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(54) Title: HETEROCYCLIC METAL COMPLEXES AND OLEFIN POLYMERIZATION PROCESS (57) Abstract Metal complexes, addition polymerisation catalysts containing the same and olefin polymerisation processes using the same comprising a boratabenzene group or divalent derivative thereof are disclosed.		

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HETEROCYCLIC METAL COMPLEXES AND OLEFIN POLYMERIZATION PROCESS

This invention relates to metal complexes and to addition polymerization catalysts formed therefrom that have improved catalytic performance. More particularly the present invention relates to an addition polymerization catalyst composition comprising a Group 3, 4, or Lanthanide metal complex containing a boratabenzene group or divalent derivative thereof bonded via its delocalized π electrons to the metal (also referred to as a boracyclohexadienyl group). In addition, the present invention relates to certain of the foregoing complexes possessing a novel bridged structure. Finally, the invention relates to a method of using the foregoing catalyst compositions in an addition polymerization process for polymerizing addition polymerizable monomers.

In EP-A-416,815 there are disclosed certain constrained geometry metal complexes and catalysts derived by reacting the metal complex with activating cocatalysts. Supported derivatives of such catalysts were prepared by contacting them with a support such as alumina, silica or MgCl_2 . In US-A-5,064,802 (EP-A-418,044) there are disclosed certain further catalysts formed by reacting metal complexes with ion forming activating cocatalysts that are salts of Bronsted acids containing a noncoordinating compatible anion. The reference discloses the fact that such complexes are usefully employed as catalysts in addition polymerizations. In EP-A-520,732 an alternative technique for preparing cationic constrained geometry catalysts using borane activators is disclosed.

In US-A-4,892,851 there are disclosed biscyclopentadienyl Group 4 metal complexes, especially complexes of zirconium or hafnium that are usefully employed with alumoxane activating cocatalysts for use in addition polymerizations, especially the polymerization of aliphatic α -olefins. In a series of patents, W. Spaelick has disclosed certain ring substituted stereorigid bisindenyl complexes and their use as olefin polymerization catalysts. The bridging group of such complexes generically includes silicon, germanium or tin containing divalent groups containing hydride, halogen, C_{1-10} alkyl, C_{1-10} fluoroalkyl, C_{6-10} aryl, C_{6-10} fluoroaryl, C_{1-10} alkoxy, C_{2-10} alkenyl, C_{7-40} aralkyl, C_{8-40} aralkenyl or C_{7-40} alkylaryl groups or ring forming

combinations thereof. Such disclosure may be found in US-A-5,243,001, US-A-5,145,819, US-A-5,304,614, US-A-5,350,817, among others.

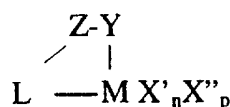
Boratabenzenes are anionic ligands which are boron containing six membered ring systems. They are previously known in the art having been
 5 described by A. Ashe, et al., J. Am. Chem. Soc., 93, 1804-1805 (1971). They may be prepared by reaction of 1,1-diorgano-1-stannacyclohexa-2,5-diene and a borontrihalide followed by substitution with a hydrocarbyl, amino, silyl or germyl group. Such ligand groups correspond to the formula:



10 wherein J is selected from the group consisting of hydrogen, hydrocarbyl, dihydrocarbylamino, silyl, germyl, halohydrocarbyl, or halocarbyl, said J having up to 20 non-hydrogen atoms.

It would be desirable if there were provided an improved catalyst system based on the foregoing boratabenzene groups as well as an improved addition
 15 polymerization process utilizing such catalyst systems.

As a result of investigations carried out by the present inventors there have now been discovered new and improved Group 3, 4, or Lanthanide metal complexes



corresponding to the formula:

or a dimer, solvated adduct, chelated derivative or mixture thereof,

20 wherein:

Y is a divalent derivative of a boratabenzene group or a hydrocarbyl-, dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

L is Y or a hydrocarbadiyl group that is bound to M by means of its delocalized
 25 π -electrons, or L is a monovalent or divalent amido group, said L group containing up to 50 nonhydrogen atoms;

M is a metal of Group 3, 4 or the Lanthanide series of the Periodic Table of the Elements;

Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms having the formula, $-(ER^2)_m-$, wherein E independently each occurrence is carbon, silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

X' is a neutral ligand having up to 20 non-hydrogen atoms;

X'' independently each occurrence is a monovalent, anionic moiety selected from hydride, halo, hydrocarbyl, silyl, germyl, hydrocarbyloxy, dihydrocarbylamide, siloxy, halohydrocarbyl, halosilyl, silylhydrocarbyl, and dihydrocarbylaminohydrocarbyl having up to 20 non-hydrogen atoms, or two X'' groups together form a divalent hydrocarbadiyl group;

n is a number from 0 to 3; and

p is an integer from 0 to 2.

According to the present invention there are further provided improved addition polymerization catalyst compositions comprising an activating cocatalyst and one or more Group 3, 4 or Lanthanide metal complexes corresponding to the formula:



or a dimer, solvated adduct, chelated derivative or mixture thereof, wherein:

Y' is a boratabenzene group or a hydrocarbyl-, dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

L' is Y' or a hydrocarbyl group that is bound to M by means of its delocalized π -electrons, or L' is an amido group, said L' group containing up to 50 nonhydrogen atoms;

L and Y are as previously defined;

M is a metal of Group 3, 4 or the Lanthanide series of the Periodic Table of the Elements;

Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms having the formula, $-(ER^2)_m-$, wherein E independently each occurrence is carbon, silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

X' is a neutral ligand having up to 20 non-hydrogen atoms;

X" independently each occurrence is a monovalent, anionic moiety selected from hydride, halo, hydrocarbyl, silyl, germyl, hydrocarbyloxy, dihydrocarbylamide, siloxy, halohydrocarbyl, halosilyl, silylhydrocarbyl, and dihydrocarbylaminohydrocarbyl having up to 20 non-hydrogen atoms, or two X" groups together form a divalent hydrocarbadiyl group;

n is a number from 0 to 3; and

p is an integer from 0 to 2,

provided that when two Y groups or two Y' groups are present in the complex, then the activating cocatalyst does not consist solely of an alumoxane.

In a further embodiment there is provided a supported catalyst system comprising one or more of the foregoing metal complexes, one or more activating cocatalysts, and a support material.

Finally there is provided an improved method for polymerization of addition polymerizable monomers using one or more of the above catalyst compositions or catalyst systems. Such addition polymerization processes may be used to prepare polymers for use in making molded articles, films, sheets, foamed materials and in other industrial applications.

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. As used herein, the term "amino" refers to a hydrocarbyl or dihydrocarbyl substituted nitrogen group attached to a nonmetal or to a metalloid.

The term "amido" refers to such a hydrocarbyl or dihydrocarbyl group attached to a metal.

Suitable L' groups for use herein include any cyclic, neutral or anionic π -electron containing moiety capable of forming a delocalized bond with the Group 3, 4 or Lanthanide metal. Examples of such neutral groups include arene moieties such as benzene, anthracene or naphthalene, as well as hydrocarbyl-, silyl- or germyl-substituted derivatives of such groups. Examples of anionic π -electron containing moieties include cyclopentadienyl groups, cyclohexadienyl groups, 1,3-pentadienyl groups, and allyl groups, as well as hydrocarbyl-, silyl- or germyl-substituted derivatives of such groups, and partially hydrogenated derivatives of the cyclic groups. In addition, suitable L' groups include the aforementioned boratabenzene or substituted boratabenzene groups represented by Y'. In complexes involving divalent derivatives of such groups, e. g. L or Y groups, it is understood that another atom of the complex is also bonded to such cyclic group thereby forming a bridged system.

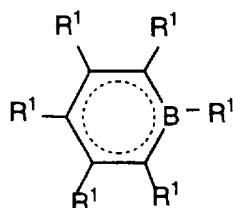
By the term "derivative" when used to describe the above cyclic substituted, delocalized π -bonded groups is meant that each atom in the delocalized π -bonded group may independently be substituted with a radical selected from the group consisting of hydrocarbyl radicals, halo-, cyano or dialkylamino- substituted-hydrocarbyl radicals, and hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements. Suitable hydrocarbyl and substituted-hydrocarbyl radicals used to form derivatives of the substituted, delocalized π -bonded group will contain from 1 to 20 carbon atoms and include straight and branched alkyl radicals, cycloalkyl radicals, aryl radicals, alkyl-substituted cycloalkyl radicals, and alkyl-substituted aromatic radicals. In addition two or more such radicals may together form a fused ring system which may be saturated or unsaturated. Examples of the latter are indenyl-, tetrahydroindenyl-, fluorenyl-, and octahydrofluorenyl- groups, as well as multicyclic, fused ring, boratabenzene derivatives. Suitable hydrocarbyl-substituted organometalloid radicals include mono-, di- and trisubstituted organometalloid radicals of Group 14 elements wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. More particularly, suitable hydrocarbyl-substituted organometalloid radicals include trimethylsilyl,

triethylsilyl, ethyldimethylsilyl, methyldiethylsilyl, triphenylgermyl, trimethylgermyl and the like.

Preferred L groups are Y, divalent hydrocarbyl substituted amido groups such as a t-butylamido group, and cyclic, hydrocarbadiyl groups. Examples of the latter
 5 include divalent derivatives of cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, and decahydroanthracenyl groups, and C₁₋₁₀ hydrocarbyl-substituted derivatives thereof. Most preferred L groups are divalent derivatives of tetramethylcyclopentadienyl, 2-methylindenyl, 3-methylindenyl, 2,3-dimethylindenyl,
 10 2, 3, 5, 6-tetramethylindenyl, and 2, 3, 5, 6, 7-pentamethylindenyl.

Preferred Z groups are 1,2-ethanediyl, dimethylsilanediyl, diphenylsilanediyl, methylisopropoxysilanediyl, and methylphenylsilanediyl.

Preferred Y' groups correspond to the formula:

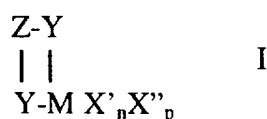


15 wherein R¹ independently each occurrence is hydrogen, hydrocarbyl, dihydrocarbylamino disilylamino, hydrocarbylsilylamino, halohydrocarbyl, halocarbyl, silyl, germlyl, or mixtures thereof, said R¹ having up to 50, preferably up to 20 non-hydrogen atoms, and optionally two such R¹ groups may be joined together thereby forming a fused ring derivative, and further optionally two such Y' groups may be
 20 joined together in a multiple ring system. In complexes involving divalent derivatives of such Y' groups, one R¹ is a covalent bond or a divalent derivative of one of the foregoing substituent groups, said R¹ being also bonded to another atom of the complex thereby forming a bridged system.

More preferred Y' groups are 1-phenyl-, 1-(N,N-di-(C₁₋₈)alkyl), 1-benzyl-, and
 25 1-methyl- substituted boratabenzene groups. Preferred Y groups are divalent derivatives of the foregoing Y' groups. Highly preferably, the divalent derivative of the boratabenzene ligand is substituted with a C₁₋₁₀ hydrocarbyl group in the ring position

that is meta to the bridgehead. The skilled artisan will appreciate that the various L and Y ligand groups may be connected at any position of the boratabenzene ring, thereby forming various isomeric products. Mixtures of such isomers may also be utilized.

