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(54) Title: MULTINUCLEAR TRANSITION METAL POLYMERIZATION CATALYSTS

(57) Abstract: Multinuclear group 4 metal complexes useful as catalyst components for addition polymerizations and polymerization process, especially suited for preparing syndiotactic polymers of vinylaromatic monomers.

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MULTINUCLEAR TRANSITION METAL POLYMERIZATION CATALYSTS

Cross Reference Statement

This application claims the benefit of U.S. Provisional Application No. 60/434,820, filed December 17, 2002.

Background of the Invention

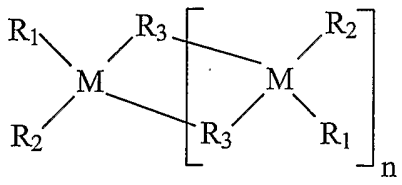
This invention relates to compositions of matter which are useful as addition polymerization catalysts, to a method for preparing these catalyst compositions and to a method of using these catalyst compositions. More particularly, this invention relates to improved addition polymerization catalyst compositions comprising a Group 4 metal complex containing multiple transition metals. The invention also relates to an improved method for polymerizing addition polymerizable monomers, especially vinylaromatic monomers, using these catalyst compositions.

Numerous Group 4 metal compounds containing one or more cyclopentadienyl ligands or multi-ring derivatives of such cyclopentadienyl ligands (also known as metallocenes), their preparation, methods of activation, active catalysts formed therefrom including cationic catalysts, and methods of use are previously known in the art. Such compounds are capable of preparing polymers of addition polymerizable monomers, especially olefins, including vinylaromatic monomers in high yields and/or narrow molecular weight distributions. Examples include those cited in United States Patents (USP's) 5,045,517, 5,196,490 and 5,536,797 wherein titanium containing compounds that are highly selective for the production of syndiotactic polymers of vinyl aromatic monomers are disclosed. Multinuclear, especially binuclear transition metal compounds useful as catalyst components are disclosed in USP 5,892,079.

Despite the advance in the art occasioned by the foregoing patented products, new catalyst compositions having favorable catalytic properties are still sought. After diligent efforts, the present investigations have led to certain improved catalyst compositions that are highly active as addition polymerization catalysts and especially suited for preparation of syndiotactic polymers of vinylaromatic monomers.

Summary of the Invention

According to the present invention, there is now provided a multi-nuclear Group 4 metal complex corresponding to the formula:



(I)

wherein,

M, independently in each occurrence is a group 4 metal, preferably titanium;

R^1 independently in each occurrence is a C_{5-50}, π-coordinated hydrocarbyl ligand, or a boron, silicon, nitrogen, phosphorus, oxygen or gallium substituted derivative thereof, optionally containing one or more halo-, halocarbyl-, halohydrocarbyl-, tri(hydrocarbyl)silyl-, or tri(hydrocarbyl)silylhydrocarbyl- substituents, preferably a cyclopentadienyl, pentamethylcyclopentadienyl, indenyl, benzindenyl, fluorenyl, or octahydrofluorenyl group;

R^2 independently in each occurrence is R^1, hydride, or a hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, trihydrocarbylsilyl, or halo group of up to 20 nonhydrogen atoms, or when n is 2 or greater, two R^2 groups on different metal centers may together form an R^3 group;

R^3 independently in each occurrence is a divalent ligand group selected from O, NR^5, PR^5, $O\text{-}R^4\text{-}O$, $NR^5\text{-}R^4\text{-}NR^5$, and $PR^5\text{-}R^4\text{-}PR^5$, which is shared by two metal centers, M, in the form of a μ-bridged structure, preferably R^3 is O;

R^4, is a divalent ligand group of up to 30 atoms, not counting hydrogen, preferably a C_{1-10} alkylene;

R^5 is an anionic ligand group of up to 30 atoms, not counting hydrogen, preferably a C_{1-6} alkyl; and

n is an integer greater than or equal to 1, preferably an integer from 1 to 3, and most preferably 3.

Further according to the present invention there is provided a process for polymerization of addition polymerizable monomers or mixtures thereof comprising contacting said monomer or mixture of monomers with a catalyst system comprising the above catalyst composition and one or more cocatalysts under addition polymerization conditions. Preferred addition polymerizable monomers are C_{8-20} vinylaromatic monomers, especially styrene, o-, m- or p- C_{1-4} alkyl- substituted styrenes, and mixtures thereof, which form highly syndiotactic polymers. Polymers prepared by the foregoing process are usefully employed for injection molding and other applications.

The catalyst compositions of this invention may also be supported on a support material and used in olefin polymerization processes in a slurry or in a gas phase. The catalyst may be prepolymerized with one or more olefin monomers *in situ* in a polymerization reactor or in a separate process with intermediate recovery of the prepolymerized catalyst prior to the primary polymerization process. Advantageously, the catalyst compositions of the present invention are relatively unaffected by air or water contamination and need not be retained under rigorously inert storage and handling conditions prior to use.

Brief Description of the Drawings

Figures 1 and 2 are computer generated (ORTEP) drawings of the metal complexes of Examples 1 and 2 determined by single crystal X-ray diffraction (XRD) analysis.

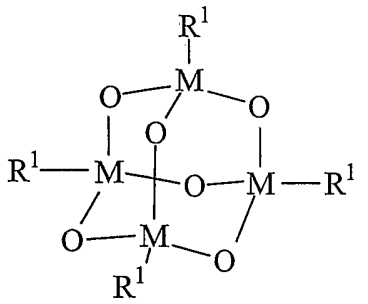
Detailed Description of the Invention

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2001. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. For purposes of United States patent practice, the contents of any patent, patent application or publication referenced herein is hereby incorporated by reference in its entirety, especially with respect to the disclosure of analytical or synthetic techniques and general knowledge in the art.

