



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US94/01647 <b>(22) International Filing Date:</b> 10 February 1994 (10.02.94)  <b>(30) Priority Data:</b> 08/034,434 19 March 1993 (19.03.93) US  <b>(71) Applicant:</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).  <b>(72) Inventors:</b> NICKIAS, Peter, N.; 4512 North Saginaw Road, Apartment 1120, Midland, MI 48642 (US). TIMMERS, Francis, J.; 4605 Lund Drive, Midland, MI 48642 (US). DEVORE, David, D.; 4881 East Shaffer Road, Midland, MI 48642 (US). ROSEN, Robert, K.; 1800 Rivercrest Drive No. 210, Sugar Land, TX 77478 (US). MUSSELL, Robert, D.; 3800 Haskin Drive, Midland, MI 48640 (US).  <b>(74) Agent:</b> DELINE, Douglas, N.; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641- 1967 (US).		<b>(81) Designated States:</b> CA, FI, JP, KR, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> PREPARATION OF ADDITION POLYMERIZATION CATALYSTS VIA LEWIS ACID MITIGATED METAL CENTER OXIDATION  <b>(57) Abstract</b>  Addition polymerization catalysts comprising a derivative of a titanium or zirconium in the +4 oxidation state prepared by metal center oxidation and cation complex formation of a reduced metal precursor complex via electron transfer in a single step by use of a neutral organic oxidant, optionally in the presence of a Lewis acid mitigator.		

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PREPARATION OF ADDITION POLYMERIZATION CATALYSTS VIA LEWIS ACID MITIGATED  
METAL CENTER OXIDATION

This invention relates to a process for preparing certain catalytically active metal  
5 complexes. More particularly, this invention relates to such a process involving oxidation of the  
metal center of a complex to form active catalyst compositions useful for polymerizing olefins,  
diolefins and/or acetylenically unsaturated monomers.

The use of homogeneous Ziegler-Natta type catalysts in the polymerization of  
addition polymerizable monomers is, of course, well known in the prior art. In general, these  
10 soluble systems comprise a Group 4 or Lanthanide metal compound and a metal alkyl  
cocatalyst, particularly an aluminum alkyl cocatalyst. Several preparations for homogeneous  
olefin polymerization catalysts are known. These involve reacting a transition metal chloride  
with an aluminum alkyl, reacting a transition metal alkyl and a aluminum alkyl, reacting a  
transition metal alkyl with a proton source, or reacting a transition metal alkyl with a cationic  
15 oxidant. In these examples the oxidation state of the transition metal remains unchanged or  
may actually be reduced.

In Polyhedron, 8(13-14), 1838-1843 (1989), M. Bochmann et al., disclosed an  
oxidative process for preparing bispentamethylcyclopentadienyltitanium methyl  
tetraphenylborate using silver tetraphenylborate oxidant in tetrahydrofuran solvent. The  
20 complex was inactive in the polymerization of ethylene.

In J. Am. Ch. Soc. 109, 4111-4113 (1987) there is disclosed a process for  
preparation of cationic zirconium (IV) benzyl complexes by one electron molecular oxidation of  
d<sup>0</sup> organometallic compounds in tetrahydrofuran or methylene chloride solvent.

In US-A-5,189,192 a metal center oxidation and cation forming process employing  
25 a cationic oxidizer is disclosed. In EP-A-416,815 there are disclosed certain novel constrained  
geometry complexes possessing unique catalytic properties. In EP-A-468,651 there is disclosed a  
unique molecular oxidative activation procedure for preparing complexes useful as addition  
polymerization catalysts.

The present invention lies in the discovery of a novel technique for preparing  
30 certain metal complexes involving both metal center oxidation and cation complex formation  
via electron transfer in a single step by use of a neutral organic oxidant. Beneficially, the use of  
neutral reactants permits the synthesis to be performed in hydrocarbon solvents normally  
employed for olefin polymerizations instead of polar or oxygenated solvents. Consequently, in  
the present invention contamination with deactivating substances is reduced and the need to  
35 substitute solvents prior to use of the resulting complexes is omitted, thereby simplifying the  
synthesis and use of the complexes as catalysts.

In one embodiment of the invention, the reduced remnant of the oxidizing agent  
comprises an anion able to ligate the metal complex. To counteract this ligating effect of the

resulting residual organic anion, a Lewis acid mitigator is additionally added to the reaction mixture. Thus the process is adaptable for use even where the byproducts may interfere with the desired metal complex formation.