- 5 Examples of highly preferred complexes according to the present invention correspond to the formula:



wherein:

- 10 M is titanium, zirconium or hafnium, preferably zirconium, in the +2, +3, or +4 formal oxidation state;

- 15 Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms having the formula, $-(\text{ER}^2)_m-$, wherein E independently each occurrence is carbon, silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

Y in each occurrence, independently is a divalent derivative of a boratabenzene group or a hydrocarbyl-, dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

- 20 X' is a conjugated diene having from 4 to 30 non-hydrogen atoms, which forms a π -complex with M when M is in the +2 formal oxidation state, whereupon n is 1 and p is 0; and

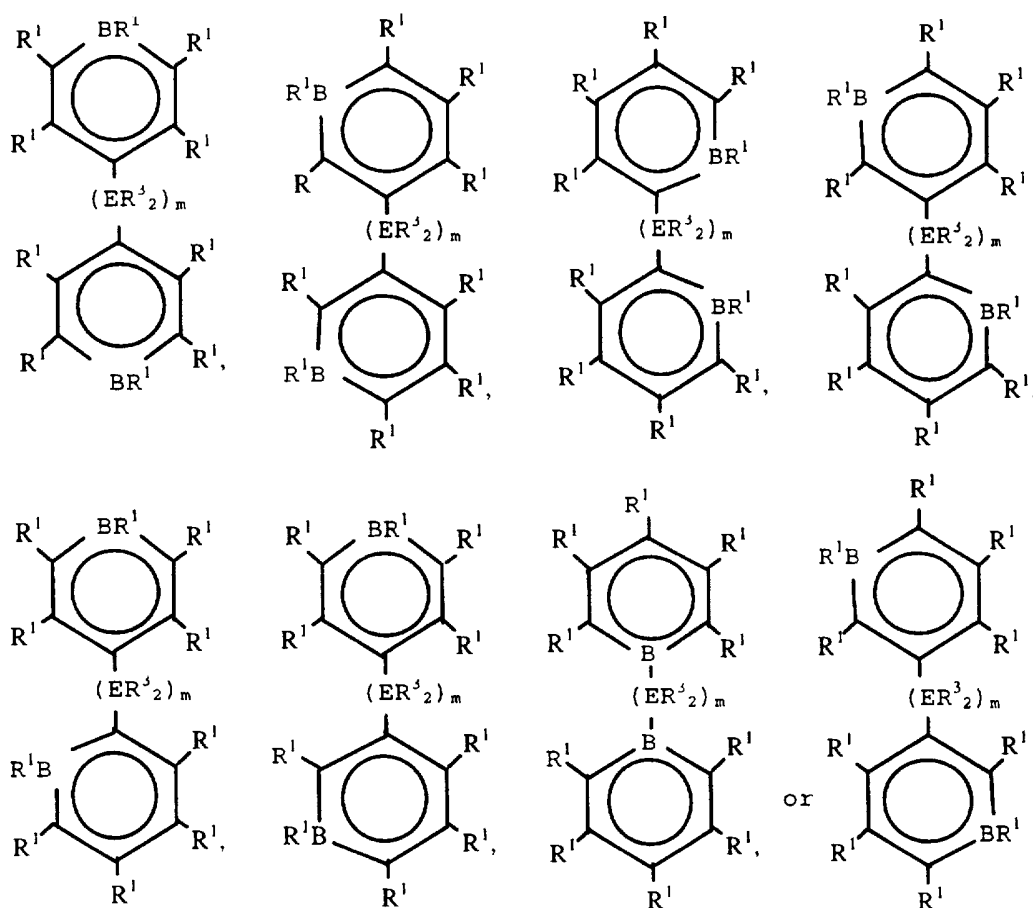
- 25 X'' each occurrence is an anionic ligand group that is covalently bonded to M when M is in the +3 or +4 formal oxidation state, whereupon n is 0 and p is 1 or 2, and optionally two X'' groups together form a divalent anionic ligand group.

- 30 Examples of suitable X' moieties include: η^4 -1,4-diphenyl-1,3-butadiene; η^4 -1,3-pentadiene; η^4 -1-phenyl-1,3-pentadiene; η^4 -1,4-dibenzyl-1,3-butadiene; η^4 -2,4-hexadiene; η^4 -3-methyl-1,3-pentadiene; η^4 -1,4-ditolyl-1,3-butadiene; and η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene. Of the foregoing 1,4-diphenyl-1,3-butadiene, 1-phenyl-1,3-pentadiene, and 2,4 hexadiene are preferred.

Examples of suitable X" moieties include chloride, methyl, benzyl, phenyl, tolyl, t-butyl, methoxide, and trimethylsilyl or two X" groups together are 1,4-butanediyl, s-cis(1,3-butadiene), or s-cis(2,3-dimethyl-1,3-butadiene).

Preferred Z groups are those wherein E is carbon and m is 2 or where E is
5 silicon and m is 1. Also preferably R² is methyl, phenyl, methoxide, ethoxide, propoxide or butoxide.

In the most preferred embodiment -Y-Z-Y- conforms to one of the following formulas:



10

Wherein:

R¹ independently each occurrence is hydrogen, hydrocarbyl, dihydrocarbylamino, perfluorohydrocarbyl, silyl substituted hydrocarbyl, or hydrocarbyl substituted silyl of up to 20 nonhydrogen atoms, and optionally two

adjacent R¹ groups together form a divalent derivative, thereby forming a multicyclic, fused, divalent derivative of a boratabenzene ring system; and

R² is as previously defined.

Most preferably R¹ independently each occurrence is hydrogen, C₆₋₂₀ aryl, secondary or tertiary C₃₋₁₀ alkyl, or di-C₁₋₆ alkylamino, and R² independently each occurrence is C₁₋₄ alkyl or alkoxy.

In the foregoing structures a negative charge is delocalized on each boratabenzene ring. Both meso and racemic isomers of the metal complexes are obtainable.

Illustrative derivatives of Group 3, 4 or Lanthanide metals of the foregoing formula that may be employed in the practice of the present invention include:

[bis(η⁶-1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (II) 1,4-diphenyl-1,3-butadiene,

[bis(η⁶-1-methyl-2-phenylboratabenzene-4-yl)dimethylsilane]zirconium (II) 1,4-diphenyl-1,3-butadiene,

[bis(η⁶-1-phenyl-2-methylboratabenzene-4-yl)dimethylsilane]zirconium (II) 1,4-diphenyl-1,3-butadiene,

[bis(η⁶-1-phenylboratabenzene-4-yl)dimethylsilane]titanium (II) 1,3-pentadiene,

[bis(η⁶-1-methylboratabenzene-4-yl)dimethylsilane]titanium (III) 2-(N,N-dimethylamino)benzyl,

[bis(η⁶-1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dimethyl,

[bis(η⁶-1-methyl-2-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dimethyl,

[bis(η⁶-1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dibenzyl,

[bis(η⁶-1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dichloride,

[bis(η⁶-1-methylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dimethyl,

[1,2-bis(η⁶-1-methyl-2-phenylboratabenzene-4-yl)ethane]zirconium (IV) dibenzyl,

[bis(η⁶-1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dichloride,

[1-(η⁶-1-phenylboratabenzene-2-yl)-2-(η⁶-1-phenylboratabenzene-3-yl)-ethane]zirconium (II) 1,4-diphenyl-1,3-butadiene,

[bis(η⁶-1-methylboratabenzene-3-yl)dimethylsilane]zirconium (II) 1,3-pentadiene,

- [(η^6 -1-phenylboratabenzene-3-yl) (η^6 -1-phenylboratabenzene-4-yl)dimethylsilane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 [(η^6 -1-phenylboratabenzene-3-yl) (η^6 -1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dimethyl,
 5 [(η^6 -1-phenylboratabenzene-2-yl) (η^6 -1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dibenzyl,
 [(η^6 -1-phenylboratabenzene-2-yl) (η^6 -1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dichloride,
 [bis(η^6 -1-phenylboratabenzene-3-yl)dimethylsilane]zirconium (IV) dimethyl,
 10 [(η^6 -1-phenylboratabenzene-2-yl) (η^6 -1-phenylboratabenzene-3-yl)dimethylsilane]zirconium (IV) dibenzyl,
 [(η^6 -1-methylboratabenzene-2-yl)(η^6 -1-phenylboratabenzene-4-yl)dimethylsilane]zirconium (IV) dichloride,

 15 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]titanium (II) 1,3-pentadiene,
 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 20 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]zirconium (IV) dimethyl,
 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]zirconium (IV) dibenzyl,
 25 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]zirconium (IV) dichloride,
 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]zirconium (IV) dimethyl,
 [bis (η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]zirconium (IV) dibenzyl,
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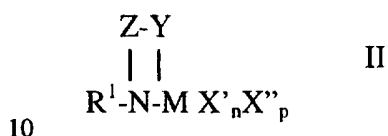
- [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)dimethylsilane]zirconium (IV) dichloride,
- [1-(η^6 -1-(N,N-dimethylamino)boratabenzene-2-yl)-2-(η^6 -1-(N,N-dimethylamino)-
 5 boratabenzene-3-yl)ethane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-3-yl)dimethylsilane]zirconium (II) 1,3-pentadiene,
 [(η^6 -1-(N,N-dimethylamino)boratabenzene-3-yl)(η^6 -1-(N,N-dimethylamino)-
 boratabenzene-4-yl)dimethylsilane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 10 [(η^6 -1-(N,N-dimethylamino)boratabenzene-3-yl) (η^6 -1-(N,N-dimethylamino)-
 boratabenzene-4-yl)dimethylsilane]zirconium (IV) dimethyl,
 [(η^6 -1-(N,N-dimethylamino)boratabenzene-2-yl) (η^6 -1-(N,N-dimethylamino)-
 boratabenzene-4-yl)dimethylsilane]zirconium (IV) dibenzyl,
 [(η^6 -1-(N,N-dimethylamino)boratabenzene-2-yl) (η^6 -1-(N,N-dimethylamino)-
 15 boratabenzene-4-yl)dimethylsilane]zirconium (IV) dichloride,
 [bis(η^6 -1-(N,N-dimethylamino)boratabenzene-3-yl)dimethylsilane]zirconium (IV) dimethyl,
 [(η^6 -1-(N,N-dimethylamino)boratabenzene-2-yl) (η^6 -1-(N,N-dimethylamino)-
 boratabenzene-4-yl)dimethylsilane]zirconium (IV) dibenzyl,
 20 [1-(η^6 -1-(N,N-dimethylamino)boratabenzene-2-yl)-2-(η^6 -1-(N,N-dimethylamino)-
 boratabenzene-4-yl)ethane]hafnium (IV) dichloride,
 [(η^6 -1-(N,N-diisopropylamino)boratabenzene-3-yl) (η^6 -1-(N,N-dimethylamino)-
 boratabenzene-4-yl)dimethylsilane]zirconium (IV) dimethyl,
 [(η^6 -1-(N,N-diisopropylamino)boratabenzene-2-yl) (η^6 -1-(N,N-dimethylamino)-
 25 boratabenzene-4-yl)dimethylsilane]zirconium (IV) dibenzyl,
 [(η^6 -1-(N,N-diisopropylamino)boratabenzene-2-yl) (η^6 -1-(N,N-dimethylamino)-
 boratabenzene-4-yl)dimethylsilane]zirconium (IV) dichloride,
 [bis(η^6 -1-(N,N-diisopropylamino)boratabenzene-3-yl)dimethylsilane]zirconium (IV) dimethyl,
 30 [(η^6 -1-(N,N-diisopropylamino)boratabenzene-2-yl) (η^6 -1-(N,N-dimethylamino)-
 boratabenzene-4-yl)dimethylsilane]zirconium (IV) dibenzyl,

- [1-(η^6 -1-(N,N-diisopropylamino)boratabenzene-2-yl)-2-(η^6 -1-(N,N-dimethylamino)-boratabenzene-4-yl)ethane]hafnium (IV) dichloride,
- [1,2-bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)ethane]zirconium (IV) dimethyl,
- [1,2-bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)ethane]zirconium (IV) dibenzyl,
- 5 [1,2-bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)ethane]zirconium (IV) dichloride,
- [1,2-bis(η^6 -1-(N,N-diisopropylamino)boratabenzene-4-yl)ethane]zirconium (IV) dimethyl,
- [1,2-bis(η^6 -1-(N,N-diisopropylamino)boratabenzene-4-yl)ethane]zirconium (IV) dibenzyl,
- 10 [1,2-bis(η^6 -1-(N,N-diisopropylamino)boratabenzene-4-yl)ethane]zirconium (IV) dichloride,
- [2,2-bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)propane]zirconium (IV) dimethyl,
- 15 [2,2-bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)propane]zirconium (IV) dibenzyl,
- [2,2-bis(η^6 -1-(N,N-dimethylamino)boratabenzene-4-yl)propane]zirconium (IV) dichloride,
- [2,2-bis(η^6 -1-(N,N-diisopropylamino)boratabenzene-4-yl)propane]zirconium (IV) dimethyl,
- 20 [2,2-bis(η^6 -1-(N,N-diisopropylamino)boratabenzene-4-yl)propane]zirconium (IV) dibenzyl,
- [2,2-bis(η^6 -1-(N,N-diisopropylamino)boratabenzene-4-yl)propane]zirconium (IV) dichloride,
- 25 [1-(η^6 -boratabenzene-2-yl)-2-(η^6 -boratabenzene-3-yl)ethane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
- [bis(η^6 -boratabenzene-3-yl)dimethylsilane]zirconium (II) 1,3-pentadiene,
- [(η^6 -boratabenzene-3-yl) (η^6 -boratabenzene-4-yl)dimethylsilane]titanium (III) 2-(N,N-
- 30 dimethylamino)benzyl,