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

The term "polymer", as used herein, includes both homopolymers, that is, polymers prepared from a single reactive compound, and copolymers, that is, polymers prepared by reaction of at least two polymer forming reactive, monomeric compounds. The term "syndiotactic" means a polymer of one or more monomers capable of forming enantiomers wherein the syndiotacticity at a racemic diad in the Carbon-13 (^{13}C) nuclear magnetic resonance (NMR) spectrum thereof is at least seventy five percent, or the syndiotacticity at a racemic pentad in the ^{13}C NMR spectrum thereof is at least thirty percent.

The metal compounds of the invention preferably are Group 4 metalloxanes having an "adamantane like" structure corresponding to the formula:



(II)

wherein,

M and R^1 are as previously defined with respect to compounds of formula (I).

Preferred metal complexes are those complexes of formula (II) wherein M each occurrence is Ti (titanoxanes), and R^1 independently each occurrence is η^5-pentamethylcyclopentadienyl or η^5-octahydrofluorenyl.

The foregoing metal complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of the transition metal and the various ligand sources. The metalloxanes in particular are prepared by reaction of the corresponding monocyclopentadienyl (monoCp) metal trialkoxide with water. The complexes may be prepared using standard dry box synthetic techniques.

Suitable activating cocatalysts useful in combination with the present metal complexes are those compounds capable of abstracting a substituent therefrom to form an inert, noninterfering counter ion, or that form a zwitterionic or other catalytically active derivative of the metal complex. Suitable activating cocatalysts for use herein include Lewis acids, such as alumoxanes, including trialkylaluminum, tris(fluoroaryl)aluminum and tris(fluoroaryl)boron modified alumoxanes, or perfluorinated tri(aryl)boron compounds, and most especially methylalumoxane (MAO) or tris(pentafluorophenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially ammonium-, phosphonium-, oxonium-, carbonium-, silylium-, sulfonium-, or ferrocenium- salts of compatible, noncoordinating anions. A combination of the foregoing activating cocatalysts may be employed as well.

More particularly, suitable ion forming compounds useful as cocatalysts in one embodiment of the present invention comprise a cation which is a Bronsted acid capable of donating a proton, and a compatible, noncoordinating anion, A^-. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as

ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

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

$$(L^*\text{-}H)^+_d\ (A)^{d-n}$$

wherein:

L* is a neutral Lewis base;

$(L^*\text{-}H)^+$ is a Bronsted acid;

A^{d-} is a noncoordinating, compatible anion having a charge of d-, and

d is an integer from 1 to 3.

More preferably A^{d-} corresponds to the formula: $[M'Q_4]^-$;

wherein:

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

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxide, halosubstituted-hydrocarbyl, hydroxy- substituted hydrocarbyl, halosubstituted hydrocarbyloxy, and halo- substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons (C_{20}) with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxide Q groups are disclosed in US-A-5,296,433 (Scheme II at column 5, lines 50-55 and Example 5 related to preparation of $(C_6F_5)_3B.2MeOH$).

In a more preferred embodiment, d is one, that is, the counter ion has a single negative charge and is A^-. Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula: $(L^*\text{-}H)^+(BQ_4)^-$;

wherein:

L* is as previously defined;

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

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

Most preferably, Q is each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this invention are tri-substituted ammonium salts such as:
trimethylammonium tetrakis(pentafluorophenyl) borate,
triethylammonium tetrakis(pentafluorophenyl) borate,
tripropylammonium tetrakis(pentafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-N-dodecylammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-N-octadecylammonium tetrakis(pentafluorophenyl) borate,
N-methyl-N,N-didodecylammonium tetrakis(pentafluorophenyl) borate,
N-methyl-N,N-dioctadecylammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate,
N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(4-(t-butyldimethylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate,
trimethylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate,
triethylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
tripropylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
dimethyl(t-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
N,N-diethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate, and
N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate;
disubstituted ammonium salts such as:
di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, and
dicyclohexylammonium tetrakis(pentafluorophenyl) borate;
trisubstituted phosphonium salts such as:
triphenylphosphonium tetrakis(pentafluorophenyl) borate,
tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and
tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate;

disubstituted oxonium salts such as:
diphenyloxonium tetrakis(pentafluorophenyl) borate,
di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and
di(2,6-dimethylphenyl)oxonium tetrakis(pentafluorophenyl) borate;
disubstituted sulfonium salts such as:
diphenylsulfonium tetrakis(pentafluorophenyl) borate,
di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and
bis(2,6-dimethylphenyl)sulfonium tetrakis(pentafluorophenyl) borate.

Preferred $(L^*\text{-}H)^+$ cations are N,N-dimethylanilinium, tributylammonium, N-methyl-N,N-di(dodecyl)ammonium, N-methyl-N,N-di(tetradecyl)ammonium, N-methyl-N,N-di(hexadecyl)ammonium, N-methyl-N,N-di(octadecyl)ammonium, and mixtures thereof. The latter three cations are the primary ammonium cations derived from a commercially available mixture of 14 to 18 carbon atoms (C_{14-18}) tallow amines, and are collectively referred to as bis-hydrogenated tallowalkyl methylammonium cation. The resulting ammonium salt of the tetrakis(pentafluorophenyl)borate anion accordingly is know as bis-hydrogenated tallowalkyl methylammonium tetrakis(pentafluorophenyl)borate.

Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula: $(Ox^{e+})_d(A^{d-})_e$.

wherein:

Ox^{e+} is a cationic oxidizing agent having a charge of e+;

e is an integer from 1 to 3; and

A^{d-} and d are as previously defined.

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

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

wherein:

$©^+$ is a C_{1-20} (1 to 20 carbon atoms) carbenium ion; and

A^- is as previously defined. A preferred carbenium ion is the trityl cation, i.e. triphenylmethylium.

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

$R^3_3Si^+ A^-$

wherein:

R^* is C_{1-10} (1 to 10 carbon atoms) hydrocarbyl, and A^- are as previously defined.

Preferred silylium salt activating cocatalysts are trimethylsilylium tetrakispentafluorophenylborate, triethylsilylium tetrakispentafluorophenylborate and ether substituted adducts thereof.

Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present invention. Such cocatalysts are disclosed in USP 5,296,433, the teachings of which are herein incorporated by reference.

Another class of suitable catalyst activators are expanded anionic compounds corresponding to the formula: $(A^{1+a^1})_{b^1}(Z^1J^1_{j^1})^{-c1}{}_{d^1}$,

wherein:

A^1 is a cation of charge $+a^1$,

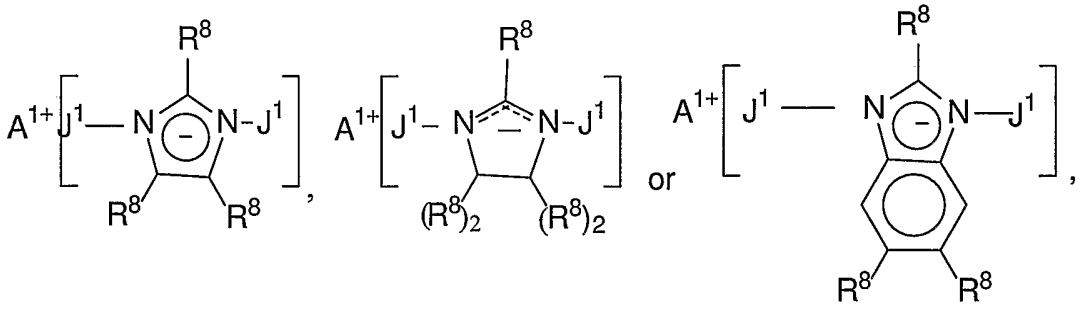
Z^1 is an anion group of from 1 to 50, preferably 1 to 30 atoms, not counting hydrogen atoms, further containing two or more Lewis base sites;

J^1 independently each occurrence is a Lewis acid coordinated to at least one Lewis base site of Z^1, and optionally two or more such J^1 groups may be joined together in a moiety having multiple Lewis acidic functionality,

j^1 is a number from 2 to 12 and

a^1, b^1, c^1, and d^1 are integers from 1 to 3, with the proviso that $a^1 \times b^1$ is equal to $c^1 \times d^1$.

The foregoing cocatalysts (illustrated by those having imidazolide, substituted imidazolide, imidazolinide, substituted imidazolinide, benzimidazolide, or substituted benzimidazolide anions) may be depicted schematically as follows:



wherein:

A^{1+} is a monovalent cation as previously defined, and preferably is a trihydrocarbyl ammonium cation, containing one or two C_{10-40} alkyl groups, especially the methylbis(tetradecyl)ammonium- or methylbis(octadecyl)ammonium- cation,

R^8, independently each occurrence, is hydrogen or a halo, hydrocarbyl, halocarbyl, halohydrocarbyl, silylhydrocarbyl, or silyl, (including mono-, di- and tri(hydrocarbyl)silyl) group of up to 30 atoms not counting hydrogen, preferably C_{1-20} alkyl, and

J^1 is tris(pentafluorophenyl)borane or tris(pentafluorophenyl)aluminane.

Examples of these catalyst activators include the trihydrocarbylammonium-, especially, methylbis(tetradecyl)ammonium- or methylbis(octadecyl)ammonium- salts of: bis(tris(pentafluorophenyl)borane)imidazolide, bis(tris(pentafluorophenyl)borane)-2-undecylimidazolide, bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolide, bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolide, bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolide, bis(tris(pentafluorophenyl)borane)imidazolinide, bis(tris(pentafluorophenyl)borane)-2-undecylimidazolinide, bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolinide, bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolinide, bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolinide, bis(tris(pentafluorophenyl)borane)-5,6-dimethylbenzimidazolide, bis(tris(pentafluorophenyl)borane)-5,6-bis(undecyl)benzimidazolide, bis(tris(pentafluorophenyl)alumane)imidazolide, bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolide, bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolide, bis(tris(pentafluorophenyl)alumane)imidazolinide, bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide, bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide, bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolide, and bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolide.