According to the present invention there is provided a process for the preparation  
5 of a cationic metal complex corresponding to the formula:

$[\text{Cp}_a(\text{ZY})_b\text{ML}_c^+]\text{q} [\text{J}_p\text{A}]^q$ , wherein:

Cp independently each occurrence is a cyclopentadienyl group  $\pi$ -bound to M, or a hydrocarbyl, silyl, halo, halohydrocarbyl, hydrocarbylmetaloid or halohydrocarbylmetaloid substituted derivative of said cyclopentadienyl group, said Cp containing up to 50  
10 nonhydrogen atoms, and, when a is 2, optionally both Cp groups may be joined together by a bridging group;

a is 1 or 2;

b is 0 or 1;

c is 1 or 2;

15 the sum of a, b and c is 3;

Z is a divalent moiety comprising oxygen, nitrogen, phosphorous, boron, or a member of Group 14 of the Periodic Table of the Elements, said moiety having up to 30 nonhydrogen atoms;

Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur covalently  
20 bonded to M and Z through said nitrogen, phosphorus, oxygen or sulfur atom;

L independently each occurrence is hydride, halo, or a monovalent anionic ligand selected from covalently bonded hydrocarbyl, silyl, amido, phosphido, alkoxy, aryloxy, and sulfido groups optionally being further substituted with one or more amino, phosphino, ether, or thioether groups, said ligand having up to 50 nonhydrogen atoms;

25 M is titanium or zirconium in the + 4 oxidation state;

p is an integer from 0 to 4;

q is 1 or 2;

J is a Lewis acid mitigating agent, and

A is a reduced remnant of a neutral organic oxidizing agent and may be ligating  
30 or nonligating,

the steps of the process comprising contacting under conditions to form the oxidized metal complex:

1) a reduced metal precursor complex corresponding to the formula:

$\text{Cp}_a(\text{ZY})_b\text{M}^*\text{L}_c$ , wherein Cp, Z, Y, L, a, b, and c are as previously defined, and

35  $\text{M}^*$  is the same metal as M but in a + 3 oxidation state;

2) a neutral organic oxidizing agent,  $\text{A}^*$ , capable of accepting one or more electrons and oxidizing  $\text{M}^*$  to M and which in reduced form is A;

and, if A is a ligating group,

3) the Lewis acid mitigating agent, J.

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. 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.

The recitation "metalloid", as used herein, includes Group 13 - 15 elements which exhibit semi-metallic characteristics especially boron, silicon, germanium, and phosphorus.

Preferably M is titanium in the + 4 oxidation state and M\* is titanium in the + 3 oxidation state.

L preferably is a monovalent anionic stabilizing ligand selected from the group consisting of:

1) covalently bonded hydrocarbyl, silyl, amido, phosphido, alkoxy, aryloxy, sulfido groups and mixtures thereof, said group being further substituted with an amino, phosphino, ether, or thioether containing substituent able to form a coordinate-covalent bond or chelating bond with M; said ligand having up to 50 nonhydrogen atoms; and

2) C<sub>3-40</sub> hydrocarbyl radicals comprising an ethylenic unsaturation able to form an  $\eta^3$  bond with M.

By the term "stabilizing ligand" is meant that the ligand group stabilizes the metal complex, and especially the reduced metal precursor complex, through either:

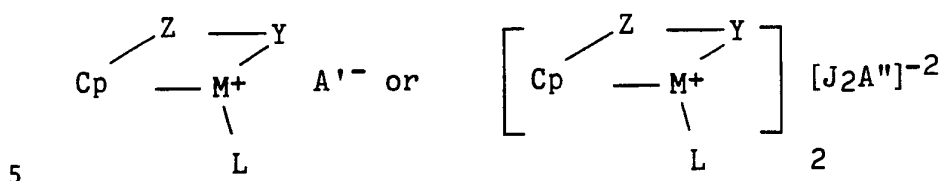
1) a nitrogen, phosphorus, oxygen or sulfur chelating bond, or  
2) an  $\eta^3$  bond with a resonant, delocalized  $\pi$ -electronic structure.

Examples of stabilizing ligands L of group 1) include silyl, hydrocarbyl, amido or phosphido ligands substituted with one or more aliphatic or aromatic ether, thioether, amino or phosphino groups, especially such amino or phosphino groups that are tertiary substituted, said stabilizing ligand having from 3 to 30 nonhydrogen atoms. Most preferred group 1) stabilizing ligands L are 2-(dialkylamino)benzyl, 2-(dialkylaminomethyl)phenyl, 2-(dialkylphosphino)benzyl or 2-(dialkylphosphinomethyl)phenyl groups containing from 1 to 4 carbons in the alkyl groups.

