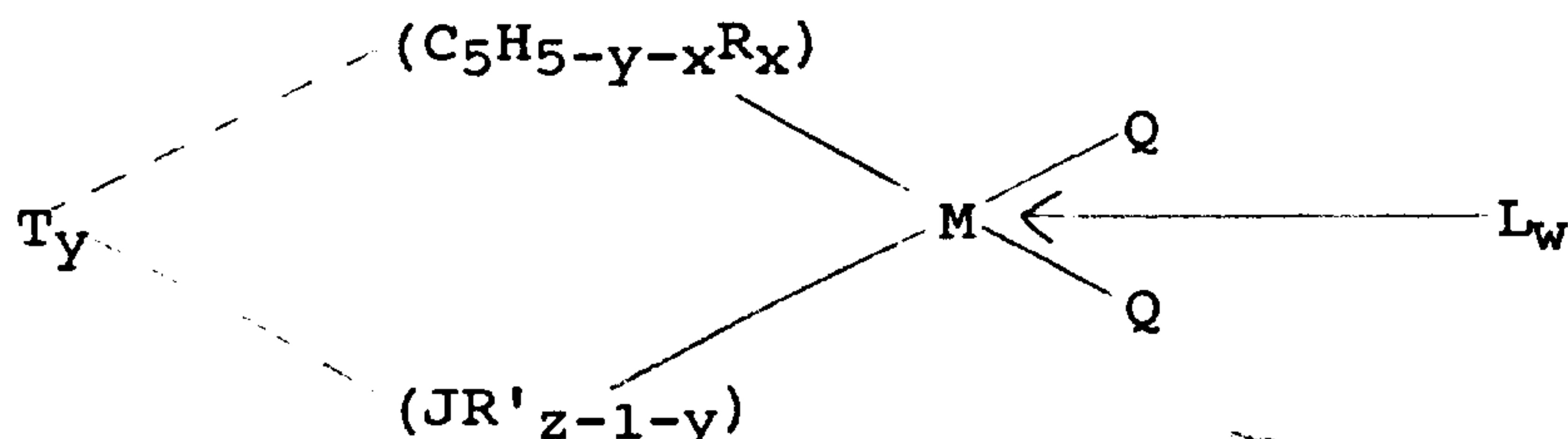


wherein M is a transition metal atom of Groups IV B, V B,
 VI B, VII B, VIII B or of the Lanthanides of the Periodic

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Table; $(C_5H_5-y-xR_x)$ is a cyclopentadienyl ligand which
 5 may be unsubstituted or substituted; $(JR'z-1-y)$ is a
 heteroatom ligand in which J is a Group V A or VI A
 element; the cyclopentadienyl and heteroatom ligands may
 be bridged together by a covalent bridging group T when
 "y" is 1; each Q is a univalent anionic ligand and "n + 2"
 10 equals the oxidation state of M; and L is a neutral Lewis
 base or L can be a second transition metal compound of
 the same type such that 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, and p + 3 equals the
 15 oxidation state of M. Particularly preferred are bridged
 transition metal compounds (i.e., y=1) wherein the
 bridging group T is of a molecular dimension which
 reduces the angle defined by the bond between the
 heteroatom to the transition metal atom and the bond
 20 between the transition metal atom to the centroid of the
 cyclopentadienyl ligand from the bonding angle which
 would otherwise exist in an analogous compound without a
 bridge. The reduction of this bonding angle by such a
 bridging group T exposes the transition metal atom to a
 25 greater accessibility by a monomer. Illustrative, but
 not limiting, examples of specific T, $(C_5H_5-y-xR_x)$,
 $(JR'z-1-y)$ and Q constituents, are given in Table 1. Of
 the transition metals, those of Group IV B are preferred.

The Group IV B transition metal component of the
 30 catalyst system is represented by the general formula:



10

wherein M is Zr, Hf or Ti in its highest formal oxidation state (+4, d^0 complex);

($C_5H_5-y-xR_x$) is a cyclopentadienyl ring which is substituted with 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 radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals, substituted C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, an alkylborido radical or any other radical containing a Lewis acidic or basic functionality, C_1 - C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, alkylborido radicals, or any other radical containing a Lewis acidic or basic functionality, or ($C_5H_5-y-xR_x$) is a cyclopentadienyl ring in which two adjacent R-groups are joined forming C_4 - C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl;

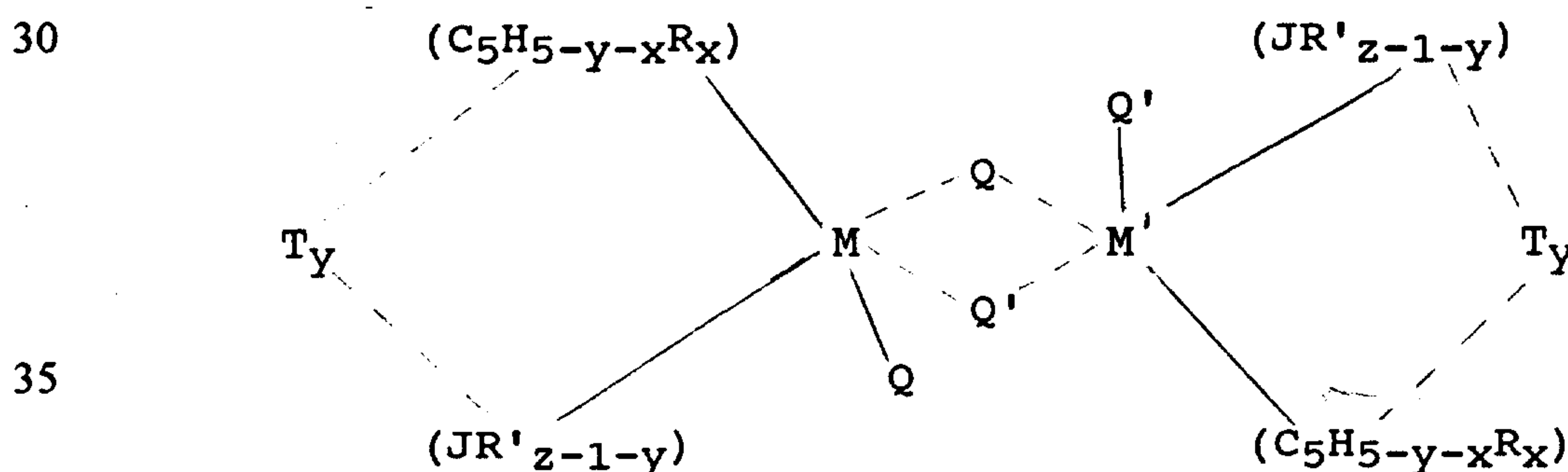
(JR'_z-1-y) is a heteroatom ligand in which J is an element with a coordination number of three from Group V A or an element with a coordination number of two from Group VI A of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur with nitrogen being preferred, and each R' is, independently a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals, substituted C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, or any other radical containing a Lewis acidic or basic functionality, and "z" is the coordination number of the element J;

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each Q is, independently, any univalent anionic
 5 ligand such as a halide, hydride, or substituted or
 unsubstituted C_1-C_{20} hydrocarbyl, alkoxide, aryloxy,
 amide, arylamide, phosphide or arylphosphide, provided
 that where any Q is a hydrocarbyl such Q is different
 from $(C_5H_5-y-xR_x)$, or both Q together may be an
 10 alkylidene or a cyclometallated hydrocarbyl or any other
 divalent anionic chelating ligand;

"y" is 0 or 1 when w is greater than 0, and y is 1
 when w equals 0; when "y" is 1, T is a covalent bridging
 group containing a Group III A, IV A, V A or VI A element
 15 such as, but not limited to, a dialkyl, alkylaryl or
 diaryl silicon or germanium radical, alkyl or aryl
 phosphine or amine radical, a hydrocarbyl radical such as
 methylene, and ethylene, an alkyl or aryl boroidoradical,
 or an oxygen or sulfur radical; and

20 L is a neutral Lewis base such as, but not limited
 to, diethylether, tetraethyl ammonium chloride,
 tetrahydrofuran, dimethylaniline, aniline,
 trimethylphosphine, and n-butylamine, and "w" is a number
 from 0 to 3; L can also be a second transition metal
 25 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. Such
 compounds are represented by the formula:



Examples of the T group which are suitable as a
 constituent group of the Group IV B transition metal

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5 component of the catalyst system are identified in column 1 of Table 1 under the heading "T".