- [(η^6 -boratabenzene-3-yl) (η^6 --boratabenzene-4-yl)dimethylsilane]zirconium (IV)
dimethyl,
- [(η^6 -boratabenzene-2-yl) (η^6 -boratabenzene-4-yl)dimethylsilane]zirconium (IV)
dibenzyl,
- 5 [(η^6 -boratabenzene-2-yl) (η^6 -boratabenzene-4-yl)dimethylsilane]zirconium (IV)
dichloride,
- [bis(η^6 -boratabenzene-3-yl)dimethylsilane]zirconium (IV) dimethyl,
- [(η^6 -boratabenzene-2-yl) (η^6 -boratabenzene-4-yl)dimethylsilane]zirconium (IV)
dibenzyl,
- 10 [1-(η^6 -boratabenzene-2-yl)-2-(η^6 -boratabenzene-4-yl)ethane]hafnium (IV) dichloride
[1,2-bis(η^6 -boratabenzene-4-yl)ethane]zirconium (IV) dimethyl,
- [1,2-bis(η^6 -boratabenzene-4-yl)ethane]zirconium (IV) dibenzyl,
- [1,2-bis(η^6 -boratabenzene-4-yl)ethane]zirconium (IV) dichloride,
- [1,2-bis(η^6 -boratabenzene-4-yl)ethane]zirconium (IV) dimethyl,
- 15 [1,2-bis(η^6 -boratabenzene-4-yl)ethane]zirconium (IV) dibenzyl,
- [1,2-bis(η^6 -boratabenzene-4-yl)ethane]zirconium (IV) dichloride,
- [1,2-bis(η^6 -boratabenzene-1-yl)ethane]zirconium (IV) dimethyl,
- [1,2-bis(η^6 -boratabenzene-1-yl)ethane]zirconium (IV) dibenzyl,
- [1,2-bis(η^6 -boratabenzene-1-yl)ethane]zirconium (IV) dichloride,
- 20 [1,2-bis(η^6 -boratabenzene-1-yl)ethane]zirconium (IV) dimethyl,
- [1,2-bis(η^6 -boratabenzene-1-yl)ethane]zirconium (IV) dibenzyl,
- [1,2-bis(η^6 -boratabenzene-1-yl)ethane]zirconium (IV) dichloride,
- [2,2-bis(η^6 -boratabenzene-4-yl)propane]zirconium (IV) dimethyl,
- [2,2-bis(η^6 -boratabenzene-4-yl)propane]zirconium (IV) dibenzyl,
- 25 [2,2-bis(η^6 -boratabenzene-4-yl)propane]zirconium (IV) dichloride,
- [2,2-bis(η^6 -boratabenzene-4-yl)propane]zirconium (IV) dimethyl,
- [2,2-bis(η^6 -boratabenzene-4-yl)propane]zirconium (IV) dibenzyl,
- [2,2-bis(η^6 -boratabenzene-4-yl)propane]zirconium (IV) dichloride,
- [2,2-bis(η^6 -boratabenzene-1-yl)propane]zirconium (IV) dimethyl,
- 30 [2,2-bis(η^6 -boratabenzene-1-yl)propane]zirconium (IV) dibenzyl,

- [2,2-bis(η^6 -boratabenzene-1-yl)propane]zirconium (IV) dichloride,
 [2,2-bis(η^6 -boratabenzene-1-yl)propane]zirconium (IV) dimethyl,
 [2,2-bis(η^6 -boratabenzene-1-yl)propane]zirconium (IV) dibenzyl,
 [2,2-bis(η^6 -boratabenzene-1-yl)propane]zirconium (IV) dichloride,
 5 [1,2-bis(η^6 -boratabenzene-1-yl)ethane]hafnium (IV) dichloride, and
 [2,2-bis(η^6 -boratabenzene-1-yl)propane]hafnium (IV) dichloride.

Further examples of preferred complexes according to the present invention correspond to the formula:



wherein:

M is titanium, zirconium or hafnium, preferably titanium, in the +2, +3 or +4 formal oxidation state;

- Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms
 15 having the formula, $-(\text{ER}^2)_m-$, wherein E independently each occurrence is carbon, silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

- Y is a divalent derivative of a boratabenzene group or a hydrocarbyl-,
 20 dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

R^1 is a C_{1-20} hydrocarbyl group,

- X' is a conjugated diene having from 4 to 30 non-hydrogen atoms, which
 forms a π -complex with M when M is in the +2 formal oxidation state, whereupon n is
 25 1 and p is 0; and

X'' each occurrence is an anionic ligand group that is covalently bonded to M when M is in the +3 or +4 formal oxidation state, whereupon n is 0 and p is 1 or 2, and optionally two X'' groups together form a divalent anionic ligand group.

Examples of suitable X' moieties include: η^4 -1,4-diphenyl-1,3-butadiene; η^4 -1,3-pentadiene; η^4 -1-phenyl-1,3-pentadiene; η^4 -1,4-dibenzyl-1,3-butadiene; η^4 -2,4-hexadiene; η^4 -3-methyl-1,3-pentadiene; η^4 -1,4-ditolyl-1,3-butadiene; and η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene. Of the foregoing 1,4-diphenyl-1,3-butadiene, 1-phenyl-1,3-pentadiene, and 2,4 hexadiene are preferred.

Examples of suitable X'' moieties include chloride, methyl, benzyl, phenyl, tolyl, t-butyl, methoxide, and trimethylsilyl or two X'' groups together are 1,4-butanediyl, s-cis(1,3-butadiene), or s-cis(2,3-dimethyl-1,3-butadiene).

Preferred Z groups are those wherein E is carbon and m is 2 or E is silicon and m is 1. In addition R² is methyl, phenyl, methoxide, ethoxide, propoxide or butoxide.

In the most preferred embodiment -Z-Y- is dimethyl(η^6 -1-phenylboratabenzene-4-yl)silyl, dimethyl(η^6 -1-N,N-dimethylaminoboratabenzene-4-yl)silyl, 1-(η^6 -1-phenylboratabenzene-4-yl)ethane-2-yl, or 1-(η^6 -1-N,N-dimethylamino)boratabenzene-4-yl)ethane-2-yl.

Examples of the foregoing metal complexes include:

[(t-butylamido)dimethyl(1-phenylboratabenzene-2-yl)silane]titanium dimethyl;
 [(t-butylamido)dimethyl(1-phenylboratabenzene-3-yl)silane]titanium dimethyl;
 [(t-butylamido)dimethyl(1-phenylboratabenzene-4-yl)silane]titanium dimethyl;
 [(t-butylamido)dimethyl(1-N,N-dimethylaminoboratabenzene-2-yl)silane]titanium dimethyl;
 [(t-butylamido)dimethyl(1-N,N-dimethylaminoboratabenzene-2-yl)silane]titanium dichloride;
 [(t-butylamido)dimethyl(1-N,N-dimethylaminoboratabenzene-4-yl)silane]titanium(II)
 1,4-diphenyl-1,3-butadiene;
 [1-(t-butylamido)-2-(1-phenylboratabenzene-2-yl)ethane]titanium dimethyl,

[(t-butylamido)dimethyl(boratabenzene-2-yl)silane]titanium dimethyl;
 [(t-butylamido)dimethyl(boratabenzene-3-yl)silane]titanium dimethyl;
 [(t-butylamido)dimethyl(boratabenzene-4-yl)silane]titanium dimethyl;
 [(t-butylamido)dimethyl(boratabenzene-4-yl)silane]titanium dibenzyl;
 [(t-butylamido)dimethyl(boratabenzene-2-yl)silane]titanium dichloride;

[(t-butylamido)dimethyl(boratabenzene-4-yl)silane]titanium(II)

1,4-diphenyl-1,3-butadiene;

[1-(t-butylamido)-2-(boratabenzene-2-yl)ethane]titanium dimethyl

5 [(cyclohexylamido)dimethyl(1-phenyl)boratabenzene-2-yl)silane]titanium dimethyl;
[(cyclohexylamido)dimethyl(1-phenyl)boratabenzene-3-yl)silane]titanium dimethyl;
[(cyclohexylamido)dimethyl(1-phenylboratabenzene-4-yl)silane]titanium dimethyl;
[(cyclohexylamido)dimethyl(1-N,N-dimethylaminoboratabenzene-2-yl)silane]titanium
dimethyl;

10 [(cyclohexylamido)dimethyl(1-N,N-dimethylaminoboratabenzene-2-yl)silane]titanium
dichloride;

[(cyclohexylamido)dimethyl(1-N,N-dimethylaminoboratabenzene-4-yl)silane]titanium(II) 1,4-diphenyl-1,3-butadiene;

[1-(cyclohexylamido)-2-(1-phenylboratabenzene-2-yl)ethane]titanium dimethyl,

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(cyclohexylamido)dimethyl(boratabenzene-2-yl)silane]titanium dimethyl;

(cyclohexylamido)dimethyl(boratabenzene-3-yl)silane]titanium dimethyl;

(cyclohexylamido)dimethyl(boratabenzene-4-yl)silane]titanium dimethyl;

(cyclohexylamido)dimethyl(boratabenzene-4-yl)silane]titanium dibenzyl;

20 (cyclohexylamido)dimethyl(boratabenzene-2-yl)silane]titanium dichloride;

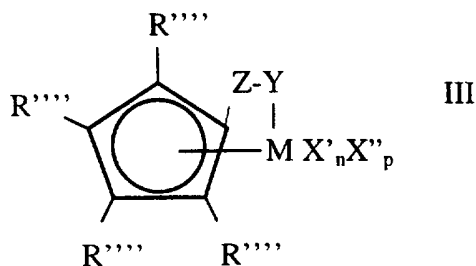
(cyclohexylamido)dimethyl(boratabenzene-4-yl)silane]titanium(II)

1,4-diphenyl-1,3-butadiene; and

1-(cyclohexylamido)-2-(boratabenzene-2-yl)ethane]titanium dimethyl.

Still further examples of complexes according to the present invention

25 correspond to the formula:



wherein:

M is titanium, zirconium or hafnium, preferably zirconium, in the +2, or +4 formal oxidation state;

Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms having the formula, $-(ER^2)_m-$, wherein E independently each occurrence is carbon, silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

Y is a divalent derivative of a boratabenzene group or a hydrocarbyl-, dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

X' is a conjugated diene having from 4 to 30 non-hydrogen atoms, which forms a π -complex with M when M is in the +2 formal oxidation state, whereupon n is 1 and p is 0;

X'' each occurrence is an anionic ligand group that is covalently bonded to M when M is in the +4 formal oxidation state, whereupon n is 0 and p is 2, and optionally two X'' groups together form a divalent anionic ligand group; and

R''' is hydrogen, hydrocarbyl, silyl, halo-, cyano, dialkylamino, halohydrocarbyl, halocarbyl, dialkylamino substituted-hydrocarbyl, or hydrocarbyl-substituted metalloid wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, said R''' , when a multi-atomic ligand group, containing up to 20 nonhydrogen atoms.

Preferably, R''' independently in each occurrence is selected from the group consisting of hydrogen, methyl, ethyl, and all isomers of propyl, butyl, pentyl and hexyl, as well as cyclopentyl, cyclohexyl, norbornyl, benzyl, and trimethylsilyl; or adjacent R''' groups are linked together thereby forming a fused ring system such as an indene-1-yl, 2-methylindene-1-yl, 3-methylindene-1-yl, 2,3-dimethylindene-1-yl, 2,3,5,6-tetramethylindene-1-yl, 2,3,5,6,7-pentamethylindene-1-yl, 2-methyl-4-phenylindene-1-yl, 2-methyl-4-naphthylindene-1-yl, tetrahydroindene-1-yl, fluorene-1-yl, tetrahydrofluorene-1-yl, or octahydrofluorene-1-yl group.

Most preferred complexes according to formula III are those containing a divalent derivative of a cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl,

tetrahydrofluorenyl, or octahydrofluorenyl group, or one of the foregoing groups further substituted with one or more methyl, ethyl, propyl, butyl, pentyl, hexyl, (including branched and cyclic isomers), norbornyl, benzyl, or phenyl groups.