Examples of stabilizing ligands L of group 2) for use according to the present invention, include C<sub>3-10</sub> hydrocarbyl groups containing ethylenic unsaturation, such as allyl, 1-methylallyl, 2-methylallyl, 1,1-dimethylallyl, or 1,2,3-trimethylallyl groups.

The ligand moiety consisting of -Cp-Z-Y-, when present, is a dianionic ligand having the ionic charges residing formally on Cp and Y. Such ligand causes the resulting complex to possess constrained geometry about the active metal catalyst site resulting in highly active Group 4 metal catalysts. Constrained geometry complexes are further described in previously mentioned EP-A-416,815.

Highly preferred Group 4 metal complexes formed according to the present invention are monocyclopentadienyl metal complexes corresponding to the formula:



wherein:

M is titanium,

10 L independently each occurrence is a covalently bonded hydrocarbonyl group substituted with an amino, phosphino, ether, or thioether containing substituent able to form a coordinate-covalent bond or chelating bond with M, said ligand having up to 50 nonhydrogen atoms, or a C<sub>3-40</sub> hydrocarbonyl radical comprising an ethylenic unsaturation able to form an  $\eta^3$  bond with M;

J is as previously defined;

15 A' is a nonligating form of A;

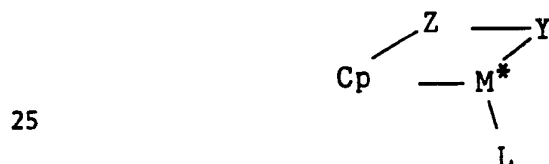
A'' is a ligating form of A;

Cp is a cyclopentadienyl or substituted cyclopentadienyl group bound in an  $\eta^5$  bonding mode to M;

Z is a divalent moiety comprising carbon or silicon; and

20 Y is a divalent linking group comprising nitrogen or phosphorus.

The monocyclopentadienyl metal complex starting reactant for preparation of the above metal complexes is



wherein:

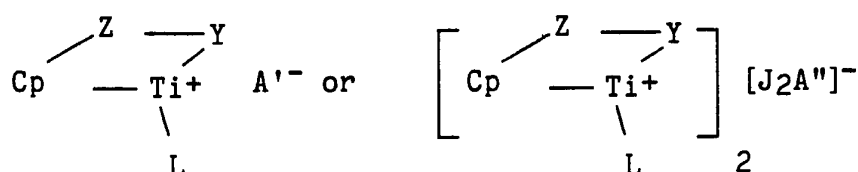
Cp, Z, Y, M\*, and L, are as previously defined with respect to the resulting complex.

30 Each carbon atom in the cyclopentadienyl radical may be unsubstituted or substituted with the same or a different radical selected from the group consisting of hydrocarbonyl radicals, substituted-hydrocarbonyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, hydrocarbonyl-substituted metalloid radicals wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, and halogen radicals. In addition two or more such substituents may together form a fused ring system. Preferred hydrocarbonyl and substituted-hydrocarbonyl radicals contain from 1 to 20 carbon atoms and include straight and branched alkyl radicals, cyclic hydrocarbon radicals, alkyl-substituted cyclic

hydrocarbon radicals, aromatic radicals and alkyl-substituted aromatic radicals. Suitable organometalloid radicals include mono-, di- and tri-substituted organometalloid radicals of Group 14 elements, preferably silicon or germanium, wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. More preferably, suitable organometalloid radicals include trimethylsilyl, triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, and trimethylgermyl. Most highly preferred Cp groups are cyclopentadienyl, tetramethylcyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl and octahydrofluorenyl.

Most highly preferred Group 4 metal complexes formed according to the present invention are amidosilane- or amidoalkanedyl-compounds corresponding to the formula:

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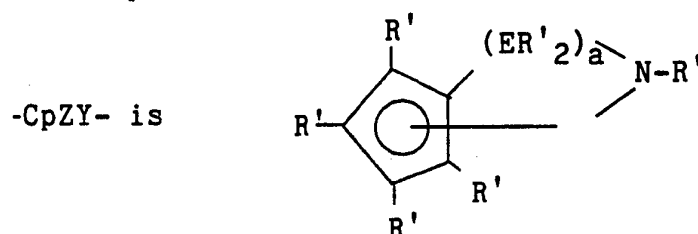


15

wherein:

L independently each occurrence is a covalently bonded hydrocarbyl group substituted with an amino, phosphino, ether, or thioether containing substituent able to form a coordinate-covalent bond or chelating bond with M, said ligand having up to 50 nonhydrogen atoms, or a C<sub>3-40</sub> hydrocarbyl radical comprising an ethylenic unsaturation able to form an  $\eta^3$  bond with M, and

20



25

wherein, R' independently each occurrence is selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms, or two such R' groups together are a C<sub>4</sub> hydrocarbylene moiety forming a fused ring with adjacent carbons of the cyclopentadienyl group;

30

E is silicon or carbon; and

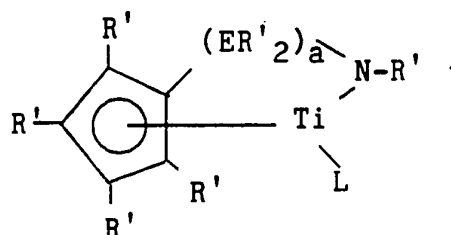
a is 1 or 2.