Exemplary hydrocarbyl radicals for Q are methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl, and phenyl, with methyl being preferred. Exemplary halogen
10 atoms for Q include chlorine, bromine, fluorine and iodine, with chlorine being preferred. Exemplary alkoxides and aryloxides for Q are methoxide, phenoxide and substituted phenoxides such as 4-methylphenoxide. Exemplary amides of Q are dimethylamide, diethylamide,
15 methylethylamide, di-t-butylamide, and diisopropylamide. Exemplary aryl amides are diphenylamide and any other substituted phenyl amides. Exemplary phosphides of Q are diphenylphospide, dicyclohexylphospide, diethylphospide, and dimethylphospide. Exemplary alkyldiene radicals for
20 both Q together are methylenidene, ethylenidene and propylenidene. Examples of the Q group which are suitable as a constituent group or element of the Group IV B transition metal component of the catalyst system are identified in column 4 of Table 1 under the heading "Q".

25 Suitable hydrocarbyl and substituted hydrocarbyl radicals, which may be substituted as an R group for at least one hydrogen atom in the cyclopentadienyl ring, will contain from 1 to about 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon
30 radicals, alkyl-substituted cyclic hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals, alkyl-substituted aromatic radicals, amido-substituted hydrocarbyl radicals, phosphide-substituted hydrocarbyl radicals, and alkoxy-substituted hydrocarbyl radicals and
35 cyclopentadienyl rings containing one or more fused saturated or unsaturated rings. Suitable organometallic radicals, which may be substituted as a R group for at least one hydrogen atom in the cyclopentadienyl ring, include, but are not limited to, trimethylsilyl,

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triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl,
5 triphenylgermyl, and trimethylgermyl. Other suitable
radicals that may be substituted for one or more hydrogen
atoms in the cyclopentadienyl ring include, but are not
limited to, halogen radicals, amido radicals, phosphido
radicals, alkoxy radicals, and alkylborido radicals.

10 Examples of cyclopentadienyl ring groups ($C_5H_5-y-xR_x$)
which are suitable as a constituent group of the Group IV
B transition metal component of the catalyst system are
identified in Column 2 of Table 1 under the heading
($C_5H_5-y-xR_x$).

15 Suitable hydrocarbyl and substituted hydrocarbyl
radicals, which may be substituted as an R' group for at
least one hydrogen atom in the heteroatom J ligand group,
contain from 1 to about 20 carbon atoms and include, but
are not limited to, straight and branched alkyl radicals,
20 cyclic hydrocarbon radicals, alkyl-substituted cyclic
hydrocarbon radicals, aromatic radicals, halogen
radicals, amido radicals, and phosphido radicals.
Examples of heteroatom ligand groups (JR'_z-1-y) which are
suitable as a constituent group of the Group IV B
25 transition metal component of the catalyst system are
identified in column 3 of Table 1 under the heading
(JR'_z-1-y).

Table 1 depicts representative constituent moieties
for the "Group IV B transition metal component", the list
30 is for illustrative purposes only and should not be
construed to be limiting in any way. A number of final
components may be formed by permuting all possible
combinations of the constituent moieties with each other.
Illustrative compounds are: dimethylsilyltetramethyl-
35 cyclopentadienyl-tert-butylamido zirconium dichloride,
methylphenylsilyltetramethylcyclopentadienyl-tert-
butylamido titanium dichloride, and dimethylsilyltetra-
methylcyclopentadienylcyclododecylamido titanium
dichloride. For illustrative purposes, the above

compounds and those permuted from Table 1 do not include
5 the neutral Lewis base ligand (L). The conditions under
which complexes containing neutral Lewis base ligands
such as ether or those which form dimeric compounds is
determined by the steric bulk of the ligands about the
metal center. For example, the t-butyl group in
10 $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-}\underline{\text{t}}\text{-Bu})\text{ZrCl}_2$ has greater steric requirements
than the phenyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NPh})\text{ZrCl}_2 \cdot \text{Et}_2\text{O}$
thereby not permitting ether coordination in the former
compound. Similarly, due to the decreased steric bulk of
the trimethylsilylcyclopentadienyl group in
15 $[\text{Me}_2\text{Si}(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{N-}\underline{\text{t}}\text{-Bu})\text{ZrCl}_2]_2$ versus that of the
tetramethylcyclopentadienyl group in $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-}\underline{\text{t}}\text{-}$
 $\text{Bu})\text{ZrCl}_2$, the former compound is dimeric and the latter
is not.

Table 1
TY - (C5H5-y-xRx) - M - (Q)n
- (JR'z-1-y)

T (when y = 1)	(C5H5-y-xRx)	(JR'z-1-y)	Q	M
dimethylsilylene diethylsilylene di-n-propylsilylene diisopropylsilylene di-n-butylsilylene di-t-butylsilylene di-n-hexylsilylene methylphenylsilylene ethylmethylsilylene diphenylsilylene di(p-t-butylphenethylsilylene) n-hexylmethylsilylene cyclopentamethylenesilylene cyclohexamethylenesilylene cyclooctamethylenesilylene dimethylgermanyli diethylgermanyli phenylamido t-butylamido methylamido t-butylphosphido ethylphosphido phenylphosphido methylene dimethylmethylene diethylmethylene ethylene diethylethylene dipropylethylene propylene dimethylpropylene diethylpropylene 1,1-dimethyl-3,3-dimethylpropylene tetramethyldisiloxane 1,1,4,4-tetramethyldisilylethylene phenyl borido ethyl borido	cyclopentadienyl methylcyclopentadienyl 1,2-dimethylcyclopentadienyl 1,3-dimethylcyclopentadienyl indenyl 1,2-diethylcyclopentadienyl tetramethylcyclopentadienyl ethylcyclopentadienyl n-butylcyclopentadienyl cyclohexylmethylcyclopentadienyl n-octylcyclopentadienyl β-phenylpropylcyclopentadienyl tetrahydroindenyl propylcyclopentadienyl t-butylcyclopentadienyl benzylcyclopentadienyl diphenylmethylcyclopentadienyl trimethylgermylcyclopentadienyl trimethylstannylcyclopentadienyl triethylphumbylcyclopentadienyl trifluoromethylcyclopentadienyl trimethylsilylcyclopentadienyl pentamethylcyclopentadienyl (when y = 0) fluorenyl octahydrofluorenyl 1,2,4-trimethylcyclopentadienyl 1-5-butyl-3-trimethylsilylcyclopentadienyl diphenylboridocyclopentadienyl dimethylamidocyclopentadienyl diphenylphosphidocyclopentadienyl methoxycyclopentadienyl	t-butylamido phenylamido cyclohexylamido p-n-butylphenylamido perfluorophenylamido n-butylamido methylamido ethylamido n-propylamido isopropylamido benzylamido t-butylphosphido ethylphosphido phenylphosphido cyclohexylphosphido oxo (when y = 1) sulfido (when y = 1) methoxide (when y = 0) ethoxide (when y = 0) methylthio (when y = 0) ethylthio (when y = 0)	hydride chloro methyl ethyl phenyl fluoro bromo iodo n-propyl isopropyl n-butyl	zirconium hafnium titanium Group: III B IV B V B VI B VII B VIII B Lanthanide