Examples of suitable X' moieties include: η^4 -1,4-diphenyl-1,3-butadiene; η^4 -1,3-pentadiene; η^4 -1-phenyl-1,3-pentadiene; η^4 -1,4-dibenzyl-1,3-butadiene; η^4 -2,4-hexadiene; η^4 -3-methyl-1,3-pentadiene; η^4 -1,4-ditolyl-1,3-butadiene; and η^4 -1,4-bis(trimethylsilyl)-1,3-butadiene. Of the foregoing 1,4-diphenyl-1,3-butadiene, 1-phenyl-1,3-pentadiene, and 2,4 hexadiene are preferred.

Examples of suitable X'' moieties include chloride, methyl, benzyl, phenyl, tolyl, t-butyl, methoxide, and trimethylsilyl or two X'' groups together are 1,4-butanediyl, s-cis(1,3-butadiene), or s-cis(2,3-dimethyl-1,3-butadiene).

Preferred Z groups are those wherein E carbon and m is 2 or E is silicon and m is 1. Also preferably R² is methyl, phenyl, methoxide, ethoxide, propoxide or butoxide.

In the most preferred embodiment -Z-Y- is (η^6 -1-phenylboratabenzene-4-yl)dimethylsilyl, (η^6 -1-N,N-dimethylaminoboratabenzene-4-yl)dimethylsilyl, 1-(η^6 -1-phenylboratabenzene-4-yl)ethane-2-yl, 1-(η^6 -1-N,N-dimethylaminoboratabenzene-4-yl)ethane-2-yl, (η^6 -1-phenylboratabenzene-4-yl)phenylmethylsilyl, or (η^6 -(1-N,N-dimethylamino)boratabenzene-4-yl)phenylmethylsilyl.

Illustrative derivatives of Group 3, 4 or Lanthanide metals of the foregoing formula that may be employed in the practice of the present invention include:

[(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,

[(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-silane]titanium (II) 1,3-pentadiene,

[(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-silane]titanium (III) 2-(N,N-dimethylamino)benzyl,

[(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-silane]zirconium (IV) dimethyl,

[1-(η^6 -1-phenylboratabenzene-4-yl)-2-(η^5 -tetramethylcyclopentadienyl)ethane]-zirconium (IV) dimethyl,

- [1-(η^6 -1-methylboratabenzene-4-yl)-2-(η^5 -tetramethylcyclopentadienyl)ethane]-
zirconium (IV) dimethyl,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-
silane]zirconium (IV) dibenzyl,
- 5 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-
silane]zirconium (IV) dichloride,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]zirconium (II)
1,4-diphenyl-1,3-butadiene,
- 10 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]zirconium (II)
1,3-pentadiene,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]titanium (III) 2-
(N,N-dimethylamino)benzyl,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]hafnium (IV)
15 dimethyl,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]zirconium (IV)
dibenzyl,
- [(η^6 -1-methyl-2-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]-
zirconium (IV) dibenzyl,
- 20 [1-(η^6 -1-methyl-2-phenylboratabenzene-4-yl)-2-(η^5 -2-methylindenyl)ethane] zirconium
(IV) dibenzyl,
- [1-(η^6 -1-methyl-2-phenylboratabenzene-4-yl)-2-(η^5 -2-methylindenyl)ethane] zirconium
(IV) dimethyl,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]zirconium (IV)
25 dichloride,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]zirconium (II)
1,4-diphenyl-1,3-butadiene,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]titanium (II) 1,3-
30 pentadiene,

- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]zirconium (IV) dimethyl,
 5 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]hafnium (IV) dibenzyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]zirconium (IV) dichloride,
 10 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]titanium (II) 1,3-pentadiene,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]titanium (III)
 15 2-(N,N-dimethylamino)benzyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (IV) dimethyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (IV) dibenzyl,
 20 [1-(η^6 -1-methyl-2-(phenyl)boratabenzene-4-yl)-2-(η^5 -2,4-dimethylindenyl)ethane]zirconium (IV) dibenzyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]hafnium (IV) dichloride,
 25 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [(η^6 -1-methyl-2-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [1-(η^6 -1-methyl-2-phenylboratabenzene-4-yl)-2-(η^5 -2-methyl-4-phenylindenyl)-ethane]zirconium (IV)dimethyl
 30

- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (II) 1,3-pentadiene,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]titanium
 (III) 2-(N,N-dimethylamino)benzyl,
- 5 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV) dimethyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV) dibenzyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV) dichloride,
- 10 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]titanium (II)
 1,4-diphenyl-1,3-butadiene,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (II)
 15 1,3-pentadiene,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]titanium (III)
 2-(N,N-dimethylamino)benzyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (IV)
 dimethyl,
- 20 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (IV)
 dibenzyl,
 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]hafnium (IV)
 dichloride,
- 25 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)silane]zirconium (II)
 1,4-diphenyl-1,3-butadiene,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)silane]titanium (II)
 1,3-pentadiene,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)silane]titanium (III)
 30 2-(N,N-dimethylamino)benzyl,

-](η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)silane]zirconium (IV)
 dimethyl,
 [1-(η^6 -boratabenzene-4-yl)-2-(η^5 -tetramethylcyclopentadienyl)ethane]zirconium (IV)
 dimethyl,
 5 [1-(η^6 -1-(methyl)boratabenzene-4-yl)-2-(η^5 -tetramethylcyclopentadienyl)-
 ethane]zirconium (IV) dimethyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)silane]zirconium (IV)
 dibenzyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)silane]zirconium (IV)
 10 dichloride,

 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]zirconium (II) 1,4-
 diphenyl-1,3-butadiene,
 [(η^6 -1(phenyl)boratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]zirconium (II)
 15 1,3-pentadiene,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]titanium (III) 2-(N,N-
 dimethylamino)benzyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]hafnium (IV) dimethyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]zirconium (IV) dibenzyl,
 20 [(η^6 -1-methyl-2-(phenyl)boratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]-
 zirconium (IV) dibenzyl,
 [1-(η^6 -1-methyl-2-phenylboratabenzene-4-yl)-2-(η^5 -2-methylindenyl)ethane] zirconium
 (IV) dibenzyl,
 [1-(η^6 -1-methyl-2-phenylboratabenzene-4-yl)-2-(η^5 -2-methylindenyl)ethane] zirconium
 25 (IV) dimethyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methylindenyl)silane]zirconium (IV) dichloride,

 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]zirconium (II) 1,4-
 diphenyl-1,3-butadiene,
 30 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]titanium (II) 1,3-
 pentadiene,

- [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]zirconium (IV) dimethyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]hafnium (IV) dibenzyl,
 5 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]zirconium (IV) dichloride,

 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]titanium (II) 1,3-
 10 pentadiene,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (IV) dimethyl,
 15 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (IV) dibenzyl,
 [1-(η^6 -1-methyl-2-(phenyl)boratabenzene-4-yl)-2-(η^5 -2,4-dimethylindenyl)ethane]zirconium (IV) dibenzyl,
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]hafnium (IV)
 20 dichloride,

 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [(η^6 -1-methyl-2-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)-
 25 silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [1-(η^6 -1-methyl-2-(phenyl)boratabenzene-4-yl)-2-(η^5 -2-methyl-4-phenylindenyl)ethane]zirconium (IV)dimethyl
 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (II) 1,3-pentadiene,
 30 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]titanium (III) 2-(N,N-dimethylamino)benzyl,

- [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV)
dimethyl,
- [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV)
dibenzyl,
- 5 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV)
dichloride,
- [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]titanium (II) 1,4-
diphenyl-1,3-butadiene,
- 10 [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (II) 1,3-
pentadiene,
- [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]titanium (III) 2-(N,N-
dimethylamino)benzyl,
- [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (IV)
15 dimethyl,
- [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (IV)
dibenzyl,
- [(η^6 -boratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]hafnium (IV)
dichloride,
- 20 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-
silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-
silane]titanium (II) 1,3-pentadiene,
- 25 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-
silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
- [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-
silane]zirconium (IV) dimethyl,
- 1-(η^6 -1-phenylboratabenzene-4-yl)-2-(η^5 -
30 tetramethylcyclopentadienyl)ethane]zirconium (IV) dimethyl,

- [1-(η^6 -1-(methyl)boratabenzene-4-yl)-2-(η^5 -
tetramethylcyclopentadienyl)ethane]zirconium (IV) dimethyl,
[(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-
silane]zirconium (IV) dibenzyl,
5 [(η^6 -1-phenylboratabenzene-4-yl)dimethyl(η^5 -tetramethylcyclopentadienyl)-
silane]zirconium (IV) dichloride,
- [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-
methylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
10 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-
methylindenyl)silane]zirconium (II) 1,3-pentadiene,
[(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-
methylindenyl)silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
[(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-
15 methylindenyl)silane]hafnium (IV) dimethyl,
[(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-
methylindenyl)silane]zirconium (IV) dibenzyl,
[(η^6 -1-diisopropylamino-3-phenylboratabenzene-4-yl)dimethyl(η^5 -2-
methylindenyl)silane]zirconium (IV) dibenzyl,
20 [1-(η^6 -1-diisopropylamino-2-phenylboratabenzene-4-yl)-2-(η^5 -2-
methylindenyl)ethane]zirconium (IV) dibenzyl,
[1-(η^6 -1-diisopropylamino-2-phenylboratabenzene-4-yl)-2-(η^5 -2-
methylindenyl)ethane]zirconium (IV) dimethyl,
[(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-
25 methylindenyl)silane]zirconium (IV) dichloride,
- [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -3-
methylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
[(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -3-
30 methylindenyl)silane]titanium (II) 1,3-pentadiene,

- [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]zirconium (IV) dimethyl,
 5 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]hafnium (IV) dibenzyl,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -3-methylindenyl)silane]zirconium (IV) dichloride,
- 10 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]titanium (II) 1,3-pentadiene,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)-
 15 silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (IV) dimethyl,
 [(η^6 -1-(N,N-diisopropylamino)boratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]zirconium (IV) dibenzyl,
- 20 [1-(η^6 -1-diisopropylamino-2-(phenyl)boratabenzene-4-yl)-2-(η^5 -2,4-dimethylindenyl)ethane]zirconium (IV) dibenzyl,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2,3-dimethylindenyl)silane]hafnium (IV) dichloride,
- 25 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [(η^6 -1-diisopropylamino-2-phenylboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (II) 1,4-diphenyl-1,3-butadiene,
 [1-(η^6 -1-diisopropylamino-2-phenylboratabenzene-4-yl)-2-(η^5 -2-methyl-4-
 30 phenylindenyl)ethane]zirconium (IV)dimethyl

[(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (II) 1,3-pentadiene,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 5 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV) dimethyl,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV) dibenzyl,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -2-methyl-4-phenylindenyl)silane]zirconium (IV) dichloride,
 10 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]titanium (II) 1,4-diphenyl-1,3-butadiene,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (II) 1,3-pentadiene,
 15 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]titanium (III) 2-(N,N-dimethylamino)benzyl,
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (IV) dimethyl,
 20 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]zirconium (IV) dibenzyl, and
 [(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethyl(η^5 -tetrahydrofluorenyl)silane]hafnium (IV) dichloride.

Other metal complexes, especially compounds containing other Group 3, 4 or
 25 Lanthanide metals will, of course, be apparent to those skilled in the art. In addition other substituted boratabenzene ligands especially 1-benzyl, and 1-methyl substituted boratabenzenes will similarly be apparent to those skilled in the art.

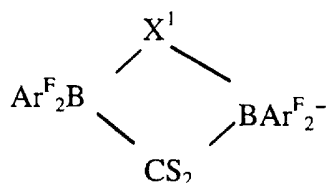
The complexes are rendered catalytically active by combination with an
 activating cocatalyst or by use of an activating technique. Suitable activating
 30 cocatalysts for use herein include polymeric or oligomeric alumoxanes, especially methylalumoxane, triisobutyl aluminum- modified methylalumoxane, or

diisobutylalumoxane; strong Lewis acids, such as C₁₋₃₀ hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron-compounds and halogenated derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, especially

5 tris(pentafluorophenyl)borane; and nonpolymeric, inert, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions). A suitable activating technique is bulk electrolysis (explained in more detail hereinafter). Combinations of the foregoing activating cocatalysts and techniques may also be employed if desired. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal
10 complexes in the following references: EP-A-277,003, US-A-5,153,157, US-A-5,064,802, EP-A-468,651, EP-A-520,732 and WO93/23412.