Preferably R' on the foregoing cyclopentadienyl groups each occurrence is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, including isomers of these radicals, norbornyl, benzyl, phenyl, or two or more such R' groups together form an indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl group.

35

Examples of the above most highly preferred Group 4 metal complexes include compounds wherein the R' on the amido group is methyl, ethyl, propyl, butyl, pentyl, hexyl, including isomers of these radicals, norbornyl, benzyl, phenyl, etc.; the cyclopentadienyl group (including R' substituents) is cyclopentadienyl, tetramethylcyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, octahydrofluorenyl, etc.; and L is methyl, neopentyl, trimethylsilyl, norbornyl, benzyl, methylbenzyl, phenyl, 2-(N,N-dialkylamino)benzyl or 2-(N,N-dialkylaminomethyl)phenyl wherein the alkyl substituents are preferably methyl radicals, and allyl.

The metal complex precursors used in the preparation of the above cationic complexes correspond to the formula:



wherein:

R', E, L and a are as previously defined with respect to the resulting complexes.

Specific titanium(III) precursor complexes include: (tert-butylamido)( $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(N,N-dimethylamino)benzyl, (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(N,N-dimethylamino)benzyl, (tert-butylamido)(ethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(N,N-dimethylamino)benzyl, (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(N,N-dimethylamino)benzyl, (methylamido)( $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(N,N-dimethylamino)benzyl, (methylamido)(ethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(N,N-dimethylamino)benzyl, (tert-butylamido)( $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium allyl, (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium allyl, (tert-butylamido)(ethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium allyl, (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium allyl, (methylamido)( $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium allyl, (methylamido)(ethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium allyl, (tert-butylamido)( $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylphosphino)benzyl, (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylphosphino)benzyl, (tert-butylamido)(ethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylphosphino)benzyl, (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylphosphino)benzyl, (methylamido)( $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylphosphino)benzyl, (methylamido)(ethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(dimethylphosphino)benzyl, (tert-butylamido)( $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-



(N,N-dipentafluorophenylamino)benzyl, (tert-butylamido)( $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(N,N-dimethylaminomethyl), (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium 2-(N,N-trimethylsilylamino)benzyl, (tert-butylamido)( $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(N,N-dimethylamino)benzyl, (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(N,N-dimethylamino)benzyl, (tert-butylamido)(ethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(N,N-dimethylamino)benzyl, (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(N,N-dimethylamino)benzyl, (methylamido)(- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(N,N-dimethylamino)benzyl, (methylamido)(ethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(N,N-dimethylamino)benzyl, (tert-butylamido)( $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium allyl, (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium allyl, (tert-butylamido)(ethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium allyl, (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium allyl, (methylamido)( $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium allyl, (methylamido)(ethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium allyl, (tert-butylamido)( $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(dimethylphosphino)benzyl, (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(dimethylphosphino)benzyl, (tert-butylamido)( $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-N,N-(dipentafluorophenylamino)benzyl, (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-N,N-(dipentafluorophenylamino)benzyl, and (methylamido)(ethyl- $\eta^5$ -cyclopentadienyl)dimethylsilanetitanium 2-(N,N-di(trimethylsilyl)amino)benzyl.

The term "organic oxidizing agent" as used herein refers to an organic compound having a reduction potential sufficient to cause oxidation of the metal,  $M^*$ , to the +4 oxidation state. Preferred organic oxidizers possess an electrochemical reduction potential from 0.30 volts more negative than the electrochemical oxidation potential of the desired oxidation to any value more positive than the electrochemical oxidation potential of the desired oxidation. More preferably, the electrochemical reduction potential for such oxidizing agent is in a range the lower endpoint of which is equal to the electrochemical oxidation potential of the desired oxidation to form the metal complex and the upper endpoint of which is 4.0 volts more positive than the electrochemical oxidation potential of the desired oxidation to form the metal complex.