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Generally the bridged species of the Group IV B transition metal compound ("y" = 1) are preferred. These compounds can be prepared by reacting a cyclopentadienyl lithium compound with a dihalo compound whereupon a lithium halide salt is liberated and a monohalo substituent is covalently bound to the cyclopentadienyl compound. The so substituted cyclopentadienyl reaction product is next reacted with a lithium salt of a phosphide, oxide, sulfide or amide (for the sake of illustrative purposes, a lithium amide) whereupon the halo element of the monohalo substituent group of the reaction product reacts to liberate a lithium halide salt and the amine moiety of the lithium amide salt is covalently bound to the substituent of the cyclopentadienyl reaction product. The resulting amine derivative of the cyclopentadienyl product is then reacted with an alkyl lithium reagent whereupon the labile hydrogen atoms, at the carbon atom of the cyclopentadienyl compound and at the nitrogen atom of the amine moiety covalently bound to the substituent group, react with the alkyl of the lithium alkyl reagent to liberate the alkane and produce a dilithium salt of the cyclopentadienyl compound. Thereafter the bridged species of the Group IV B transition metal compound is produced by reacting the dilithium salt cyclopentadienyl compound with a Group IV B transition metal preferably a Group IV B transition metal halide.

Unbridged species of the Group IV B transition metal compound can be prepared from the reaction of a cyclopentadienyl lithium compound and a lithium salt of an amine with a Group IV B transition metal halide.

Suitable, but not limiting, Group IV B transition metal compounds which may be utilized in the catalyst system of this invention include those bridged species ("y" = 1) wherein the T group bridge is a dialkyl, diaryl or alkylaryl silane, or methylene or ethylene.

Exemplary of the more preferred species of bridged Group IV B transition metal compounds are dimethylsilyl, methylphenylsilyl, diethylsilyl, ethylphenylsilyl, diphenylsilyl, ethylene or methylene
5 bridged compounds. Most preferred of the bridged species are dimethylsilyl, diethylsilyl and methylphenylsilyl bridged compounds.

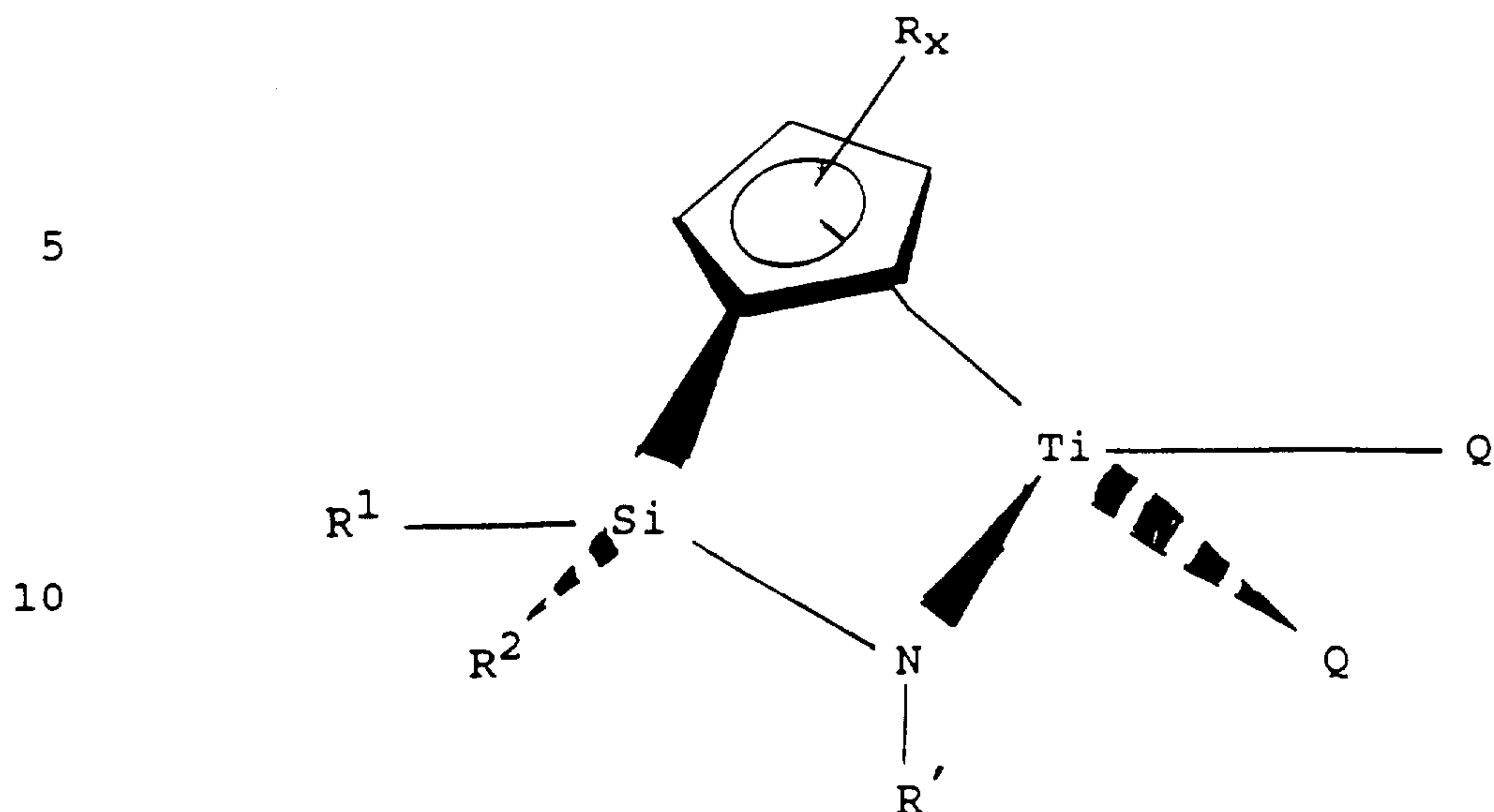
Suitable Group IV B transition metal compounds which are illustrative of the unbridged ("y" = 0)
10 species which may be utilized in the catalyst systems of this invention are exemplified by pentamethylcyclopentadienyldi-t-butylphosphinodimethyl hafnium; pentamethylcyclopentadienyldi-t-butylphosphinomethylethyl hafnium; cyclopentadienyl-2-
15 methylbutoxide dimethyl titanium.

To illustrate members of the Group IV B transition metal component, select any combination of the species in Table 1. An example of a bridged species would be dimethylsilylcyclopentadienyl-t-butylamidodichloro
20 zirconium; an example of an unbridged species would be cyclopentadienyldi-t-butylamidodichloro zirconium.

Generally, wherein it is desired to produce an α -olefin copolymer which incorporates a high content of α -olefin, the species of Group IV B transition metal
25 compound preferred is one of titanium. The most preferred species of titanium metal compounds are represented by the formula:

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wherein Q, L, R', R, "x" and "w" are as previously defined and R¹ and R² are each independently a C₁ to C₂₀ hydrocarbyl radicals, substituted C₁ to C₂₀ hydrocarbyl radicals wherein one or more hydrogen atom is replaced by a halogen atom; R¹ and R² may also be joined forming a C₃ to C₂₀ ring which incorporates the silicon bridge.

The alumoxane component of the catalyst system is an oligomeric compound which may be represented by the general formula (R³-Al-O)_m which is a cyclic compound, or may be R⁴(R⁵-Al-O-)_m-AlR⁶₂ which is a linear compound. An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula R³, R⁴, R⁵ and R⁶ are, independently a C₁-C₅ alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "m" is an integer from 1 to about 50. Most preferably, R³, R⁴, R⁵ and R⁶ are each methyl and "m" is at least 4. When an alkyl aluminum halide is employed in the preparation of the alumoxane, one or more R³⁻⁶ groups may be halide.