Suitable nonpolymeric, inert, compatible, noncoordinating, ion forming compounds useful as cocatalysts in one embodiment of the present invention
15 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 is formed when the two components are combined. Also, said
20 anion can 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
25 or metalloid atom are well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

Additional suitable anions include sterically shielded diboron anions corresponding to the formula:



wherein:

S is alkyl, fluoroalkyl, aryl, or fluoroaryl (and where two S groups are present additionally hydrogen),

5 Ar^F is fluoroaryl, and
 X^1 is either hydrogen or halide.

Such diboron anions are disclosed in US-A-5,447,895.

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



wherein:

L^* is a neutral ligand;

$(L^*-H)^+$ is a Bronsted acid;

15 A^{d-} is a noncoordinating, compatible anion having a charge of d-, and
d is an integer from 1 to 3.

More preferably d is one, that is, A^{d-} is A^- .

Highly preferably, A^- corresponds to the formula: $[BQ_4]^-$

wherein:

B is boron in the +3 formal oxidation state; and

20 Q independently each occurrence is selected from hydride, dialkylamino, halide, alkoxide, aryloxy, hydrocarbyl, halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide.

25 In a more highly preferred embodiment, Q is a fluorinated C_{1-20} hydrocarbyl group, most preferably, a fluorinated aryl group, especially, pentafluorophenyl.

Illustrative, but not limiting, examples of ion forming compounds comprising proton donatable cations which may be used as activating cocatalysts in the preparation of the catalysts of this invention are tri-substituted ammonium salts such

as:

- trimethylammonium tetraphenylborate,
 triethylammonium tetraphenylborate,
 tripropylammonium tetraphenylborate,
 5 tri(n-butyl)ammonium tetraphenylborate,
 tri(t-butyl)ammonium tetraphenylborate,
 N,N-dimethylanilinium tetraphenylborate,
 N,N-diethylanilinium tetraphenylborate,
 N,N-dimethyl(2,4,6-trimethylanilinium) tetraphenylborate, trimethylammonium tetrakis-
 10 (penta-fluorophenyl) 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-dimethylanilinium tetrakis(pentafluorophenyl)
 borate, N,N-diethylanilinium tetrakis(pentafluoro-phenyl) borate, N,N-dimethyl(2,4,6-
 15 trimethyl-anilinium) 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)
 20 borate,
 tri(n-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl)
 borate,
 dimethyl(t-butyl)ammonium tetrakis(2,3,4,6-
 tetrafluorophenyl) borate,
 25 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-
 30 tetrafluorophenyl) borate.

Dialkyl ammonium salts such as:

di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, and
dicyclohexylammonium tetrakis(pentafluorophenyl) borate.

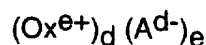
Tri-substituted phosphonium salts such as: triphenylphosphonium
5 tetrakis(pentafluorophenyl) borate, tri(o-tolyl)phosphonium tetrakis(penta-
fluorophenyl)

borate, and

tri(2,6-dimethylphenyl)-phosphonium tetrakis(penta-fluorophenyl) borate.

Preferred are N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and
10 tributylammonium 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:



15 wherein:

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

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-
20 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 or silylium ion and a noncoordinating, compatible
25 anion represented by the formula:



wherein:

C^+ is a C_{1-20} carbenium ion or silylium ion; and

A^- is as previously defined.

30 A preferred carbenium ion is the trityl cation, that is triphenylcarbenium. A
preferred silylium ion is triphenylsilylium.

The foregoing activating technique and ion forming cocatalysts are also preferably used in combination with a tri(hydrocarbyl)aluminum compound having from 1 to 4 carbons in each hydrocarbyl group, an oligomeric or polymeric alumoxane compound, or a mixture of a tri(hydrocarbyl)aluminum compound having from 1 to 4 carbons in each hydrocarbyl group and a polymeric or oligomeric alumoxane.

An especially preferred activating cocatalyst comprises the combination of a trialkyl aluminum compound having from 1 to 4 carbons in each alkyl group and an ammonium salt of tetrakis(pentafluorophenyl)borate, in a molar ratio from 0.1:1 to 1:0.1, optionally up to 1000 mole percent of an alkylalumoxane with respect to M, is also present.

The activating technique of bulk electrolysis involves the electrochemical oxidation of the metal complex under electrolysis conditions in the presence of a supporting electrolyte comprising a noncoordinating, inert anion. In the technique, solvents, supporting electrolytes and electrolytic potentials for the electrolysis are used such that electrolysis byproducts that would render the metal complex catalytically inactive are not substantially formed during the reaction. More particularly, suitable solvents are materials that are: liquids under the conditions of the electrolysis (generally temperatures from 0 to 100°C), capable of dissolving the supporting electrolyte, and inert. "Inert solvents" are those that are not reduced or oxidized under the reaction conditions employed for the electrolysis. It is generally possible in view of the desired electrolysis reaction to choose a solvent and a supporting electrolyte that are unaffected by the electrical potential used for the desired electrolysis. Preferred solvents include difluorobenzene (all isomers), DME, and mixtures thereof.

The electrolysis may be conducted in a standard electrolytic cell containing an anode and cathode (also referred to as the working electrode and counter electrode respectively). Suitably materials of construction for the cell are glass, plastic, ceramic and glass coated metal. The electrodes are prepared from inert conductive materials, by which are meant conductive materials that are unaffected by the reaction mixture or reaction conditions. Platinum or palladium are preferred inert conductive materials. Normally, an ion permeable membrane such as a fine glass frit separates the cell into separate compartments, the working electrode compartment

and counter electrode compartment. The working electrode is immersed in a reaction medium comprising the metal complex to be activated, solvent, supporting electrolyte, and any other materials desired for moderating the electrolysis or stabilizing the resulting complex. The counter electrode is immersed in a mixture of the solvent and supporting electrolyte. The desired voltage may be determined by theoretical calculations or experimentally by sweeping the cell using a reference electrode such as a silver electrode immersed in the cell electrolyte. The background cell current, the current draw in the absence of the desired electrolysis, is also determined. The electrolysis is completed when the current drops from the desired level to the background level. In this manner, complete conversion of the initial metal complex can be easily detected.

Suitable supporting electrolytes are salts comprising a cation and an inert, compatible, noncoordinating anion, A^- . Preferred supporting electrolytes are salts corresponding to the formula:

G^+A^- ;

wherein:

G^+ is a cation which is nonreactive towards the starting and resulting complex, and

A^- is a noncoordinating, compatible anion.

Examples of cations, G^+ , include tetrahydrocarbyl substituted ammonium or phosphonium cations having up to 40 nonhydrogen atoms. A preferred cation is the tetra-n-butylammonium cation.

During activation of the complexes of the present invention by bulk electrolysis the cation of the supporting electrolyte passes to the counter electrode and A^- migrates to the working electrode to become the anion of the resulting oxidized product. Either the solvent or the cation of the supporting electrolyte is reduced at the counter electrode in equal molar quantity with the amount of oxidized metal complex formed at the working electrode.

Preferred supporting electrolytes are tetrahydrocarbylammonium salts of tetrakis(perfluoroaryl) borates having from 1 to 10 carbons in each hydrocarbyl group, especially tetra-n-butylammonium tetrakis(pentafluorophenyl) borate.

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 1:10 to 1:2.

In general, the catalysts can be prepared by combining the two components (metal complex and activator) in a suitable solvent at a temperature within the range from -100°C to 300°C. The catalyst may be separately prepared prior to use by combining the respective components or prepared *in situ* by combination in the presence of the monomers to be polymerized. It is preferred to form the catalyst *in situ* due to the exceptionally high catalytic effectiveness of catalysts prepared in this manner. The catalysts' components are sensitive to both moisture and oxygen and should be handled and transferred in an inert atmosphere.

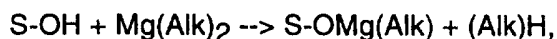
As previously mentioned the present metal complexes are highly desirable for use in preparing supported catalysts. In this regard, the presence of the alkoxy functionality in the bridging group is particularly beneficial in allowing the complexes to chemically bind to hydroxyl, silane or chlorosilane functionality of the substrate materials. Especially suited substrates include alumina or silica. Suitable supported catalyst systems are readily prepared by contacting the present metal complexes with the substrate optionally while subjecting to heating and/or reduced pressures. A Lewis base, especially a trialkylamine can be present to assist in the reaction between the support and the alkoxy functionality of the metal complexes if desired.

Preferred supports for use in the present invention include highly porous silicas, aluminas, aluminosilicates, and mixtures thereof. The most preferred support material is silica. The support material may be in granular, agglomerated, pelletized, or any other physical form. Suitable materials include, but are not limited to, silicas available from Grace Davison (division of W.R. Grace & Co.) under the designations SD 3216.30, Davison Syloid 245, Davison 948 and Davison 952, and from Degussa AG under the designation Aerosil 812; and aluminas available from Akzo Chemicals Inc. under the designation Ketzen Grade B.

Supports suitable for the present invention preferably have a surface area as determined by nitrogen porosimetry using the B.E.T. method from 10 to 1000 m²/g, and preferably from 100 to 600 m²/g. The pore volume of the support, as determined by nitrogen adsorption, advantageously is between 0.1 and 3 cm³/g,

preferably from 0.2 to 2 cm³/g. The average particle size is not critical, but typically is from 0.5 to 500 µm, preferably from 1 to 100 µm.

Both silica and alumina are known to inherently possess small quantities of hydroxyl functionality attached to the crystal structure. When used as a support herein, these materials are preferably subjected to a heat treatment and/or chemical treatment to reduce the hydroxyl content thereof. Typical heat treatments are carried out at a temperature from 30 to 1000°C for a duration of 10 minutes to 50 hours in an inert atmosphere or under reduced pressure. Typical chemical treatments include contacting with Lewis acid alkylating agents such as trihydrocarbyl aluminum compounds, trihydrocarbylchlorosilane compounds, trihydrocarbylalkoxysilane compounds or similar agents. Preferred silica or alumina materials for use herein have a surface hydroxyl content that is less than 0.8 mmol hydroxyl groups per gram of solid support, more preferably less than 0.5 mmol per gram. The hydroxyl content may be determined by adding an excess of dialkyl magnesium to a slurry of the solid support and determining the amount of dialkyl magnesium remaining in solution via known techniques. This method is based on the reaction:



wherein S is the solid support, and Alk is a C₁₋₄ alkyl group.

The support may be unfunctionalized (excepting for hydroxyl groups as previously disclosed) or functionalized by treating with a silane or chlorosilane functionalizing agent to attach thereto pendant silane -(Si-R)=, or chlorosilane -(Si-Cl)= functionality, wherein R is a C₁₋₁₀ hydrocarbyl group. Suitable functionalizing agents are compounds that react with surface hydroxyl groups of the support or react with the silicon or aluminum of the matrix. Examples of suitable functionalizing agents include phenylsilane, diphenylsilane, methylphenylsilane, dimethylsilane, diethylsilane, dichlorosilane, and dichlorodimethylsilane. Techniques for forming such functionalized silica or alumina compounds were previously disclosed in US-A-3,687,920 and US-A-3,879,368.

The support may also be treated with an aluminum component selected from an alumoxane or an aluminum compound of the formula $\text{AlR}^4_x\text{R}^5_y$, wherein R⁴ independently each occurrence is hydride or C₁₋₂₀ hydrocarbyl, R⁵ is

hydride, C₁₋₁₀ hydrocarbyl or C₁₋₁₀ hydrocarbyloxy, x' is 2 or 3, y' is 0 or 1 and the sum of x' and y' is 3. Examples of suitable R⁴ and R⁵ groups include methyl, methoxy, ethyl, ethoxy, propyl (all isomers), propoxy (all isomers), butyl (all isomers), butoxy (all isomers), phenyl, phenoxy, benzyl, and benzyloxy. Preferably, the aluminum
5 component is selected from the group consisting of aluminoxanes and tri(C₁₋₄ hydrocarbyl)aluminum compounds. Most preferred aluminum components are aluminoxanes, trimethyl aluminum, triethyl aluminum, tri-isobutyl aluminum, and mixtures thereof.