Examples of suitable neutral, organic oxidizing agents for use according to the present invention are organic compounds containing quinone functionality containing up to 50 carbons and closed caged, carbon structures known as "fullerenes". Fullerene oxidizing agents do not form ligating reduction species that interfere with the operation of the metal complex. Preferred are  $C_{60}$  fullerene and  $C_{70}$  fullerene. Preferred quinone functional organic oxidizing agents are benzoquinone, diphenquinone, anthroquinone, and

C<sub>1-4</sub> alkyl substituted derivatives thereof. Highly preferred organic oxidizing agents are 2,3,5,6-tetramethylbenzoquinone, 2,3,5,6-tetratert-butylbenzoquinone, 2,2',6,6'-tetramethyldiphenquinone, 2,2',6,6'-tetratert-butylidiphenquinone. A most preferred quinone functional organic oxidizing agent is 2,2',6,6'-tetratert-butylidiphenquinone.

5           Upon reduction, the above quinone functional oxidizing agents form an organic anion remnant which may coordinate to (ligate) the metal complex. However, because the mitigating agent is an electron pair acceptor, the organic anion and one or more Lewis acid mitigating agents together form the noncoordinating, noninterfering, complex counter ion, J<sub>p</sub>A<sup>-q</sup>.

10           Preferred Lewis acid mitigating agents are C<sub>1-10</sub> trialkylaluminum compounds, C<sub>1-10</sub> trialkylboron compounds, C<sub>1-10</sub> tri(haloalkyl)boron compounds, and C<sub>1-10</sub> trialkylborate compounds. Most preferred Lewis acid mitigating agents are trimethylaluminum, triethylaluminum, trimethylboron, triethylboron, tris(pentafluorophenyl)borane, tris(2,3,5,6-tetrafluorophenyl)borane, tris(2,3,4,5-tetrafluorophenyl)borane, tris(3,4,5-trifluorophenyl)borane,  
15 tris(1,2,2-trifluoroethenyl)borane, phenylbis(perfluorophenyl)borane, and tris(perfluorophenyl) borate.

          The above Lewis acid mitigating agents may be prepared according to known techniques such as those of Marks, et al. J. Am. Chem. Soc. 1991, 113, 3623-3625, or J. Pohlman, et al., Naturforsch. 1965, 20b, 5-11. The preferred technique is to combine a boron or  
20 aluminum halide compound such as boron trichloride or boron trifluoride with an alkali metal or alkaline earth derivative of the desired substituent or substituents. Additionally, borate esters such as tris(perfluorophenyl) borate may be prepared by the reaction of pentafluorophenylphenol and borane-methyl sulfide complex according to the method of J. Org. Chem., 43(13) 2731-32 (1978).

25           In general, the complexes can be prepared by combining the components in a suitable noninterfering, noncoordinating solvent at a temperature from -100°C to 300°C, preferably from 0 to 200°C. Suitable solvents are noncoordinating, 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  
30 cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C<sub>4-10</sub> alkanes, and the like, and aromatic, or alkyl-substituted aromatic compounds such as benzene, toluene and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-  
35 pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, 4-vinylcyclohexene, and vinyltoluene (including all isomers alone or in admixture). Mixtures of the foregoing are also suitable.

The catalyst formed by the method of this invention may be retained in solution or separated from the solvent, isolated, and stored for subsequent use. As previously indicated *supra*, the catalyst may also be prepared *in situ* during a polymerization reaction by passing the separate components into the polymerization vessel where the components will contact and  
5 react to produce the improved catalyst of this invention.

The equivalent ratio of reduced metal precursor complex to oxidizing agent employed in the process is preferably in a range from 0.1:1 to 10:1, more preferably from 0.75:1 to 5:1, most preferably 1:1 to 2:1. The equivalent ratio of Lewis acid mitigating agent to oxidizing agent employed in the process is preferably in a range from 0:1 to 50:1, more  
10 preferably from 0.75:1 to 10:1, most preferably 1:1 to 2.5:1.