As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl aluminum may be reacted with water, in the form of a

moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. In another method wherein a supported form of catalyst is desired, a non-dehydrated or wet gel, such as a wet silica gel may be reacted with a trialkyl aluminum to prepare the alumoxane in situ on the support. Generally, however prepared, the reaction of a trialkyl aluminum with a limited amount of water yields a mixture of both linear and cyclic species of alumoxane.

Suitable alumoxanes which may be utilized in the catalyst systems of this invention are those prepared by the hydrolysis of a trialkylaluminum; such as, but not limited to, trimethylaluminum, triethylaluminum, tripropylaluminum; triisobutylaluminum, and dimethylaluminumchloride. The most preferred alumoxane for use is methylalumoxane (MAO). Methylalumoxanes having an average degree of oligomerization of from about 4 to about 25 ("m" = 4 to 25), with a range of 13 to 25, are the most preferred.

Generally, the modifier component is a Lewis base or a compound containing one or more Lewis basic functionalities which are capable of reacting with a Lewis acid such as trimethylaluminum. Such modifiers are represented by, but not limited to N,N-dimethylaniline, ethylamine, diethylamine, triethylamine, triphenylamine, triphenylphosphine, hexamethylphosphorous triamide, diethylether, water, deuterium oxide, ethanol, phenol, thiophenol, 2,6-di-t-butyl-4-methylphenol), tetraethoxysilane, phenyltriethoxysilane, diphenyldiethoxysilane, triphenylethoxysilane, and diethyldihydroxysilane. The modifier component can be represented by the formula:

$$R''_{a-c}E(G-R''_{b-1})_c \text{ or } R''(G-R''_{b-1})$$

wherein G is a Group V A or VI A element and "b" is equal to the coordination number of G, E is a Group IV A or V A element and "a" is equal to the coordination number of E, "c" is an integer from 1 to 4, but not greater than "a", and each R" is independently a hydrogen, hydrocarbyl or substituted hydrocarbyl radical. Likewise, dimeric, trimeric, tetrameric or oligomeric versions of these compounds could be used. Examples of such compounds include, but are not limited to, N,N,N',N'-tetramethylethylenediamine, 2,2',2''-triaminotriethylamine, hexamethylenetetraamine, 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane, 1,2-bis(diphenylphosphino)ethane, tris(2-diphenylphosphinoethyl)phosphine, 1,1,1-tris(diphenylphosphinomethyl)ethane, 4,7,13,16,21,24-hexaoxa-1, 10-diazabicyclo[8.8.8]hexacosane, 12-crown-4, 15-crown-5, 18-crown-6, 1,4,7,10,13,16-hexathiacyclooctadecane, and hexamethylcyclotrisiloxane.

The catalyst system in soluble unsupported form is prepared by comixing the transition metal compound, alumoxane and modifier component in any order of addition or simultaneously in a hydrocarbon solvent which, preferably is suitable for use as a polymerization diluent.

Where the hydrocarbon solvent utilized is also suitable for use as a polymerization diluent, the catalyst system may be prepared in situ in the polymerization reactor. Alternatively, the catalyst system may be separately prepared, in concentrated form, and added to the polymerization diluent in a reactor. Or, if desired, the components of the catalyst system may be prepared as separate solutions and added to the polymerization diluent in a reactor, in appropriate ratios, as is suitable for a continuous liquid phase polymerization reaction procedure. Alkane and aromatic hydrocarbons suitable as solvents for formation of the

catalyst system and also as a polymerization diluent are exemplified by, but are not necessarily limited to, straight and branched chain hydrocarbons such as isobutene, butane, pentane, hexane, heptane, and octane. 5 cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, and methylcycloheptane, and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, and xylene. Suitable solvents also include, but are not limited to, liquid olefins 10 which may act as monomers or comonomers including ethylene, propylene, 1-butene, and 1-hexene.

The transition metal compound and alumoxane are employed in quantified such that the transition metal compound is present in solution in a concentration of 15 from about 0.00001 to about 1.0 millimoles/liter and the alumoxane is present in an amount to provide a ratio of aluminum atom to transition metal atom of from about 1:1 to about 20,000:1. The modifier is employed in an amount to provide a mole ratio of modifier to transition metal 20 compound of from about 1:1 to about 5,000:1.

The catalyst system ingredients -- that is, the Group IV B transition metal, the alumoxane, the modifier and polymerization diluent (optional) -- can be added to the reaction vessel rapidly or slowly. The temperature 25 maintained during the contact of the catalyst components can vary widely, such as, for example, from -100° C to 300° C. Greater or lesser temperatures can also be employed. Preferably, during formation of the catalyst system, the reaction is maintained within a temperature 30 of from about 25° C to 100° C, most preferably about 25° C.

At all times, the individual catalyst system components, as well as the catalyst system once formed, are protected from oxygen and moisture. Therefore, the 35 reactions to prepare the catalyst system are performed in an oxygen and moisture free atmosphere and, where the

catalyst system is recovered separately it is recovered in an oxygen and moisture free atmosphere. Preferably, therefore, the reactions are performed in the presence of an inert dry gas such as, for example, helium or
5 nitrogen.

If desired the catalyst may also be prepared in a supported form. The normally hydrocarbon soluble transition metal component and alumoxane are prepared as a supported catalyst by deposition on a support material.
10 The modifier may also be, and preferably is, deposited on a support or the modifier may be used in conjunction with a supported transition metal compound-alumoxane/component by addition of the modifier to a polymerization diluent to which the supported transition metal compound-
15 alumoxane component is ultimately added. The support material for preparing the supported catalyst may be any resinous support material such as a polyolefin or any finely divided inorganic solid porous support, such as talc, silica, alumina, silica-alumina, or mixtures
20 thereof. Other inorganic oxides that may be employed either alone or in combination with silica or silica-alumina are oxides such as magnesia, titania, and zirconia. The inorganic oxides may be dehydrated, as is well known in the art, to remove water. If desired, the
25 residual surface hydroxyl groups in the inorganic solid porous support may be removed by additional heating or by reaction with chemical dehydrating agents such as lithium alkyl, silylchlorides, aluminum alkyls, or preferably with alumoxane. Preferred catalyst supports include
30 dehydrated inorganic oxide treated with an alumoxane, more preferably with methylalumoxane. A suitable support material of this type is a dehydrated silica-gel treated with methylalumoxane. When such an alumoxane-treated support is utilized in the production of the supported
35 catalyst, it may not be necessary to include additional alumoxane in the catalyst composition. Also preferred as

a catalyst support is a wet gel, more preferably a wet silica gel, containing up to approximately 20% by weight absorbed water. Wet gels may be directly mixed with trialkyl aluminums to form the alumoxane component of the catalyst system directly on the support.

A suitable inorganic support such as silica would have a particle diameter in the range of 0.1-600 microns, preferably 0.3-100 microns; a surface area of 50-1000 m²/g, preferably 100-500 m²/g; and a pore volume of 0.5 - 3.5 cm³/g. To insure its use in dehydrated form, the support material may be heat treated at 100-1000°C for a period of 1-100 hours, preferably 3-24 hours. The treatment may be carried out in a vacuum or while purging with a dry inert gas such as nitrogen. As an alternative, the support material may be chemically dehydrated. The chemical dehydration is accomplished by slurrying the support in an inert low boiling solvent such as, for example, heptane, in the presence of the dehydrating agent such as for example, triethylaluminum in a moisture and oxygen-free atmosphere.