A further class of suitable activating cocatalysts include cationic Group 13 salts corresponding to the formula: $[M''Q^1{}_2L'_{r'}]^+ (Ar^f{}_3M'Q^2)^-$

wherein:

M" is aluminum, gallium, or indium;

M' is boron or aluminum;

Q^1 is C_{1-20} hydrocarbyl, optionally substituted with one or more groups which independently each occurrence are hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbylsilyl)amino, hydrocarbylamino, di(hydrocarbyl)amino, di(hydrocarbyl)phosphino, or hydrocarbylsulfido groups having from 1 to 20 atoms other than hydrogen, or, optionally, two or

more Q^1 groups may be covalently linked with each other to form one or more fused rings or ring systems;

Q^2 is an alkyl group, optionally substituted with one or more cycloalkyl or aryl groups, said Q^2 having from 1 to 30 carbons;

L' is a monodentate or polydentate Lewis base, preferably L' is reversibly coordinated to the metal complex such that it may be displaced by an olefin monomer, more preferably L' is a monodentate Lewis base;

l' is a number greater than zero indicating the number of Lewis base moieties, L', and

Ar^f independently in each occurrence is an anionic ligand group; preferably Ar^f is selected from the group consisting of halide, C_{1-20} halohydrocarbyl, and Q^1 ligand groups, more preferably Ar^f is a fluorinated hydrocarbyl moiety of from 1 to 30 carbon atoms, most preferably Ar^f is a fluorinated aromatic hydrocarbyl moiety of from 6 to 30 carbon atoms (C_{6-30}), and most highly preferably Ar^f is a perfluorinated aromatic hydrocarbyl moiety of from 6 to 30 carbon atoms.

Examples of the foregoing Group 13 metal salts are alumicinium tris(fluoroaryl)borates or gallicinium tris(fluoroaryl)borates corresponding to the formula: $[M''Q^1{}_2L'_{l'}]^+ (Ar^f{}_3BQ^2)^-$, wherein M" is aluminum or gallium; Q^1 is C_{1-20} hydrocarbyl, preferably C_{1-8} alkyl; Ar^f is perfluoroaryl, preferably pentafluorophenyl; and Q^2 is C_{1-8} alkyl, preferably C_{1-8} alkyl. More preferably, Q^1 and Q^2 are identical C_{1-8} alkyl (respectively, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl) groups, most preferably, methyl, ethyl or octyl.

The foregoing activating cocatalysts may also be used in combination. An especially preferred combination is a mixture of a tri(hydrocarbyl)aluminum or tri(hydrocarbyl)borane compound having from 1 to 4 carbons (C_{1-4}) in each hydrocarbyl group or an ammonium borate with an oligomeric or polymeric alumoxane compound.

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

The most preferred activating cocatalysts are methylalumoxanes, including tri(C_{3-12} alkyl)aluminum modified alumoxanes, trispentafluorophenylborane and a mixture of long chain ammonium salts of tetrakis(pentafluorophenyl)borate, especially N,N-dioctadecyl-N-methylammonium tetrakpentafluorophenylborate, N-methyl-N,N-di(hexadecyl)ammonium

tetrakpentafluorophenylborate and N,N-ditetradecyl-N-methylammonium tetrakpentafluorophenylborate. C_{3-8} alkyls are noted above. C_{9-12} alkyls are, respectively, nonyl, decyl, undecyl and dodecyl. The latter mixture of borate salts is derived from hydrogenated tallow amine, and is referred to as bis-hydrogenated tallow alkyl methylammonium tetrakis(pentafluorophenyl)borate.

Additional components, such as scavengers, especially trialkylaluminum compounds, dialkylaluminum alkoxides, dialkylaluminum N,N-di(hydrocarbyl)amides, alkylaluminum dialkoxide compounds and hydroxyl containing compounds, especially triphenylmethanol, and the reaction products of such hydroxyl containing compounds with alkylaluminum compounds, may be included in the catalyst composition of the invention if desired. A particularly preferred scavenger is triisobutylaluminum (TIBA). Generally such additional components are present in the reaction mixture in molar ratios from 1:1 to 500:1 based on metal complex, preferably from 10:1 to 100:1.

The process may be used to polymerize ethylenically unsaturated monomers having from 2 to 20 carbon atoms (C_{2-20}) either alone or in combination. Preferred monomers include monovinylidene aromatic monomers, 4-vinylcyclohexene, vinylcyclohexane, norbornadiene and C_{2-10} aliphatic α-olefins (especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, and 1-octene), C_{4-40} dienes, and mixtures thereof. Of the dienes typically used to prepare ethylene/propylene/diene monomer polymers (EPDMs), the particularly preferred dienes are 1,4-hexadiene (HD), 5-ethylidene-2-norbornene (ENB), 5-vinylidene-2-norbornene (VNB), 5-methylene-2-norbornene (MNB), and dicyclopentadiene (DCPD). The especially preferred dienes are 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene (HD). Most preferred monomers are ethylene, mixtures of ethylene, propylene and ethylidenenorbornene, mixtures of ethylene and a C_{4-8} α-olefin, especially 1-butene, 1-hexene or 1-octene, styrene, and mixtures of styrene and p-methylstyrene.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250 degrees centigrade (°C), preferably 30 to 200 °C and pressures from atmospheric to 30,000 atmospheres or higher. Suspension, solution, slurry, gas phase, solid state powder polymerization or other process condition may be employed if desired. A support, especially silica, alumina, or a polymer (especially poly(tetrafluoroethylene) or a polyolefin) may be employed, and desirably is employed when the catalysts are used in a gas phase polymerization process. The support is preferably employed in an amount to provide a weight ratio of catalyst (based on metal):support from 1:100,000 to 1:10, more preferably from 1:50,000 to 1:20, and most preferably from 1:10,000 to 1:30.

In most polymerization reactions, the molar ratio of catalyst:polymerizable compounds employed is from 10^{-12}:1 to 10^{-1}:1, more preferably from 10^{-9}:1 to 10^{-5}:1.

Suitable solvents for polymerization are inert liquids. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C_{4-10} alkanes, and the like and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene, ethylbenzene and the like. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 1-hexane, 4-vinylcyclohexene, vinylcyclohexane, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, vinyltoluene (including all isomers alone or in admixture), and the like. Mixtures of the foregoing are also suitable.