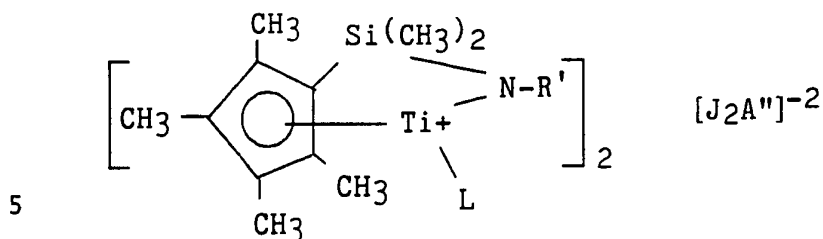
The complexes may be used to polymerize ethylenically and/or acetylenically unsaturated monomers having from 2 to 18 carbon atoms either alone or in combination. Preferably they are used to polymerize C<sub>2-10</sub>  $\alpha$ -olefins, especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene, including mixtures  
15 thereof. Other suitable monomers include vinyl aromatic monomers such as styrene which may advantageously be interpolymerized with one or more  $\alpha$ -olefins. 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 0-250°C and pressures from atmospheric to 1000 atmospheres. Suspension, solution, slurry, gas-phase or  
20 other process conditions may be employed. A support may be employed but preferably the catalysts are used in a homogeneous manner. In most polymerization reactions the equivalent ratio of complex:polymerizable monomer employed is from 10<sup>-12</sup>:1 to 10<sup>-1</sup>:1, more preferably from 10<sup>-8</sup>:1 to 10<sup>-5</sup>:1. The complexes generally need no activating agent in order to be catalytically effective.

25 Having described the invention the following examples are provided as further illustration thereof and are not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis.

#### Examples 1-4

##### Example 1

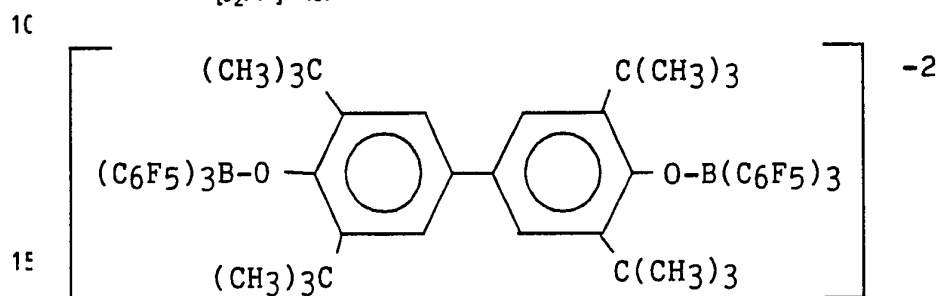
30 20 mg (46  $\mu$ mol) of (t-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanetitanium(III) 2-(N,N-dimethylamino)benzyl and 9.5 mg (23  $\mu$ mol) of 4-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]-2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadien-1-one (2,2',6,6'-tetratert-butylidiphenquinone), were dissolved in 1 ml of benzene-d<sub>6</sub> for <sup>1</sup>H NMR analysis. 23.7 mg (46  $\mu$ mol) of B(C<sub>6</sub>F<sub>5</sub>) Lewis acid mitigating agent  
35 were also added to the reaction mixture. The spectrum clearly showed that oxidation of the Ti(III) complex had occurred. The resulting complex was determined to be



wherein:

L is 2-(N,N-dimethylamino)benzyl, and

$[\text{J}_2\text{A}']^{-2}$  is:



When the above procedure was repeated excepting that no Lewis acid mitigating agent was added, the resulting spectrum clearly showed that oxidation of the Ti(III) complex had occurred to give an asymmetric Ti(IV) complex that was different than that obtained in the presence of the Lewis acid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 7.61 (s), 7.2-6.8 (m), 4.94 (s), 2.47 (s), 2.33 (s), 2.14 (s), 1.64 (s), 1.50 (s), 1.43 (s), 0.87 (s), 0.74 (s), 0.69 (s) ppm.

#### Example 2

A 2 L stirred reactor was charged with 740 g of mixed alkane solvent (Isopar™ E, available from Exxon Inc.) and 118 g of 1-octene comonomer. Hydrogen chain transfer agent was added from a 75 ml addition tank at a differential pressure of 170 Kpa. The reactor was heated to 140°C and saturated with ethylene at 3448 Kpa. Catalyst was prepared in a drybox by adding 2 μmol of (t-butylamido)dimethyl(tetramethyl-η<sup>5</sup>-cyclopentadienyl)silanetitanium(III) 2-(N,N-dimethylamino)benzyl in 2 mL of Isopar™ E to a combination of 1.6 mL of a 0.0050M solution of tris(perfluorophenyl)borane in Isopar™ E and 0.20 mL of a 0.0050 M solution of the diquinone 4-[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]-2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadien-1-one in Isopar™ E. The resulting solution was then transferred to a catalyst addition tank and injected into the reactor. The polymerization was allowed to proceed for 15 minutes and the solution was removed from the reactor and quenched with hindered phenol anti-oxidant and isopropanol. The polymer was dried in a vacuum oven to give 16.8 grams of ethylene/1-octene copolymer.