Method of Use

The catalyst system may be most usefully employed in liquid, solution, slurry, high pressure fluid, bulk or gas phase processes, all of which are known to those of skill in the art. These processes may be employed singularly or in series. Thus, polymerizations using the invention catalyst system may be conducted by any of these processes, generally at a temperature in the range of about 0° to about 220°C or even higher, and under atmospheric, subatmospheric or superatmospheric pressure conditions.

A slurry polymerization process can utilize sub-or super-atmospheric pressures and temperatures in the range of -80 to 250°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene, α -olefin,

diolefin, cyclic olefin or acetylenically unsaturated comonomer, hydrogen (optional) and catalyst are added. Alkanes and cycloalkanes, such as butane, pentane, hexane, or cyclohexane, are preferred with C₄ to C₂₀ alkanes especially preferred. Preferred solvents also include liquid olefins which may act as monomers or comonomers including, but not limited to, ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, and substituted styrenes.

A gas-phase polymerization process utilizes superatmospheric pressure and temperatures in the range of about 50°C - 120°C. Gas-phase polymerization can be performed in a stirred or fluidized bed of catalyst and product particles in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Thermostated ethylene, comonomer, including α -olefins, diolefins, cyclic olefins or acetylenically unsaturated comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated so as to maintain the particles at a temperature of 50° - 120°C. The polymer product can be withdrawn continuously or semi-continuously at a rate such as to maintain a constant product inventory in the reactor. After polymerization and deactivation of the catalyst, the product polymer can be recovered by any suitable means. In commercial practice, the polymer product can be recovered directly from the gas phase reactor, freed of residual monomer with a nitrogen purge, and used without further deactivation or catalyst removal.

The liquid phase process comprises the steps of contacting an olefin monomer with the catalyst system in a suitable polymerization diluent and reacting said monomer in the presence of said catalyst system for a time and at a temperature sufficient to produce a polyolefin of high molecular weight.

The monomer for such process may comprise ethylene alone, for the production of a homopolyethylene, or ethylene in combination with an α -olefin having 3 to 20 carbon atoms for the production of an ethylene- α -olefin copolymer. Homopolymers of higher α -olefin such as propylene, butene, styrene and copolymers thereof with ethylene and/or C_4 or higher α -olefins and diolefins can also be prepared. Conditions most preferred for the homo-or copolymerization of ethylene are those wherein ethylene is submitted to the reaction zone at pressures of from about 344,738 kPa (0.019 psia) to about 131 kPa (50,000 psia) and the reaction temperature is maintained at from about -100° to about 300°C . The aluminum to transition metal molar ratio is preferably from about 1:1 to 20,000 to 1. A more preferable range would be 1:1 to 2000:1. The reaction time is preferably from about 10 seconds to about 1 hour. Without limiting in any way the scope of the invention, one means for carrying out the process of the present invention for production of a copolymer is as follows: in a stirred-tank reactor liquid α -olefin monomer is introduced, such as 1-butene. The catalyst system is introduced via nozzles in either the vapor or liquid phase. Feed ethylene gas is introduced either into the vapor phase of the reactor, or sparged into the liquid phase as is well known in the art. The reactor contains a liquid phase composed substantially of liquid α -olefin comonomer, together with dissolved ethylene gas, and a vapor phase containing vapors of all monomers. The reactor temperature and pressure may be controlled via reflux of vaporizing α -olefin monomer (autorefrigeration), as

well as by cooling coils, jackets etc. The polymerization rate is controlled by the concentration of catalyst. The ethylene content of the polymer product is determined by the ratio of ethylene to α -olefin comonomer in the reactor, which is controlled by manipulating the relative feed rates of these components to the reactor.

While it is a characteristic of the catalyst system that the produced polymers have a narrow molecular weight distribution, if desired broad molecular weight distribution polymers may be produced by using two or more transition metal compounds or two or more activators.

The invention is illustrated in actual practice by the following non-limiting examples.

Examples

All procedures were performed under an inert atmosphere of helium or nitrogen. Solvent choices are often optional, for example, in most cases either pentane or 30-60 petroleum ether can be interchanged. The lithiated amides were prepared from the corresponding amines and either *n*-BuLi or MeLi. Published methods for preparing LiHC_5Me_4 include C.M. Fendrick et al. Organometallics, 3, 819 (1984) and F.H. Köhler and K.H. Doll, Z. Naturforsch, 376, 144 (1982). Other lithiated substituted cyclopentadienyl compounds are typically prepared from the corresponding cyclopentadienyl ligand and *n*-BuLi or MeLi, or by reaction of MeLi with the proper fulvene. TiCl_4 was purchased from either Aldrich Chemical Company or Cerac. TiCl_4 was typically used in its etherate form. The etherate, $\text{TiCl}_4 \cdot 2\text{Et}_2\text{O}$, can be prepared by gingerly adding TiCl_4 to diethylether. Amines, silanes and lithium reagents were purchased from Aldrich Chemical Company or Petrarch Systems. Methylalumoxane was supplied by either Schering or Ethyl Corp.

Part 1. MePhSiCl₂ (14.9 g, 0.078 mol) was diluted with 250 ml of thf. Me₄HC₅Li (10.0 g, 0.078 mol) was slowly added as a solid. The reaction solution was allowed to stir overnight. The solvent was removed via a vacuum to a cold trap held at -196°C. Petroleum ether was added to precipitate the LiCl. The mixture was filtered through Celite and the pentane was removed from the filtrate. MePhSi(Me₄C₅H)Cl (20.8 g, 0.075 mol) was isolated as a yellow viscous liquid.

Part 2. LiHN-t-Bu (4.28 g, 0.054 mol) was dissolved in ~100 ml of thf. MePhSi(C₅Me₄H)Cl (15.0 g, 0.054 mol) was added dropwise. The yellow solution was allowed to stir overnight. The solvent was removed in vacuo. Petroleum ether was added to precipitate the LiCl. The mixture was filtered through Celite, and the filtrate was evaporated. MePhSi(C₅Me₄H)(NH-t-Bu) (16.6 g, 0.053 mol) was recovered as an extremely viscous liquid.

Part 3. MePhSi(C₅Me₄H)(NH-t-Bu) (17.2 g, 0.055 mol) was diluted with ~20 ml of ether. n-BuLi (60 ml in hexane, 0.096 mol, 1.6 M) was slowly added and the reaction mixture was allowed to stir for ~3 hours. The solvent was removed in vacuo to yield 15.5 g (0.48 mol) of a pale tan solid formulated as Li₂[MePhSi(C₅Me₄)(N-t-Bu)].

Part 4. Li₂[MePhSi(C₅Me₄)(N-t-Bu)] (8.75 g, 0.027 mol) was suspended in ~125 ml of cold ether (-30°C). TiCl₄·2Et₂O (9.1 g, 0.027 mol) was slowly added. The reaction was allowed to stir for several hours prior to removing the ether via vacuum. A mixture of toluene and dichloromethane was then added to solubilize the product. The mixture was filtered through Celite to remove the LiCl. The solvent was largely removed via vacuum and petroleum ether was added. The mixture was cooled to maximize product precipitation. The crude product was filtered off and

redissolved in toluene. The toluene insolubles were filtered off. The toluene was then reduced in volume and petroleum ether was added. The mixture was cooled to maximize precipitation prior to filtering off 3.34 g (7.76 mmol) of the yellow solid $\text{MePhSi}(\text{C}_5\text{Me}_4)(\text{N-t-Bu})\text{TiCl}_2$.

The examples are all based on the transition metal compound $(\text{MePhSi}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{TiCl}_2)$ with methylalumoxane (MAO).