The catalysts may be utilized in combination with at least one additional homogeneous or heterogeneous polymerization catalyst in the same or separate reactors connected in series or in parallel to prepare polymer blends having desirable properties.

The catalyst composition may be prepared as a homogeneous catalyst by addition of the requisite components to a solvent. The catalyst composition may also be prepared and employed as a heterogeneous catalyst by adsorbing the requisite components on a catalyst support material such as silica gel, alumina or other suitable inorganic support material. When prepared in heterogeneous or supported form, it is preferred to use silica as the support material. The heterogeneous form of the catalyst system is desirably employed in a slurry or gas phase polymerization. As a practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization is one or more hydrocarbons with less than 5 carbon atoms. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. Likewise the α-olefin monomer or a mixture of different α-olefin monomers may be used in whole or part as the diluent. Most preferably the diluent comprises in at least major part the α-olefin monomer or monomers to be polymerized.

In contrast, solution polymerization conditions utilize a solvent for the respective components of the reaction, particularly the resulting polymer, at the temperature of operation. Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperatures. Illustrative examples of useful solvents include alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane, as well as mixtures of alkanes including kerosene and Isopar E™, a blend of iso-octane and iso-nonane which is available from Exxon Chemicals Inc.;

cycloalkanes such as cyclopentane and cyclohexane; and aromatics such as benzene, toluene, xylenes, ethylbenzene and diethylbenzene.

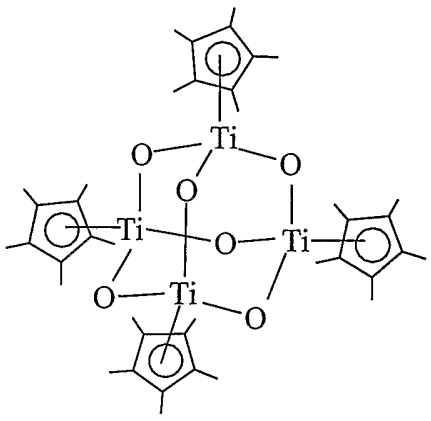
At all times, the individual ingredients as well as the recovered catalyst components must be protected from oxygen and moisture. Therefore, the catalyst components and catalyst compositions must be prepared and recovered in an oxygen and moisture free environment. Preferably, therefore, the syntheses are performed in the presence of a dry, inert gas such as, for example, nitrogen.

Generally the polymerization of olefin monomers is carried out with a differential pressure from about 10 to about 1000 psi (70 to 7000 kPa), most preferably from about 40 to about 400 psi (30 to 300 kPa). The polymerization is generally conducted at a temperature of from 25 to 200 °C, preferably from 75 to 170 °C, and most preferably from greater than 95 to 160 °C. Generally polymerization of vinylaromatic monomers is conducted in a solid, powder bed polymerization reactor at temperatures from 25 to 120°C, preferably from 50 to 90 °C under conditions to avoid substantial formation of atactic vinylaromatic polymer.

The polymerization may be carried out as a batchwise or a continuous polymerization process. A continuous process is preferred, in which event the catalyst composition or the individual components thereof, monomer(s), and optionally solvent are continuously supplied to the reaction zone and polymer product continuously or semicontinuously removed therefrom.

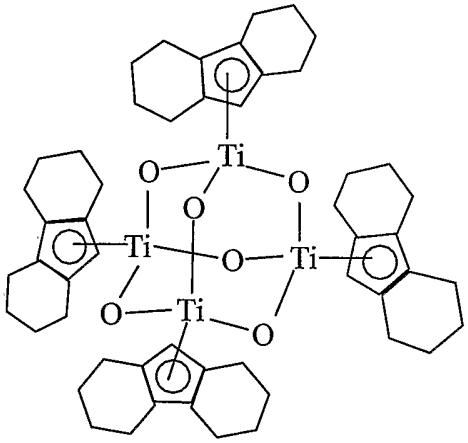
The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component which has not been specifically disclosed. The following examples are provided as further illustration of the invention and are not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis.

Example 1 Tetrakis(pentamethylcyclopentadienyl)titanoxane



To a crimp sealed ampoule equipped with a stirring bar under nitrogen atmosphere, 5 grams (g) (18.1 millimoles (mmol)) of η^5-pentamethylcyclopentadienyltitanium trimethoxide were added. Then, 10 g, (0.556 mol) of degassed distilled water were slowly added by syringe at room temperature. After a complete reaction, the mixture was filtered under air and dried under vacuum at room temperature for three days. The desired product was recovered as a light yellow powder. Yield 3.47 g, 93 percent. After preparing crystals, the product was subjected to analysis by X-ray crystallography. The resulting structure (ORTEP) is shown in Figure 1.

Example 2 Tetrakis(octahydrofluorenyl)titanoxane



In a glass flask under an inert atmosphere, 5 g (15.9 mmol) of η^5-octahydrofluorenyl-titanium trimethoxide were dissolved in 150 ml of degassed acetone. While refluxing 40 ml (2.22 mol) of degassed distilled water were added slowly by syringe. After completion of the addition, refluxing was continued for 30 minutes. The light yellow precipitate that formed was separated, washed with a 15:4 volume mixture of acetone and water and dried under reduced pressure. The desired product was recovered as a light yellow powder. Yield 3.50 g, 90 percent. The X-ray crystal structure of the product (ORTEP) is shown in Figure 2.