Alumoxanes (also referred to as aluminoxanes) are oligomeric or
10 polymeric aluminum oxy compounds containing chains of alternating aluminum and oxygen atoms, whereby the aluminum carries a substituent, preferably an alkyl group. The structure of alumoxane is believed to be represented by the following general formulae $(-\text{Al}(\text{R}^6)-\text{O})_{m'}$, for a cyclic alumoxane, and $\text{R}^6_2\text{Al}-\text{O}(-\text{Al}(\text{R}^6)-\text{O})_{m'}-\text{AlR}^6_2$, for a linear compound, wherein R⁶ is C₁₋₁₀ alkyl, and m' is an integer ranging from 1 to 50,
15 preferably at least 4. Alumoxanes are typically the reaction products of water and an aluminum alkyl, which in addition to an alkyl group may contain halide or alkoxide groups. Reacting several different aluminum alkyl compounds, such as for example trimethyl aluminum and tri-isobutyl aluminum, with water yields so-called modified or mixed alumoxanes. Preferred alumoxanes are methylalumoxane and
20 methylalumoxane modified with minor amounts of C₂₋₄ alkyl groups, especially isobutyl. Alumoxanes generally contain minor to substantial amounts of starting aluminum alkyl compound.

Particular techniques for the preparation of alumoxane type compounds by contacting an aluminum alkyl compound with an inorganic salt
25 containing water of crystallization are disclosed in U.S. 4,542,119. In a particular preferred embodiment an aluminum alkyl compound is contacted with a regeneratable water-containing substance such as hydrated alumina, silica or other substance. This is disclosed in EP-A-338,044. Thus the alumoxane may be incorporated into the support by reaction of a hydrated alumina or silica material,
30 which has optionally been functionalized with silane, siloxane, hydrocarbyloxysilane, or chlorosilane groups, with a tri(C₁₋₁₀ alkyl) aluminum compound according to known techniques.

The treatment of the support material in order to also include optional alumoxane or trialkylaluminum loadings involves contacting the same before, after or simultaneously with addition of the complex or activated catalyst hereunder with the alumoxane or trialkylaluminum compound, especially triethylaluminum or triisobutylaluminum. Optionally the mixture can also be heated under an inert atmosphere for a period and at a temperature sufficient to fix the alumoxane, trialkylaluminum compound, complex or catalyst system to the support. Optionally, the treated support component containing alumoxane or the trialkylaluminum compound may be subjected to one or more wash steps to remove alumoxane or trialkylaluminum not fixed to the support.

Besides contacting the support with alumoxane the alumoxane may be generated *in situ* by contacting an unhydrolyzed silica or alumina or a moistened silica or alumina with a trialkyl aluminum compound optionally in the presence of an inert diluent. Such a process is well known in the art, having been disclosed in EP-A-250,600, US-A-4,912,075, and US-A-5,008,228. Suitable aliphatic hydrocarbon diluents include pentane, isopentane, hexane, heptane, octane, isooctane, nonane, isononane, decane, cyclohexane, methylcyclohexane and combinations of two or more of such diluents. Suitable aromatic hydrocarbon diluents are benzene, toluene, xylene, and other alkyl or halogen substituted aromatic compounds. Most preferably, the diluent is an aromatic hydrocarbon, especially toluene. After preparation in the foregoing manner the residual hydroxyl content thereof is desirably reduced to a level less than 1.0 meq of OH per gram of support, by any of the previously disclosed techniques.

The catalysts, whether or not supported in any of the foregoing methods, may be used to polymerize ethylenically and/or acetylenically unsaturated monomers having from 2 to 100,000 carbon atoms either alone or in combination. Preferred monomers include the C_{2-20} α -olefins especially ethylene, propylene, isobutylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, long chain macromolecular α -olefins, and mixtures thereof. Other preferred monomers include styrene, C_{1-4} alkyl substituted styrene, tetrafluoroethylene, vinylbenzocyclobutane, ethylidenenorbornene, 1,4-hexadiene, 1,7-octadiene, vinylcyclohexane, 4-vinylcyclohexene, divinylbenzene, and mixtures thereof with

ethylene. Long chain macromolecular α -olefins are vinyl terminated polymeric remnants formed *in situ* during continuous solution polymerization reactions. Under suitable processing conditions such long chain macromolecular units are readily polymerized into the polymer product along with ethylene and other short chain olefin monomers to give small quantities of long chain branching in the resulting polymer.

The catalysts of the invention are particularly adapted for use in the preparation of high molecular weight α -olefin homopolymers and copolymers, especially crystalline propylene homopolymers and copolymers having a high degree of isotacticity. In this regard the preferred catalysts are the corresponding racemic isomers of the metal complexes disclosed herein.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, such as temperatures from 0-250°C and pressures from atmospheric to 1000 atmospheres (0.1 to 100 MPa). Suspension, solution, slurry, gas phase or other process conditions may be employed if desired. The support, if present, 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. Suitable gas phase reactions may utilize condensation of the monomer or monomers employed in the reaction, or of an inert diluent to remove heat from the reactor.

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^{-12} :1 to 10^{-5} :1.

Suitable solvents for polymerization via a solution process 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 cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C₄₋₁₀ alkanes, and aromatic and 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, 1-butene, butadiene, cyclopentene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1,7-octadiene, 1-

octene, 1-decene, styrene, divinylbenzene, ethylenenorbornene, allylbenzene, vinyltoluene (including all isomers alone or in admixture), 4-vinylcyclohexene, and vinylcyclohexane. Mixtures of the foregoing are also suitable.

The catalysts may also be utilized in combination with at least one additional
5 homogeneous or heterogeneous polymerization catalyst in the same or in separate reactors connected in series or in parallel to prepare polymer blends having desirable properties. An example of such a process is disclosed in WO 94/00500. Alternatively, the two catalysts may be utilized in sequential or simultaneous polymerizations while being supported on a highly porous support or carrier, including
10 a prepolymerized support that is capable of being permeated by an α -olefin.

Such polymerization process may comprise contacting, optionally in a solvent or in a nonsolvent, one or more α -olefins with a catalyst according to the present invention, in one or more continuous stirred tank or tubular reactors, or in the absence of solvent, optionally in one or more fluidized bed gas phase reactors,
15 connected in series or parallel, and recovering the resulting polymer. Condensed monomer or solvent may be added to the gas phase reactor as is well known in the art. In the preparation of polypropylene the foregoing polymerization may further involve use of a porous inert carrier particle which optionally may be prepolymerized with polypropylene or other polymer.

20 In another process an ethylene / α -olefin interpolymer composition is prepared by:

(A) contacting ethylene and at least one other α -olefin under polymerization conditions in the presence of a catalyst composition of the present invention in at least one reactor to produce a first interpolymer or optionally a solution of a first
25 interpolymer,

(B) contacting ethylene and at least one other α -olefin under polymerization conditions and at a higher polymerization reaction temperature than used in step (A) in the presence of a heterogeneous Ziegler catalyst in at least one other reactor to produce a second interpolymer optionally in solution, and

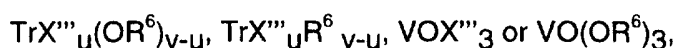
30 (C) combining the first interpolymer and second interpolymer to form an ethylene/ α -olefin interpolymer blend composition, and

(D) recovering the ethylene/ α -olefin interpolymer blend composition.

Preferably the heterogeneous Ziegler catalyst comprises:

(i) a solid support component comprising magnesium halide, silica, modified silica, alumina, aluminum phosphate, or a mixture thereof, and

5 (ii) a transition metal component represented by the formula:



wherein:

Tr is a Group 4, 5, or 6 metal,

u is a number from 0 to 6 that is less than or equal to v,

10 v is the formal oxidation number of Tr,

X^{v-u} is halogen, and

R⁶ independently each occurrence is a C₁₋₁₀ alkyl group.

These polymerizations are generally carried out under solution conditions to facilitate the intimate mixing of the two polymer-containing streams. The foregoing
15 technique allows for the preparation of ethylene/ α -olefin interpolymer compositions having a broad range of molecular weight distribution and composition distribution. Preferably, the heterogeneous catalyst is also chosen from those catalysts which are capable of efficiently producing the polymers under high temperature, especially, temperatures greater than or equal to 180°C under solution process conditions.

20 In a still further embodiment, there is provided a process for preparing polypropylene homopolymer or copolymer compositions, comprising:

(A) polymerizing propylene and, optionally, at least one other α -olefin in a solution, slurry or gas phase process under suitable polymerization temperatures and pressures in at least one reactor containing a catalyst composition of the present
25 invention, optionally supported on an inert support to produce a first polymer,

(B) optionally passing the polymer of (A) into at least one other reactor in the presence of one other α -olefin under polymerization conditions to form a polypropylene/propylene/ α -olefin interpolymer composition blend, and

(C) recovering the resulting composition.

30 The foregoing technique also allows for the preparation of polypropylene and polypropylene/propylene/ α -olefin interpolymer composition blends having a broad range of molecular weight distributions and composition distributions. Particularly

desirable α -olefins for use in the foregoing processes are ethylene, C_{4-8} α -olefins, most desirably ethylene.

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.

Example 1 [1,2-bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)ethane]zirconium dichloride

10 a) 1,2-Bis(1,1-dibutylstannacyclohexa-2,5-dien-4-yl)ethane

A solution of 1,1-dibutyl-1-stannacyclohexadienyllithium prepared from 1,1-dibutyl-1-stannacyclohexa-2,5-diene (0.08 g, 2.67 mmol) and 2.67 mmol of lithium diisopropylamide (LDA) in 20 mL of THF was added to a solution of 1,1-dibutyl-4-(2-bromoethyl)-1-stannacyclohexa-2,5-diene (1.0 g, 2.46 mmol) in 5 mL THF at -78°C .

15 After stirring approximately 16 hours, 10 mL of water were added and the product was extracted with pentane, dried over MgSO_4 , and evaporated to dryness. The red residue left contained 1.25 g (81 percent) of crude product.

^1H NMR (C_6D_6): δ 0.9-1.5 (m, Bu), 1.62 (m, $-\text{CH}_2\text{CH}_2$), 3.11 (m, H_γ), 6.26 (dd, $J=14.2, 1.5$), 6.61 (dd, $J=14.2, 4.3$)

20 ^{13}C NMR (C_6D_6): δ 151.0 (C_β), 126.4 (C_α), 45.1 (C_γ), 33.7 (CH_2CH_2), 30.0, 27.8, 14.4, 11.4 (Bu)

HRMS (EI): calculated for $\text{C}_{24}\text{H}_{41}^{120}\text{Sn}_2$ (M-Bu): 569.1252, found 569.1237

b) 1,2-Bis(1-chloro-1-boracyclohexa-2,5-dien-4-yl)ethane

25 A solution of 1,2-bis(1,1-dibutylstannacyclohexa-2,5-dien-4-yl)ethane (1.25 g, 2.0 mmol) in pentane was added to a pentane solution of BCl_3 (1.0 g, 8.5 mmol) at -78°C . After stirring for two hours at room temperature, the solvent was removed and the product was extracted with pentane. The isolated product contained minor quantities of Bu_2SnCl_2 .

30 ^1H -NMR (C_6D_6): δ 6.51m (8H), δ 2.34t, (H_γ) δ 0.91 (m, CH_2CH_2)

C-NMR (C_6D_6): δ 161.4 (C_β), δ 133.9 (C_α), δ 45.8 (C_γ), δ 28.3 (CH_2CH_2),

B-NMR (C_6D_6) 51.7

c) 1,2-Bis(1-N,N-diisopropylamino-1-boracyclohexa-2,5-dien-4-yl)ethane

5 1,2-Bis(1-chloro-1-boracyclohexa-2,5-dien-4-yl)-ethane (1.5 g) was treated with excess diisopropylamine in pentane and left to stir for 2 hours. The solution was filtered and the filtrate was cooled at $-20^\circ C$. Upon standing for several hours, solid formed which was separated from the filtrate. The filtrate was concentrated and left to stand at $-20^\circ C$ for approximately 16 hours which caused the separation of more
10 solid. The filtrate was separated and the pentane was removed under reduced pressure leaving an oily product containing small amounts of Bu_2SnCl_2 in addition to the desired product.