The examples are collected in Table II. The general procedure is the same for all the runs. The codes to the modifiers is as follows: BHT (2,6-di-*t*-butyl-4-methylphenol), DMA (N,N-dimethylaniline), TEOS (tetraethoxysilane), DPDEOS (diphenyldiethoxysilane), and PTEOS (phenyltriethoxysilane). Trimethylaluminum is abbreviated as TMA and is provided as a counter example. Methylalumoxane is abbreviated as MAO. MW is weight average molecular weight, MWD is molecular weight distribution, and short chain branching per 1000 carbon atoms (SCB/1000C) was determined by either IR(a), ^1H NMR (b) or ^{13}C NMR (c).

Polymerization

General Catalyst Preparation and Polymerization

Procedure:

The polymerization run was performed in a 1-liter autoclave reactor equipped with a paddle stirrer, an external water jacket for temperature control, a regulated supply of dry nitrogen, ethylene, propylene, 1-butene and hexane, and a septum inlet for introduction of other solvents or comonomers, transition metal compound and alumoxane solutions. The reactor was dried and degassed thoroughly prior to use. A typical run consisted of injecting into the reactor 300 ml of toluene, 100 ml of 1-butene, the specified amount of 1.0 M methylalumoxane (MAO) which had been

mixed with the specified modifier (MOD), and 1 ml of a toluene solution of the transition metal compound. Exact amounts are collected in Table II. The reactor was then heated to 80°C and the ethylene (65 psi) was introduced into the system. The polymerization reaction was limited to the specified time (30 to 35 minutes). The reaction was ceased by rapidly cooling and venting the system and the ethylene-butene copolymer was recovered and allowed to dry under a stream of nitrogen.

The invention has been described with reference to its preferred embodiments. Those of ordinary skill in the art may, upon reading this disclosure, appreciate that there are alternate embodiments of the invention that, though not illustrated herein, are within the scope of the invention as described above or claimed hereafter.

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TABLE II

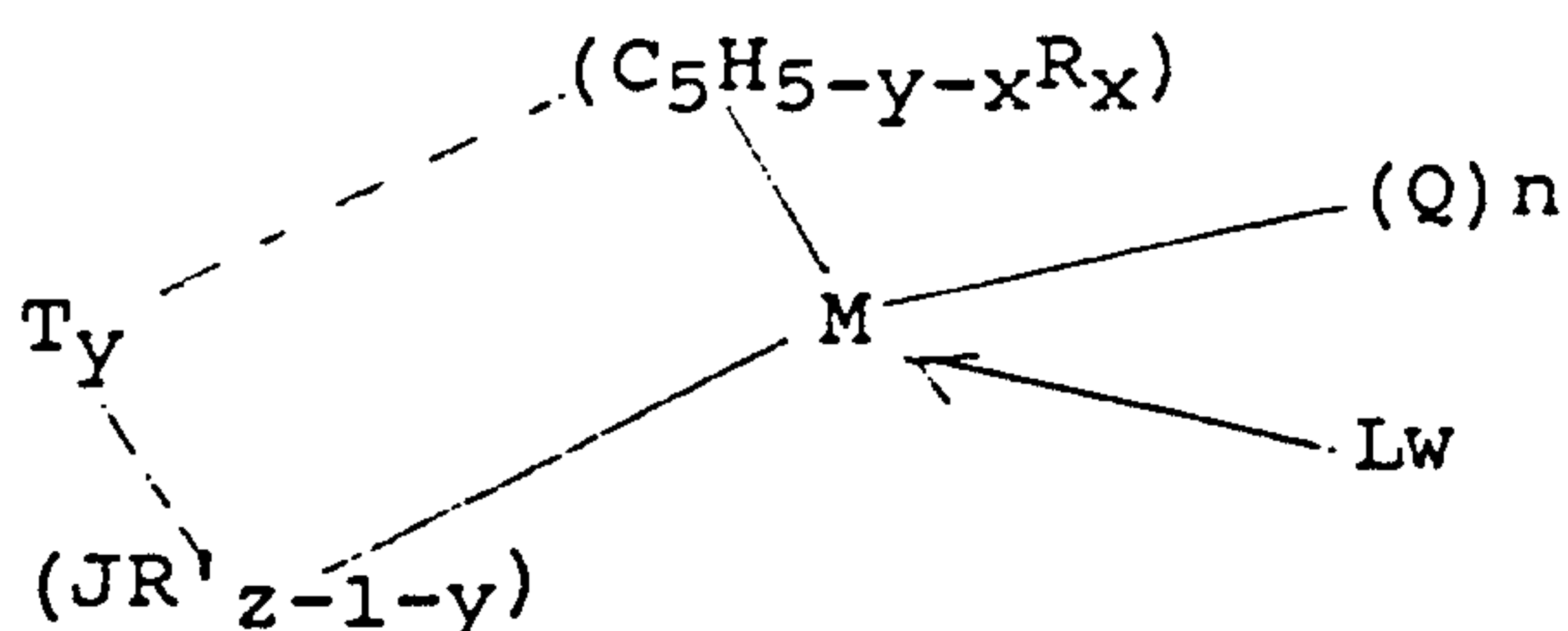
A	C	D	E	F	G	H
Exp #	Modifier	mmol TM	mmol MAO	mmol Mod	Al/TM(mol)	Al/MOD(mol)
1	None	0.00244	7.5		3074	
2	BHT	0.00244	7.5	0.00908	3074	826
3	BHT	0.00244	7.5	0.01815	3074	413
4	DMA	0.00302	5.0	0.01271	1656	393
5	DMA	0.00304	7.5	0.25747	2467	29
6	TEOS	0.00302	7.5	0.0192	2483	391
7	DPDEOS	0.00302	7.5	0.01652	2483	454
8	PTEOS	0.00321	4.0	0.0208	1248	192
9	TMA	0.00302	4.0	0.02774	1325	144
10	TMA	0.00302	6.0	0.02774	1987	216

TABLE II (continued)

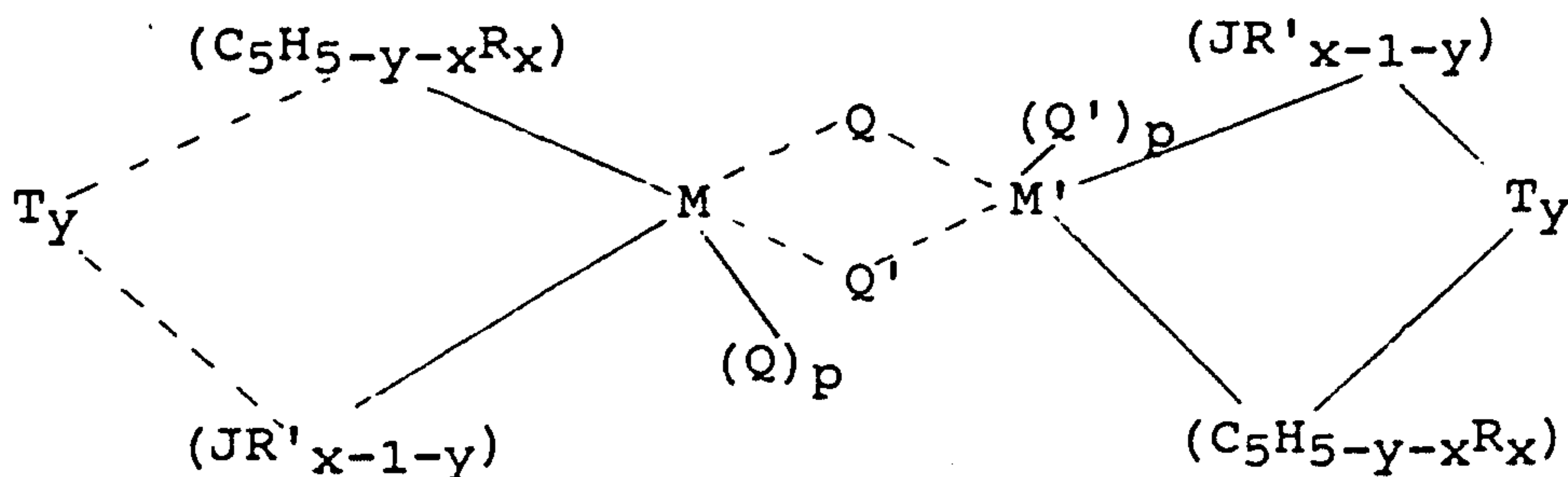
Exp.	I Mod/TM (mol)	J T(C)	K KPA (psi)	L C4(ml)	M t(hr)	N Mw	O MWD	P SCB/1000C	Q Yield (g)
1		80	413.69 (60)	100	0.58	87,900	2.122	55.5(a)	35.0
2	3.2	80	448.16 (65)	100	0.5	71,700	2.254	57.0(a)	46.7
3	7.44	80	448.16 (65)	100	0.5	55,600	2.159	66.0(a)	41.9
4	4.21	80	448.16 (65)	100	0.5	72,600	2.308	154.2(c)	91.6
5	84.69	80	448.16 (65)	100	0.5	81,600	1.913	133.0(b)	86.8
6	6.36	80	448.16 (65)	100	0.5	77,800	2.043	146.0(b)	97.9
7	5.47	80	448.16 (65)	100	0.5	95,900	1.900	86.6(a)	42.6
8	6.49	80	448.16 (65)	100	0.5	26,600	3.150	71.0(b)	130.4
9	9.19	80	448.16 (65)	100	0.5	40,100	3,460	131.1(c)	23.6
10	9.19	80	448.16 (65)	100	0.58	64,800	3.557	91.6(a)	27.6