Styrene Polymerization

All preparations were carried out under inert gas atmosphere. Catalyst premix solutions were prepared in a 5 milliliters (ml) glass flask by combining a toluene solution of methylalumoxane (MAO), triisobutylaluminum (TIBA), and 8.0 milligrams (mg) of Ex. 1 complex or 9.4 mg of Ex. 2 complex along with additional toluene to make 5 ml total volume.

Styrene polymerizations were conducted in glass ampoules charged with 10 ml of deoxygenated styrene that had been passed through activated alumina and hydrogenated using Pd on alumina to remove impurities. The flasks were capped with a septum, crimp sealed and placed in a water bath at the desired temperature for 10 minutes to equilibrate. Polymerization was initiated by addition of the desired quantity of catalyst premix via microliter syringe. After

polymerization for the desired time the reaction was quenched by addition of methanol. The resulting polymer was isolated and dried under vacuum for 30 minutes at 150 °C followed by 35 minutes at 250 °C. Results are contained in Table 1 where "Tc" means crystallization temperature, "Mn" means number average molecular weight and "Mw" means weight average molecular weight.

Table 1

Run	Catalyst	Styrene/MAO /TIBA/Ti[1]	Temp.[2] (°C)	Time (min)	Conversion (percent)	Tc (°C)	Mn (x 10^3)	Mw/Mn
1	Ex. 1	$2.52x10^6$/720/360/1	60	120	5.13	266	304	5.2
2*	"	"	"	"	3.48	266	301	5.2
3**	Ex. 2	$2.56x10^6$/732/366/1	"	"	8.46	269	188	3.42
4**	"	"	"	"	9.57	268	53	2.91
5	"	$1.28x10^6$/274/91/1	50	60	8.64	267	317	2.61
6***	"	"	"	"	9.92	268	267	3.17

* metal complex stored in air for 5 days prior to polymerization

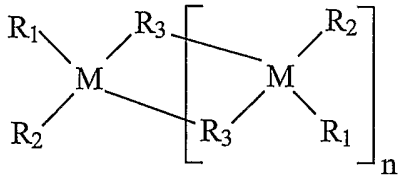
** 18.7 µl of a toluene solution containing 1.4 µmol triphenylmethanol and 1.7 µmol TIBA additionally added to styrene monomer before polymerization

*** Hydrogen (4 psi, 28 kPa) added to polymerization flask during polymerization

1. molar ratio
2. reaction temperature

CLAIMS:

1. A multi-nuclear Group 4 metal complex corresponding to the formula:



(I)

;

wherein,

M, independently each occurrence is a group 4 metal, preferably titanium;

R^1 independently each occurrence is a C_{5-50}, π-coordinated hydrocarbyl ligand, or a boron, silicon, nitrogen, phosphorus, oxygen or gallium substituted derivative thereof, optionally containing one or more halo-, halocarbyl-, halohydrocarbyl-, tri(hydrocarbyl)silyl-, or tri(hydrocarbyl)silylhydrocarbyl-, substituents, preferably a cyclopentadienyl, pentamethylcyclopentadienyl, indenyl, benzindenyl, fluorenyl, or octahydrofluorenyl group;

R^2 independently each occurrence is R^1, hydride, or a hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, trihydrocarbylsilyl, or halo group of up to 20 nonhydrogen atoms, or when n is 2 or greater, two R^2 groups on different metal centers may together form an R^3 group;

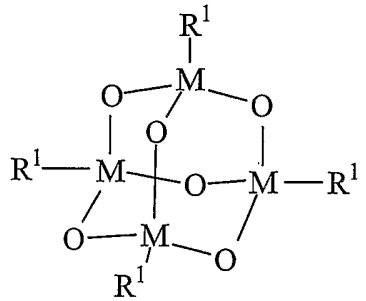
R^3 independently each occurrence is a divalent ligand group selected from O, NR^5, PR^5, O-R^4-O, NR^5-R^4-NR^5, and PR^5-R^4-PR^5, which is shared by two metal centers, M, in the form of a μ-bridged structure, preferably R^3 is O;

R^4, is a divalent ligand group of up to 30 atoms, not counting hydrogen, preferably C_{1-10} alkylene;

R^5 is an anionic ligand group of up to 30 atoms, not counting hydrogen, preferably C_{1-6} alkyl; and

n is an integer greater than or equal to 1, preferably an integer from 1 to 3, and most preferably 3.

2. A metal complex according to claim 1 corresponding to the formula:



(II)

wherein,

M and R^1 are as previously defined with respect to compounds of formula (I).

3. A metal complex according to claim 2 wherein M each occurrence is Ti, and R^1 independently each occurrence is η^5-pentamethylcyclopentadienyl or η^5-octahydrofluorenyl.

4. A process for polymerization of addition polymerizable monomers or mixtures thereof comprising contacting said monomer or mixture of monomers with a catalyst system comprising the metal complex of claim 1 and one or more activating cocatalysts under addition polymerization conditions.

5. A process according to claim 4 wherein the molar ratio of metal complex to cocatalyst is from 1:1 to 1:10,000.

6. A process according to claim 4 wherein the activating cocatalyst comprises methylalumoxane, N-methyl-N,N-dioctadecylammonium tetrakis(pentafluorophenyl)borate, or bis-hydrogenated tallowalkyl methylammonium tetrakis(pentafluorophenyl)borate.