Example 3

The polymerization conditions of Example 2 were repeated excepting that 4 mL of a 0.0050 M solution of triethylborane mitigating agent in Isopar™ E was substituted for the tris(perfluorophenyl)borane solution of Example 2. Polymer yield was 13.8 g. of ethylene/1-octene copolymer.

Examples 4 and 5

A two liter stirred reactor was charged with 660 g of Isopar-E® and the quantity of 1-octene specified in Table I. Hydrogen was added by differential pressure expansion from a 75 mL addition tank from 2070 Kpa to 1929 Kpa. The contents of the reactor were heated to 100°C and saturated with ethylene at 3448 Kpa. In a drybox, the desired volume of a 0.0050 M solution of buckminsterfullerene oxidizing agent in toluene was added to 1.0 micromoles of (t-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane titanium(III) 2-(N,N-dimethylamino)benzyl in toluene. In Example 5, Lewis acid mitigating agent,  $B(C_6F_5)_3$ , was added as a 0.005M toluene solution. The combined solution was transferred to a catalyst addition tank and injected into the reactor. The polymerization was allowed to proceed for the desired reaction time and the reactor contents were combined with a mixture of anti-oxidant (Irganox 1010™ available from Ciba Geigy) and isopropanol. The polymer was dried in a vacuum over overnight at 130°C. Results are contained in Table I.

Table I

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Example	Octene (g)	Oxidizing Agent ( $\mu$ mol)	$B(C_6F_5)_3$ ( $\mu$ mol)	Run Time (min)	Yield (g)
4	210	1.0	None	20	138
5	200	1.0	2.0	15	86

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Claims :

1. A process for the preparation of a cationic metal complex corresponding to the formula:  

$$[\text{Cp}_a(\text{ZY})_b\text{ML}_c^+]\text{J}_p\text{A}]^q$$
 wherein:  
 Cp independently each occurrence is a cyclopentadienyl group  $\pi$ -bound to M, or a hydrocarbyl, silyl, halo, halohydrocarbyl, hydrocarbylmetalloid or halohydrocarbylmetalloid substituted derivative of said cyclopentadienyl group, said Cp containing up to 50 nonhydrogen atoms, and, when a is 2, optionally both Cp groups may be joined together by a bridging group;  
 a is 1 or 2;  
 b is 0 or 1;  
 c is 1 or 2;  
 the sum of a, b and c is 3;  
 Z is a divalent moiety comprising oxygen, nitrogen, phosphorous, boron, or a member of Group 14 of the Periodic Table of the Elements, said moiety having up to 30 nonhydrogen atoms;  
 Y is a linking group comprising nitrogen, phosphorus, oxygen or sulfur covalently bonded to M and Z through said nitrogen, phosphorus, oxygen or sulfur atom;  
 L independently each occurrence is hydride, halo, or a monovalent anionic ligand selected from covalently bonded hydrocarbyl, silyl, amido, phosphido, alkoxy, aryloxy, and sulfido groups optionally being further substituted with one or more amino, phosphino, ether, or thioether groups, said ligand having up to 50 nonhydrogen atoms;  
 M is titanium or zirconium in the + 4 oxidation state;  
 p is an integer from 0 to 4;  
 q is 1 or 2;  
 J is a Lewis acid mitigating agent, and  
 A is a reduced remnant of a neutral organic oxidizing agent and may be ligating or nonligating,  
 the steps of the process comprising contacting under conditions to form the oxidized metal complex:  
 1) a reduced metal precursor complex corresponding to the formula:  

$$\text{Cp}_a(\text{ZY})_b\text{M}^*\text{L}_c$$
 wherein Cp, Z, Y, L, a, b, and c are as previously defined, and  
 M\* is the same metal as M but in a + 3 oxidation state;  
 2) an organic oxidizing agent, A\*, capable of accepting one or more electrons and oxidizing M\* to M and which in reduced form is A;  
 and, if A is a ligating group,  
 3) the Lewis acid mitigating agent, J.

2. A process according to Claim 1 wherein the organic oxidizing agent has an electrochemical reduction potential from 0.30 volts more negative than the electrochemical oxidation potential of the reaction to form the oxidized metal complex to any value more positive than the electrochemical oxidation potential of the reaction to form the desired metal complex.

3. A process according to Claims 1 or 2 wherein the organic oxidizing agent is an organic compound containing quinone functionality containing up to 50 carbons or a fullerene.