CLAIMS:

1. A catalyst system comprising:
 - (1) a transition metal compound of the formula:



or



wherein M is a transition metal atom; (C₅H₅-y-xR_x) is a cyclopentadienyl ring which is substituted with 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 radical selected from a group consisting of C₁-C₂₀ hydrocarbyl radicals; substituted C₁-C₂₀ hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, or an alkylborido radical; C₁-C₂₀ hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, or alkylborido radicals; or (C₅H₅-y-xR_x) is a cyclopentadienyl ring in which two adjacent R-groups are joined forming C₄-C₂₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

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(JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group V A or an element with a coordination number of two from Group VI A of the Periodic Table of Elements, each R' is, independently a radical selected from a group consisting of C₁-C₂₀ hydrocarbyl radicals; substituted C₁-C₂₀ hydrocarbyl radicals wherein one or more hydrogen atom is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, or an alkylborido radical; and "z" is the coordination number of element J;

each Q is, independently, an univalent anionic ligand selected from halide, hydride, or a substituted or unsubstituted C₁-C₂₀ hydrocarbyl, alkoxide, aryloxy, amide, or phosphide, provided that where Q is a hydrocarbyl ligand such Q cannot be represented by the formula (C₅H_{5-y-x}R_x) or both Q together are an alkylidene, a cyclometallated hydrocarbyl or a divalent anionic chelating ligand;

"n" and "p" are an integer number such that n + 2 and p + 3 are equal to the oxidation state of M and the oxidation state of M is 3 or greater;

"y" is 0 or 1 when "w" is greater than 0; "y" is 1 when "w" is 0; when "y" is 1, T is a dialkyl, diaryl, or alkyaryl silane, or methylene or ethylene;

L is a neutral Lewis base where "w" denotes a number from 0 to 3; M' has the same meaning as M; Q' has the same meaning as Q; and

(B) an alumoxane; and

(C) a modifier consisting of N, N-dimethylaniline, ethylamine, diethylamine, triethylamine, triphenylamine, triphenylphosphine, hexamethylphosphorous triamide, diethylether, water, deuterium oxide, ethanol, phenol, thiophenol, 2, 6-di-t-butyl-4-methylphenol), tetraethoxysilane, phenyltriethoxysilane, diphenyldiethoxysilane, triphenylethoxysilane, and diethyldihydroxysilane and dimeric, trimeric, tetrameric or oligomeric versions of these compounds.

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2. The catalyst system of claim 1, wherein the transition metal atom is from Group IV B, V B, or VI B of the Periodic Table of Elements.

3. The catalyst system of claim 2, wherein M is Zr, Hf or Ti in its highest formal oxidation state and p is 0.

4. The catalyst system of claim 1, 2 or 3 wherein the heteroatom ligand group J element is nitrogen, phosphorous, oxygen or sulfur.

5. The catalyst system of any one of claims 1 to 4 wherein O is a halogen or hydrocarbyl radical.

6. The catalyst system of any one of claims 1 to 5 wherein the aluminum atom to transition metal atom mole ratio is from 10:1 to 3,000:1.

7. The catalyst system of any one of claims 1 to 6 further comprising an inert support.

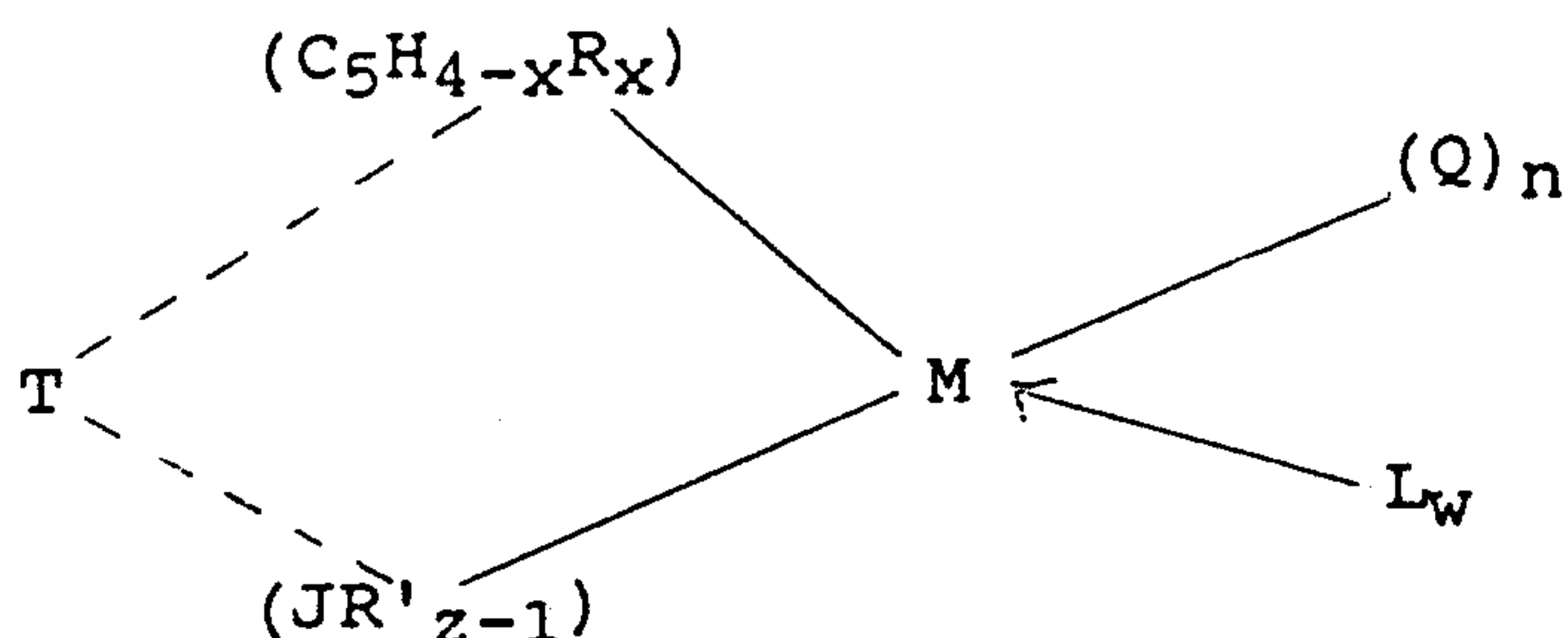
8. The catalyst system of claim 7, wherein the support comprises talc, silica, alumina, silica-alumina, magnesia, magnesium chloride, titania, or zirconia.