7. The process of claim 4 wherein the addition polymerizable monomer is styrene, p-methylstyrene, or a mixture thereof.

8. The process of claim 7 wherein a syndiotactic polymer is prepared.

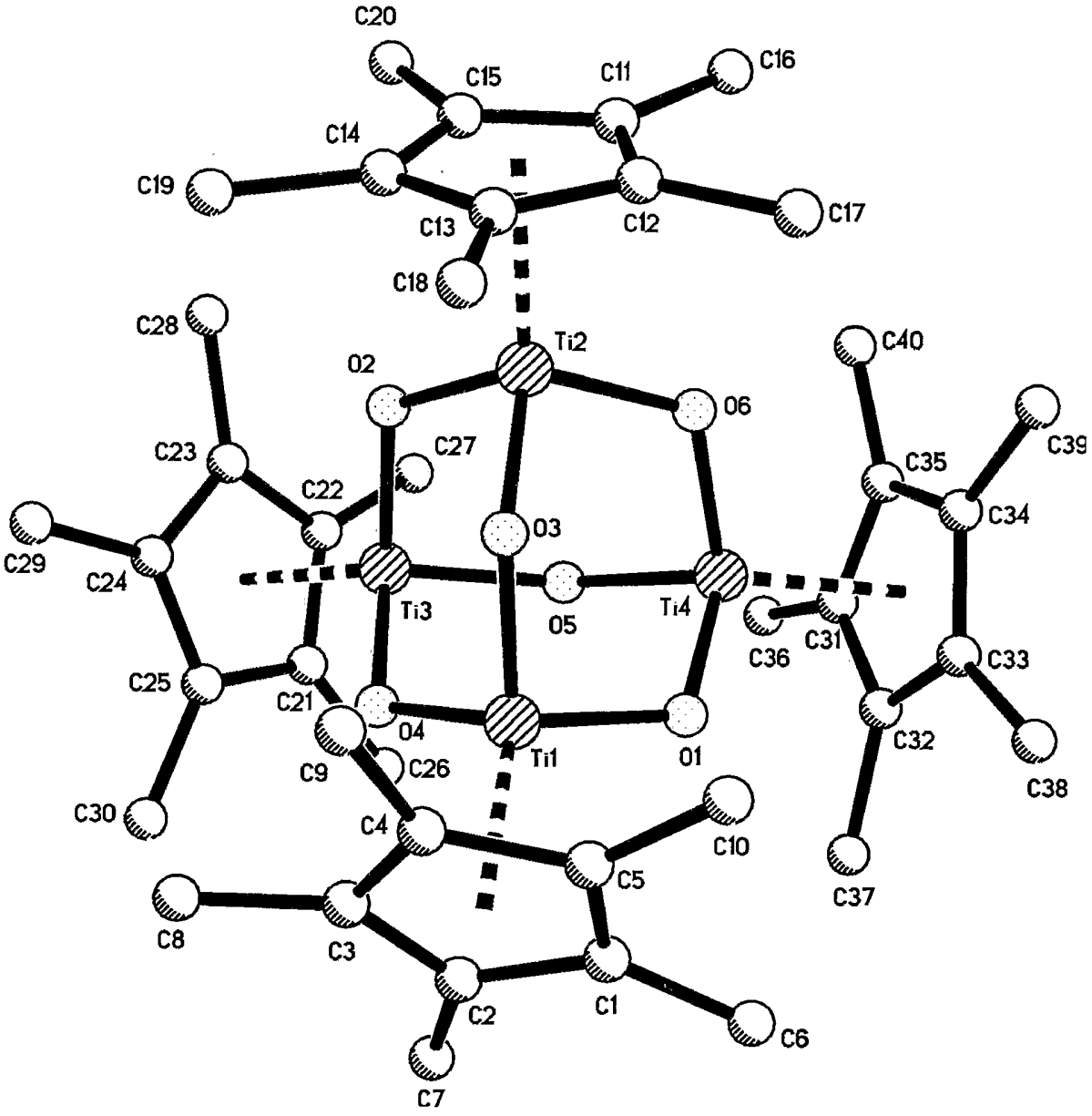

C20
C15
C11
C16
C14
C19
C13
C12
C17
C18
C28
Ti2
C40
O2
O6
C39
C23
C27
C35
C22
O3
C34
C29
C24
Ti3
O5
Ti4
C31
C36
C25
C21
O4
C33
Ti1
O1
C32
C9
C26
C38
C30
C4
C10
C5
C37
C8
C3
C2
C1
C6
C7