^1H NMR (C_6D_6): δ 6.73 (d, $J=12.8$), 6.55 (d, $J=12.8$), 3.69 (m, NCH), 2.82 (m, H_γ), 1.76 (m, CH_2CH_2), 1.12 (d, CH_3)

15 ^{13}C NMR (C_6D_6): δ 151.2 (C_β), 131.3 (C_α), 47.5 (NCH) 43.7 (C_γ), 31.6 (CH_2CH_2), 25.1 (CH_3)

HRMS (EI): calculated for $C_{23}H_{39}B_2N_2$, 365.3299, found 365.3312

d) [1,2-Bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)ethane]zirconium
20 dichloride

A solution of 1,2-bis(1-N,N-diisopropylamino-1-boracyclohexa-2,5-dien-4-yl)ethane (1.0 g, 2.7 mmol) in ether was treated with 2 equivalents of LDA in ether at $-78^\circ C$ and left to stir for 2 hours at room temperature. The resulting suspension was transferred to an ether suspension of $ZrCl_4$ 0.63 g (2.7 mmol) at $-78^\circ C$. The reaction
25 was stirred at room temperature about 16 hours. Solvent removed and the residue was extracted with CH_2Cl_2 and treated with pentane and cooled at $-20^\circ C$ for 24 hours. The crystals formed were collected and washed with pentane. The yield was 0.2 g (14 percent) based on the estimated purity of the starting material. Melting point = $249^\circ C$.

^1H NMR (C_6D_6): δ 6.61 (d, $J=11.4$), 6.11 (d, $J=11.4$), 3.75 (m, CHN), 2.52 (s, CH_2CH_2), 1.31 (d, CH_3)

^{13}C NMR (C_6D_6): δ 138 (C_β), 37.7, (CH_2CH_2), 47.1 (CHN), 23.9 (CH_3)

^{11}B NMR (C_6D_6): δ 30.0

5 HRMS (EI): Calculated for $\text{C}_{23}\text{H}_{37}\text{B}_2\text{N}_2\text{Cl}_2\text{Zr}$: 523.1567, found 523.1581

Example 2 [(tert-butylamido)dimethyl(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)silane]zirconium dichloride

10 a) dimethylchloro(1-N,N-diisopropylamino-1-boracyclohexa-2,5-dien-4-yl)silane

A solution of BuLi (2.5 M in hexane, 3.6 ml, 6.98 mmol) was added dropwise with stirring to a solution of 1-(N,N-diisopropylamino)boracyclohexa-2,5-diene (prepared by reaction of 1,1-dibutyl-1-stannacyclohexadiene and BCl_3 followed by reaction with excess diisopropylamine at 20-25 °C) (1.22 g, 6.89 mmol) in THF (10 ml) at -78 °C. The mixture was allowed to warm to 20-25 °C and stirred for 2 hours. The mixture was slowly added to Me_2SiCl_2 (8.4 ml, 68.9 mmol) in a Shlenk vessel at -78 °C via cannula. After complete addition, the mixture was warmed to 20-25 °C and stirred for 2 hours. THF was removed under reduced pressure, pentane (5 ml) was added to assist THF removal. Pentane (20 ml) was added, the resulted white suspension was filtered through a sintered glass filter, and the solid was washed with pentane (10 ml). Pentane was removed under reduced pressure to afford product (1.81 g, 98 percent) as a yellowish oil:

25 ^1H NMR (300 MHz, C_6D_6) δ 0.22 (s, 6H, SiCH_3), 1.17 (d, 12H, $J=6.9$ Hz, NCHCH_3), 3.19 (tt, 1H, $J=4.1$, 1.0 Hz H(4)), 3.72 (m, 2H, NCH), 6.64 (dd, 2H, $J=12.5$, 1.0 Hz, H(2,6)), 6.95 (dd, 2H, $J=12.5$, 4.1 Hz, H(3,5))

^{13}C NMR (90 MHz, C_6D_6) δ -0.3 (SiCH_3), 23.7 (CH_3), 24.0 (CH_3), 44.8 (C(4)), 47.3 (NCH), 132.6 (br, C(2,6)), 144.7 (C(3,5))

^{11}B NMR (115.5 MHz, C_6D_6) δ 31.2

MS(EI) [m/e (intensity)]: 269 (10, M^+), 254 (100), 212 (18)

MS(EI) exact mass (m/z): calculated for $C_{13}H_{25}BSiNCl$, 269.1538; found 269.1535

b) (t-butylamino)dimethyl(1-N,N-diisopropylaminoboratabenzene-4-yl)silane

5 To a solution of dimethylchloro(1-N,N-diisopropylaminoboratabenzene-4-yl)silane (0.30 g, 1.11 mmol) in THF (10 ml) at $-78^{\circ}C$ was added *tert*-butylamine (0.46 ml, 4.44 mmol). The mixture was allowed to warm to $20-25^{\circ}C$ and stirred for approximately 16 hours. THF was removed under reduced pressure, pentane (15 ml) was added, the resulting suspension was filtered through a sintered glass filter, the
10 white solid was washed with pentane (5 ml). The filtrate was dried under reduced pressure to afford the product (0.34 g, 100 percent) as a yellowish oil.

^1H NMR (300 MHz, C_6D_6) δ 0.12 (s, 6H, $SiCH_3$), 1.08 (s, 9H, $C(CH_3)_3$), 1.22 (d, 12H, $J=6.9$ Hz, $NCHCH_3$), 3.14 (t, 1H, $J=4.1$ Hz, H(4)), 3.81 (m, 2H, NCH), 6.62 (d, 2H, $J=12.4$ Hz, H(2,6)), 7.07 (dd, 2H, $J=12.4$, 3.8 Hz, H(3,5))

15 ^{13}C NMR (75 MHz, C_6D_6) δ 0.4 ($SiCH_3$), 24.0 (CH_3), 24.3 (CH_3), 34.4 ($C(CH_3)_3$), 46.7, 47.3, 49.4 ($C(CH_3)_3$), 130.3 (br, C(2,6)), 148.0 (C(3,5))

^{11}B NMR (115.5 MHz, C_6D_6) δ 31.9

MS(Cl with NH_3) exact mass (m/z): calcd for $C_{17}H_{35}BSiN_2H$, 307.2741; found 307.2725

20

c) (tert-butylamido)dimethyl(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)silane]zirconium dichloride

To a solution of (t-butylamino)dimethyl(1-(N,N-diisopropylamino)boratabenzene-4-yl)silane (1.64 g, 5.36 mmol) in ether (20 ml) at $-78^{\circ}C$ was added dropwise *t*BuLi (1.7 M in pentane, 6.30 ml, 10.72 mmol). The
25 mixture was warmed to $20-25^{\circ}C$ and stirred for 3 hours, a dark red solution was formed. The solution was added dropwise *via* cannula at $-78^{\circ}C$ to a suspension of $ZrCl_4$ (1.28 g, 5.36 mmol) in ether (10 ml). The mixture was gradually warmed to $20-25^{\circ}C$ and stirred about 16 hours. Ether was removed under reduced pressure,
30 pentane (2x5 ml) was added to assist removal of ether. Residue was extracted with

pentane (4x7 ml), and filtered through a sintered glass filter. The filtrate was concentrated to about 15 ml and cooled to -78 °C to give the crude product as a yellow solid. Recrystallization from pentane at -78 °C afforded the product (0.66 g, 26 percent) as yellow crystals: m.p.=200-200.5 °C.

5 ^1H NMR (360 MHz, C_6D_6) δ 0.26 (s, 6H, SiCH_3), 1.21 (d, 6H, $J=6.8$ Hz, NCHCH_3), 1.25 (d, 6H, $J=6.8$ Hz, NCHCH_3), 1.35 (s, 9H, $\text{C}(\text{CH}_3)_3$), 3.69 (m, 2H, NCH), 6.73 (d, 2H, $J=11.2$ Hz, $\text{H}(2,6)$), 7.08 (d, 2H, $J=11.3$ Hz, $\text{H}(3,5)$)

^{13}C NMR (90 MHz, C_6D_6) δ 0.4 (SiCH_3), 22.8 (CH_3), 23.4 (CH_3), 33.3 ($\text{C}(\text{CH}_3)_3$), 47.2, 58.0, 95.7, 130.3 (br, $\text{C}(2,6)$), 144.4 ($\text{C}(3,5)$)

10 ^{11}B NMR (115.5 MHz, C_6D_6) δ 29.2

MS (CI with Methane) [m/e (intensity)]: 465(4.0, M^+ observed isotope pattern matches predicted), 451 (6.0), 450 (4.0)

MS (EI) exact mass (m/z): calculated for $\text{C}_{16}\text{H}_{30}\text{BCl}_2\text{N}_2\text{SiZr}$ ($[\text{M}-\text{CH}_3]^+$) 449.0695; found 449.0697

15 Elemental Analysis: calculated for $\text{C}_{17}\text{H}_{33}\text{BCl}_2\text{N}_2\text{SiZr}$: C, 43.68; H, 7.28; N, 6.00; found C, 44.00; H, 7.39; N, 5.64

Example 3 [2-(η^5 -cyclopentadienyl)-2-(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)propane]zirconium dichloride

20

a) 2-(Cyclopentadienyl)-2-(1-N,N-diisopropylaminoboratabenzene-4-yl)propane

25 A solution of 6,6-dimethylfulvene (0.6 g, 5.7 mmol) in 5 mL of THF was added to (1-N,N-diisopropylaminoboratabenzene-4-yl)lithium, which had been prepared from 1-N,N-diisopropylamino-1-boracyclohexa-2,5-diene (1.0 g, 5.6 mmol) and BuLi (7.3 mmol), at -78 °C. The reaction was allowed to warm to room temperature and stirred for 3 hours. To the resulting red solution was added 1 mL of water and the solvent was removed under reduced pressure. The residue was extracted with pentane and dried over MgSO_4 , then the solvent was removed leaving an oily residue 1.0 g (62 percent yield) of crude product. The H-NMR indicated a mixture of isomers.

HRMS (EI): calculated for $C_{19}H_{30}BN$: 283.2471, found 283.2468

b) [2-(η^5 -Cyclopentadienyl)-2-(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)propane]zirconium dichloride

5 A solution of the dilithium salt of 2-(cyclopentadienyl)-2-(1-N,N-diisopropylaminoboratabenzene-4-yl)propane (prepared from 0.8 g (2.8 mmol) of the ligand and 5.6 mmol of lithium diisopropylamide) in ether was added to 0.65 g (2.8 mmol) $ZrCl_4$ in ether at $-78^\circ C$. The reaction mixture was stirred at $20-25^\circ C$ for about 16 hours. The solvent was removed under reduced pressure and the residue
10 was washed with pentane. The remaining residue was extracted with toluene and treated with pentane. Upon standing about 16 hours in the freezer, microcrystalline product formed. The product was isolated and washed with pentane and dried. The yield is 0.3 g (24 percent). Mp, $234^\circ C$

^1H NMR (C_6D_6): δ 6.71 (d, $J=12.1$), 6.51 (d, $J=12.1$) 6.3 (m, Cp), 5.0 (m, Cp),
15 3.88 (m, CHN), 1.12 (2, CMe_2), 1.12 (d, $CHMe_2$)

^{13}C NMR (C_6D_6): δ 133.2 (C_β), 124.1 (Cp), 104.2 (Cp), 60.4 (CMe_2), 47.0 (NCH), 30.5 ($CHMe_2$), 23.5 (CH_3); Cd not observed

^{11}B NMR (C_6D_6): δ 27.3

HRMS (EI): Calculated for $C_{18}H_{25}BCl_2NZr$: 426.0504, found 426.0524

20

Example 4 [bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethylsilane]-zirconium dichloride

a) Bis(1-N,N-diisopropylaminoboratabenzene-4-yl)dimethylsilane

25 To a solution of (1-N,N-diisopropylaminoboracyclohexa-2,5-diene (1.54 g, 8.70 mmol) in THF (15 ml) at $-78^\circ C$ was added BuLi (2.5 M hexane, 3.83 ml, 9.57 mmol). The mixture was allowed to warm to $20-25^\circ C$ and stirred for 2 hours. The resulting red solution was then added to a solution of (1-N,N-diisopropylaminoboratabenzene-4-yl)chlorodimethylsilane (2.27 g, 8.70 mmol) in THF (10 ml) at $-78^\circ C$. The mixture
30 was stirred about 16 hours at $20-25^\circ C$. Solvent was then removed and the residue

was extracted with pentane (4x6 ml). Removal of pentane gave the desired product (4.63 g, 100 percent) as a yellow solid. A small portion of the product was recrystallized from pentane at -78 °C to give an analytically pure product. Melting point = 100-102 °C