9. The catalyst system of any one of claims 1 to 8 wherein said modifier comprises a siloxane, tetraethoxysilane, triphenylethoxysilane, diphenylethoxysilane, phenyltriethoxysilane, N,N-dimethylaniline, or 2,6-di-t-butyl-4-methylphenol.

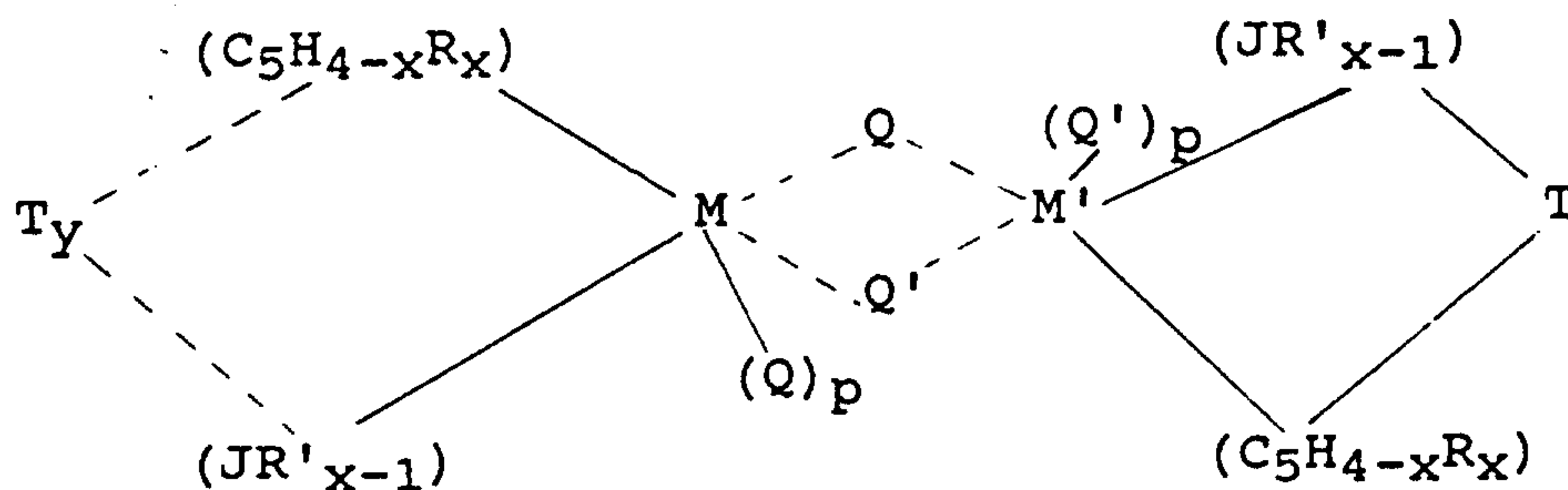
10. A process for producing polyolefins which comprises subjecting an olefinic monomer and optionally one or more comonomers to polymerizing conditions in the presence of a catalyst system according to any one of claims 1 to 9.

11. A process according to claim 10, wherein the olefinic monomer has from 2 to 20 carbon atoms and the optional comonomers comprise a C₂-C₂₀ olefin other than said olefinic monomer and/or polyene.

12. A catalyst system comprising:
 (A) a transition metal compound of the
 formula:



or



wherein M is a transition metal atom; $(C_5H_4-xR_x)$ is a cyclopentadienyl ring which is substituted with from zero to five substituent groups R, "x" is 0, 1, 2, 3, or 4 denoting the degree of substitution, and each substituent group R is, independently, a radical selected from a group consisting of C_1 - C_{20} hydrocarbyl radicals; substituted C_1 - C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, or an alkylborido radical; C_1 - C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; and halogen radicals, amido radicals, phosphido radicals, alkoxy radicals, or an alkylborido radical; or $(C_5H_4-xR_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming C_4 - C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

(JR'_{z-1}) is a heteroatom ligand in which J is an element with a coordination number of three from Group V A or an element with a coordination number of two from Group VI A of the Periodic Table of Elements, each R' is, independently a radical selected from a group consisting of C₁-C₂₀ hydrocarbyl radicals; substituted C₁-C₂₀ hydrocarbyl radicals wherein one or more hydrogen atom is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, or an alkylborido radical; and "z" is the coordination number of element J;

each Q is, independently, an univalent anionic ligand selected from halide, hydride, or a substituted or unsubstituted C₁-C₂₀ hydrocarbyl, alkoxide, aryloxy, amide, phosphide or arylphosphide, provided that where Q is a hydrocarbyl ligand such Q cannot be represented by the formula (C₅H_{4-x}R_x) or both Q together are an alkylidene, a cyclometallated hydrocarbyl or a divalent anionic chelating ligand;

"n" and "p" are an integer number such that n + 2 and p + 3 are equal to the oxidation state of M and the oxidation state of M is 3 or greater;

"y" is 1, and T is a dialkyl, diaryl, alkylaryl silane, methylene or ethylene;

L is a neutral Lewis base where "w" denotes a number from 0 to 3; M' has the same meaning as M; Q' has the same meaning as Q; and

(B) an alumoxane; and

(C) a modifier consisting of N,N-dimethylaniline, ethylamine, diethylamine, triethylamine, triphenylamine, triphenylphosphine, hexamethylphosphorous triamide, diethylether, water, deuterium oxide, ethanol, phenol, thiophenol, 2,6-di-t-butyl-4-methylphenol), tetraethoxysilane, phenyltriethoxysilane, diphenyldiethoxysilane, triphenylethoxysilane, and diethyldihydroxysilane.

13. The catalyst system of claim 12, wherein the transition metal atom is from Group IV B, V B, or VI B of the Periodic Table of Elements.

14. The catalyst system of claim 13, wherein M is Zr, Hf or Ti in its highest formal oxidation state and p is 0.

15. The catalyst system of claim 12, 13 or 14 wherein the heteroatom ligand group J element is nitrogen, phosphorous, oxygen or sulfur.

16. The catalyst system of any one of claims 1 to 9 or 12 to 15 wherein O is a halogen or hydrocarbyl radical.

17. The catalyst system of any one of claims 1 to 9 or 12 to 16 wherein the aluminum atom to transition metal atom mole ratio is from 10:1 to 3,000:1.

18. The catalyst system of any one of claims 1 to 9 or 12 to 17 further comprising an inert support.

19. The catalyst system of claim 18, wherein the support comprises talc, silica, alumina, silica-alumina, magnesia, magnesium chloride, titania, or zirconia.

20. The catalyst system of any one of claims 1 to 9 or 12 to 19 wherein said modifier comprises a siloxane, tetraethoxysilane, triphenylethoxysilane, diphenylethoxysilane, phenyltriethoxysilane, N,N-dimethylaniline, or 2,6-di-t-butyl-4-methylphenol.

21. A process for producing polyolefins which comprises subjecting an olefinic monomer and optionally one or more comonomers to polymerizing conditions in the presence of a catalyst system according to any one of claims 12 to 20.

22. A process according to claim 21, wherein the olefinic monomer has from 2 to 20 carbon atoms and the optional comonomers comprise a C₂-C₂₀ olefin other than said olefinic monomer and/or polyene.