Figure 1

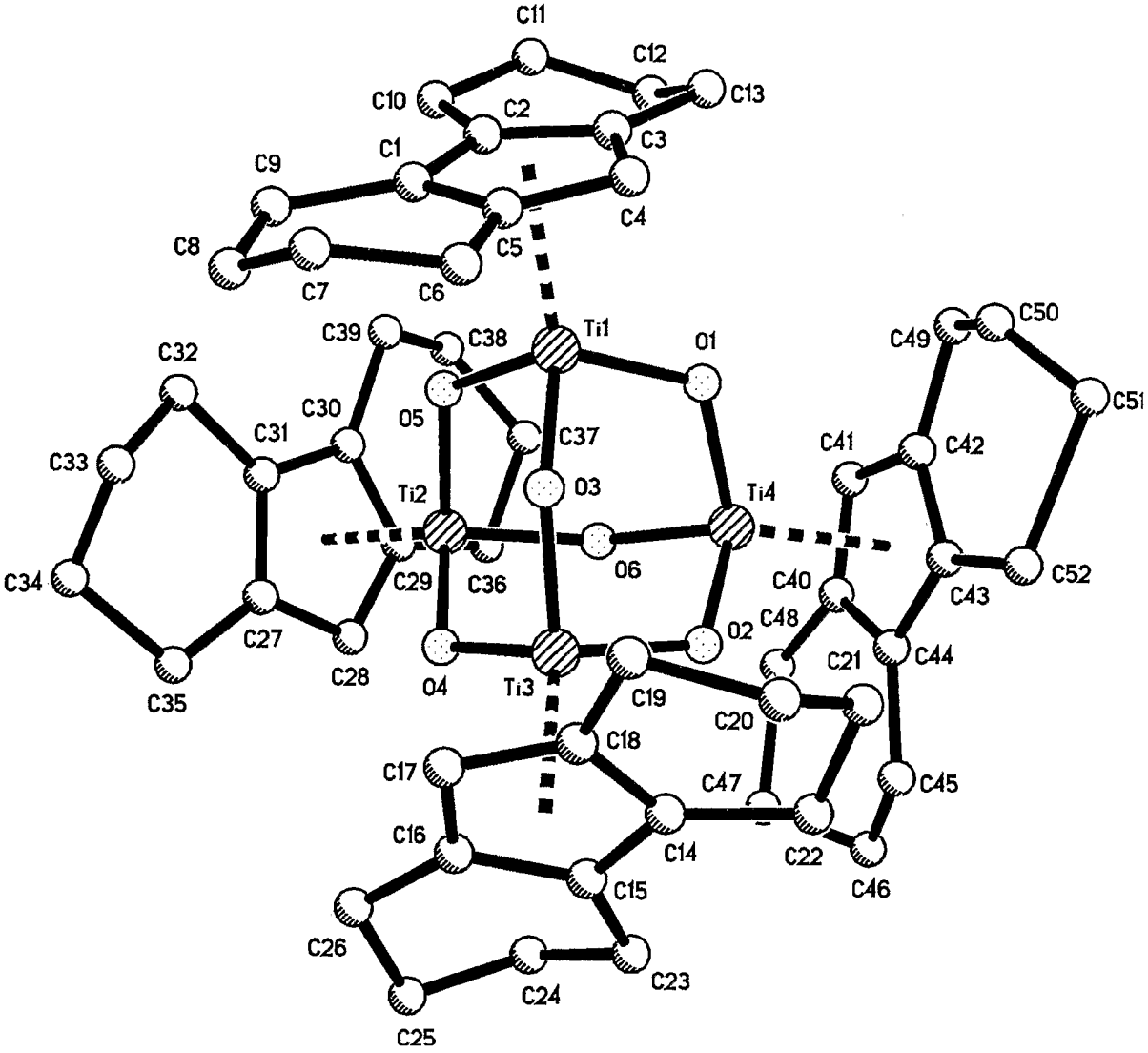

C11
C12
C13
C10
C2
C3
C1
C9
C4
C8
C5
C7
C6
C39
C38
Ti1
O1
C49
C50
C32
C30
O5
C37
C51
C31
C41
C42
C33
Ti2
O3
Ti4
C34
C29
C36
O6
C40
C52
C43
C48
C27
O2
C21
C44
C28
O4
Ti3
C19
C20
C35
C18
C17
C47
C45
C16
C14
C22
C15
C46
C26
C23
C24
C25

Figure 2

INTERNATIONAL SEARCH REPORT

Ir onal Application No
PCT/US 03/34817

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F17/00 C08F4/00 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FANDOS, ROSA ET AL: "Isolation and characterization of the first bis(2-pyridyl)carbyltitanium(IV) complex derived from the C-O bond cleavage of the alkoxide ligand in Cp*TiMe2(OCMePy2). X-Ray crystal structure of 'Cp*Ti(.mu.-O)(CMePy2)!2 (Cp* = C5Me5)" JOURNAL OF THE CHEMICAL SOCIETY, DALTON TRANSACTIONS (2002), (1), 11-13 , 2002, XP002274069 the whole document --- -/--	1

[X] Further documents are listed in the continuation of box C.

[ ] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 March 2004	08/04/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Rinkel, L

INTERNATIONAL SEARCH REPORT

Int ɔnal Application No
PCT/US 03/34817

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZAGOREVSKII, DMITRI V. ET AL: "Tandem Mass Spectrometry Study of the Zirconocenium Ion: Generation of Neutral Zirconocene in the Gas Phase" ORGANOMETALLICS (1995), 14(11), 5041-3 , 1995, XP002274070 the whole document	1
X	GOMEZ-SAL, PILAR ET AL: "Hydrolysis of (pentamethylcyclopentadienyl)titanium(IV) carbamates. X-ray structure of '{Cp*Ti(.eta.2-O2CNEt2)}2(.mu.-O)2!" JOURNAL OF ORGANOMETALLIC CHEMISTRY (1995), 494(1-2), C19-C21 , 1995, XP002274071 the whole document	1
X	OKUDA, JUN ET AL: "Synthesis and structural characterization of an organotitanium complex containing a planar bis(.mu.-oxo)dititanium core" INORGANIC CHEMISTRY (1991), 30(7), 1516-20 , 1991, XP002274072 the whole document	1
X	OKUDA, JUN: "Komplee mit sterisch anspruchsvollen Liganden. IX. Sterische Effekte bei de Hydrolyse von Cyclopentadienyl-Titan-Komplexen" JOURNAL OF ORGANOMETALLIC CHEMISTRY (1990), 397(3), C37-C40 , 1990, XP002274073 the whole document	1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/34817

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Continuation of Box I.2

Present claims 1,4-8 relate to an extremely large number of possible compounds and their uses. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of these compounds and their use. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds of Formula (I) wherein R3 is an oxygen atom

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.