4. A process according to Claim 3 wherein the organic oxidizing agent is 2,3,5,6-tetramethylbenzoquinone, 2,3,5,6-tetratert-butylbenzoquinone, 2,2',6,6'-tetramethyldiphenquinone, and 2,2',6,6'-tetratertbutyldiphenquinone

5. A process according to any of the Claims 1-4 wherein the Lewis acid mitigating agent is tris(pentafluorophenyl)borane, tris(2,3,5,6-tetrafluorophenyl)borane, tris(2,3,4,5-tetrafluorophenyl)borane, tris(3,4,5-trifluorophenyl)borane, tris(1,2,2-trifluoroethenyl)borane, phenylbis(perfluorophenyl)borane, tris(perfluorophenyl) borate, or triethyl borane.

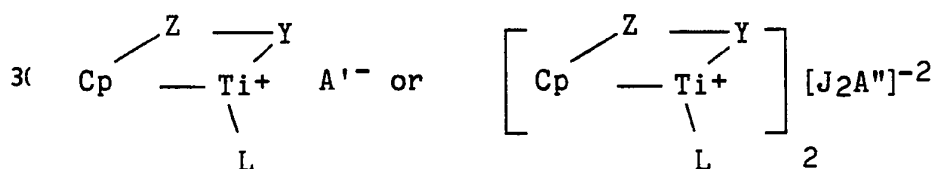
6. A process according to any of the Claims 1-5 wherein M is titanium.

7. A process according to any of the Claims 1-6 wherein L is a monovalent anionic stabilizing ligand selected from the group consisting of:

1) covalently bonded hydrocarbyl, silyl, amido, phosphido, alkoxy, aryloxy, sulfido groups and mixtures thereof, said group being further substituted with an amino, phosphino, ether, or thioether containing substituent able to form a coordinate-covalent bond or chelating bond with M; said ligand having up to 50 nonhydrogen atoms; and

2) C<sub>3-40</sub> hydrocarbyl radicals comprising an ethylenic unsaturation able to form an η<sup>3</sup> bond with M.

8. A process according to any of the Claims 1-7 wherein the complex corresponds to the formula:



wherein:

L independently each occurrence is a covalently bonded hydrocarbyl group substituted with an amino, phosphino, ether, or thioether containing substituent able to form a coordinate-covalent bond or chelating bond with M, said ligand having up to 50

nonhydrogen atoms, or a C<sub>3-40</sub> hydrocarbyl radical comprising an ethylenic unsaturation able to form an  $\eta^3$  bond with M;

Cp is a cyclopentadienyl or substituted cyclopentadienyl group bound in an  $\eta^5$  bonding mode to M;

5 Z is a divalent moiety comprising carbon or silicon; and

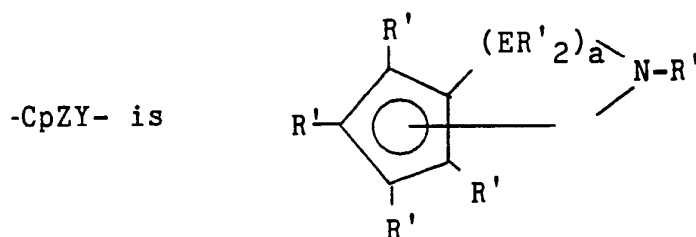
Y is a divalent linking group comprising nitrogen or phosphorus;

J is as previously defined;

A' is a nonligating form of A; and

A'' is a ligating form of A.

10 9. A process according to Claim 8 wherein:



wherein, R' each occurrence is independently selected from the group consisting of hydrogen, silyl, alkyl, aryl and combinations thereof having up to 10 carbon or silicon atoms, or two such R' groups together are a C<sub>4</sub> hydrocarbylene moiety forming a fused ring with adjacent carbons of the cyclopentadienyl group;

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E is silicon or carbon; and

a is 1 or 2.

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/01647

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08F4/74 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 5 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)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 495 375 (THE DOW CHEMICAL COMPANY) 22 July 1992 see claim 1 & US,A,5 189 192 cited in the application ---	1
A	EP,A,0 418 044 (THE DOW CHEMICAL COMPANY) 20 March 1991 see claim 1 -----	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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# INTERNATIONAL SEARCH REPORT

...information on patent family members

International Application No

PCT/US 94/01647

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0495375	22-07-92	US-A- 5189192 AU-A- 1023392 JP-A- 5086120	23-02-93 23-07-92 06-04-93
US-A-5189192	23-02-93	AU-A- 1023392 EP-A- 0495375 JP-A- 5086120	23-07-92 22-07-92 06-04-93
EP-A-0418044	20-03-91	US-A- 5064802 AU-B- 632620 AU-A- 6247390 CA-A- 2025332 CN-A- 1050194 JP-A- 3139504 US-A- 5132380	12-11-91 07-01-93 21-03-91 15-03-91 27-03-91 13-06-91 21-07-92