5 ^1H NMR (300 MHz, CDCl_3) δ -0.13 (s, 6H, SiCH_3), 1.23 (d, 24H, $J=6.9$ Hz, NCHCH_3), 3.20 (t, 2H, $J=4.1$ Hz, H(4)), 3.79 (m, 2H, NCH), 6.42 (d, 4H, $J=11.9$ Hz, H(2,6)), 6.90 (dd, 2H, $J=11.5$, 6.2 Hz, H(3,5))

^{13}C NMR (75 MHz, CDCl_3) δ -6.6 (SiCH_3), 23.6 (CH_3), 24.0 (CH_3), 42.3, 46.9 130.3 (br, C(2,6)), 146.0 (C(3,5))

10 ^{11}B NMR (115.5 MHz, C_6D_6): δ 31.9

MS (EI) exact mass (m/z): calculated for $\text{C}_{24}\text{H}_{44}\text{B}_2\text{N}_2\text{Si}$: 410.3460; found 410,3457

Elemental analysis, calculated for $\text{C}_{24}\text{H}_{44}\text{B}_2\text{N}_2\text{Si}$: C, 70.31; H, 10.74; N, 6.84, found C. 70.27; H, 10.92; N, 7.02

15

b) [Bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethylsilane]zirconium dichloride

To a solution of bis(1-N,N-diisopropylaminoboracyclohexa-2,5-dienyl)dimethylsilane (2.47 g, 5.85 mmol) in ether (17 ml) at -78 °C was added
20 dropwise $t\text{BuLi}$ (1.7 M in pentane, 6.89 ml, 11.71 mmol). The mixture was warmed to 20-25 °C and stirred for 2 hours, during which time a dark red solution was formed. The solution was added dropwise via cannula at -78 °C to a suspension of ZrCl_4 (1.37 g, 5.90 mmol) in ether (10 ml). The mixture was gradually warmed to 20-25 °C and stirred about 16 hours. Ether was removed under reduced pressure and pentane
25 (2x5 ml) was added to assist removal of ether. The residue was extracted with dichloromethane (3x8 ml) and filtered through a sintered glass filter. The filtrate was concentrated and recrystallized at -78 °C to give the desired product as a green solid. Melting point = 152-153 °C

^1H NMR (300 MHz, CDCl_3) δ 0.73 (s, 6H, SiCH_3), 1.24 (d, 12H, $J=6.8$ Hz, NCHCH_3), 1.25 (d, 12H, $J=6.8$ Hz, NCHCH_3), 3.75 (m, 4H, NCH), 6.35 (d, 4H, $J=11.2$ Hz, H(2,6)), 6.98 (d, 2H, $J=11.2$ Hz, H(3,5))

^{13}C NMR (90 MHz, CDCl_3 - C_6D_6) δ -5.3 (SiCH_3), 23.5 (CH_3), 23.8 (CH_3),
 5 46.7, 91.4 (C(4)), 134.2 (br, C(2,6)), 139.3 (C(3,5))

^{11}B NMR (115.5 MHz, C_6D_6) δ 29.9

MS (EI) exact mass (m/z), calculated for $\text{C}_{23}\text{H}_{39}\text{B}_2\text{Cl}_2\text{N}_2\text{SiZr}$ ($[\text{M}-\text{CH}_3]^+$):
 553.1493, found 553,1497

Elemental analysis: calculated for $\text{C}_{24}\text{H}_{44}\text{B}_2\text{Cl}_2\text{N}_2\text{SiZrLiCl}$: C, 47.18; H,
 10 6.88; N, 4.59, found C. 47.09; H, 6.92; N, 4.54, ($[\text{M}-\text{CH}_3]^+$) 449.0695, found
 449.0697

Propylene polymerization

A two liter reactor is charged with mixed alkane solvent (Isopar- E^{TM}).
 15 Hydrogen is added by differential pressure expansion from a 75 ml addition tank from
 300 psig (2.1 MPa) to near 275 psig (1.9 MPa). The reactor is then charged with 150
 g of propylene monomer. The reactor and contents are then heated to and
 maintained at 70°C , the polymerization temperature. In an inert atmosphere glove
 box the appropriate quantities of metal complex and methyl alumoxane (MAO)
 20 cocatalyst solutions (0.00500 M and 1.5 M, respectively, in toluene) are combined
 and this catalyst solution is transferred to a catalyst addition tank. The polymerization
 is initiated by injecting this catalyst solution into the contents of the reactor. The
 polymerization conditions are maintained for the run time. Additional catalyst solution
 prepared and transferred in the same way may be added to the reactor throughout
 25 the course of the reaction. The polymer solution is removed from the reactor and
 combined with a hindered phenol antioxidant and isopropyl alcohol. Volatile
 components are removed from the polymer in a vacuum oven set at 140°C for about
 20 hours. The dried polymers are analyzed by ^{13}C NMR spectroscopy and gel
 permeation chromatography (GPC). Results are contained in Table 1.

Table 1

complex* (μ mol)	MAO mmol	Isopar (g)	H ₂ (Δ psi)	Run Time (min.)	yield (g)	Peak Molecular Weight	mmmm (%)	(mm)/(mr, rm)/(rr)
Ex. 1 (18.0)	18.0	652	26	70	1.6	158,900	22	34/35/31
Ex. 3 (30.0)	30.0	652	26	60	2.7	109,000	small	25/41/34
Ex. 4 (15.0)	15.0	655	25	44	3.0	800	small	23/43/37

* Ex. 1= [1,2-bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)ethane]zirconium dichloride

Ex. 3= [2-(η^5 -cyclopentadienyl)-2-(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)propane]zirconium dichloride

5 Ex. 4= [bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethylsilane]zirconium dichloride

Ethylene/Octene copolymerization

A two liter reactor is charged with mixed alkane solvent (Isopar-E) and 1-octene. Hydrogen is added by differential pressure expansion from a 75 ml addition tank from 300 psig (2.1 MPa) to near 275 psig (1.9 MPa). The reactor and contents are then heated to and maintained at 140°C, the polymerization temperature and saturated with ethylene at 500 psig (3.4 MPa). In an inert atmosphere glove box the appropriate quantities of metal complex and methyl alumoxane (MAO) cocatalyst solutions (0.00500 M and 1.5 M, respectively, in toluene) are combined and this catalyst solution transferred to a catalyst addition tank. The polymerization is initiated by injecting this catalyst solution into the contents of the reactor. The polymerization conditions are maintained for the run time with ethylene provided on demand at 500 psig (3.4 MPa). Additional catalyst solution prepared and transferred in the same way may be added to the reactor throughout the course of the reaction. The polymer solution is removed from the reactor and combined with a hindered phenol antioxidant and isopropyl alcohol. Volatile components are removed from the polymer in a vacuum oven set at 140°C for about 20 hours. The dried polymers were analyzed by ¹³C NMR spectroscopy and GPC. Results are contained in Table 2.

Table 2

complex* (μ mol)	MAO mmol	Isopar (g)	1-octene (g)	H ₂ (Δ psi)	Run Time (min.)	yield (g)	Peak Molecular Weight	1-octene (mole %)
Ex. 1 (12.0)	12.0	747	120	26	48	26.1	15,700	1.0
Ex. 2 (12.0)	12.0	743	120	25	45	20.8	3,700	0.8
Ex. 3 (3.0)	3.0	743	123	26	30	26.2	83,900	0.7
Ex. 4 (12.0)	12.0	740	123	26	46	9.5	70,300	0.7

* Ex. 1= [1,2-bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)ethane]zirconium dichloride

Ex. 2= [(tert-butylamido)dimethyl(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)silane]zirconium dichloride

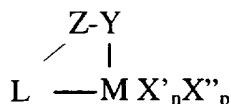
Ex. 3= [2-(η^5 -cyclopentadienyl)-2-(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)propane]zirconium dichloride

Ex. 4= [bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethylsilane]zirconium dichloride

5

WHAT IS CLAIMED IS:

1. A metal complex corresponding to the formula:



or a dimer, solvated adduct, chelated derivative or mixture thereof,
wherein:

Y is a divalent derivative of a boratabenzene group or a hydrocarbyl-,
dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up
to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

L is Y or a hydrocarbadiyl group that is bound to M by means of its delocalized
 π -electrons, or L is a monovalent or divalent amido group, said L group containing up
to 50 nonhydrogen atoms;

M is a metal of Group 3, 4 or the Lanthanide series of the Periodic Table of
the Elements;

Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms
having the formula, $-(\text{ER}^2)_m-$, wherein E independently each occurrence is carbon,
silicon or germanium, R^2 independently each occurrence is selected from the group
consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other
than hydrogen, and m is an integer from 1 to 3;

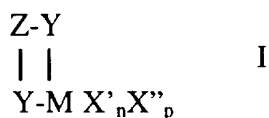
X' is a neutral ligand having up to 20 non-hydrogen atoms;

X'' independently each occurrence is a monovalent, anionic moiety selected
from hydride, halo, hydrocarbyl, silyl, germyl, hydrocarbyloxy, amide, siloxy,
halohydrocarbyl, halosilyl, silylhydrocarbyl, and dihydrocarbylaminohydrocarbyl
having up to 20 non-hydrogen atoms, or two X'' groups together form a divalent
hydrocarbadiyl group;

n is a number from 0 to 3; and

p is an integer from 0 to 2.

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



wherein:

- M is titanium, zirconium or hafnium, preferably zirconium, in the +2, +3, or +4 formal oxidation state;

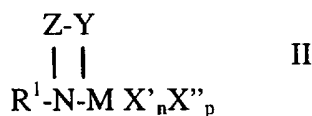
- Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms having the formula, $-(\text{ER}^2)_m-$, wherein E independently each occurrence is carbon, silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

Y in each occurrence, independently is a divalent derivative of a boratabenzene group or a hydrocarbyl-, dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

- X' is a conjugated diene having from 4 to 30 non-hydrogen atoms, which forms a π -complex with M when M is in the +2 formal oxidation state, whereupon n is 1 and p is 0; and

- X'' each occurrence is an anionic ligand group that is covalently bonded to M when M is in the +3 or +4 formal oxidation state, whereupon n is 0 and p is 1 or 2, and optionally two X'' groups together form a divalent anionic ligand group.

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



wherein:

- M is titanium, zirconium or hafnium, preferably titanium, in the +2, +3 or +4 formal oxidation state;

Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms having the formula, $-(\text{ER}^2)_m-$, wherein E independently each occurrence is carbon,

silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

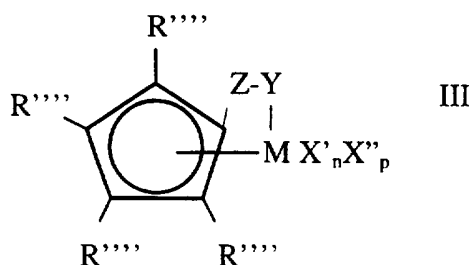
Y is a divalent derivative of a boratabenzene group or a hydrocarbyl-,
 5 dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

R^1 is C_{1-20} hydrocarbyl,

X' is a conjugated diene having from 4 to 30 non-hydrogen atoms, which
 forms a π -complex with M when M is in the +2 formal oxidation state, whereupon n is
 10 1 and p is 0; and

X'' each occurrence is an anionic ligand group that is covalently bonded to M
 when M is in the +3 or +4 formal oxidation state, whereupon n is 0 and p is 1 or 2,
 and optionally two X'' groups together form a divalent anionic ligand group.

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



wherein:

M is titanium, zirconium or hafnium, preferably zirconium, in the +2, or +4 formal oxidation state;

20 Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms having the formula, $-(ER^2)_m-$, wherein E independently each occurrence is carbon, silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

Y is a divalent derivative of a boratabenzene group or a hydrocarbyl-, dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

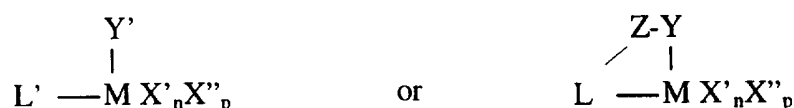
X' is a conjugated diene having from 4 to 30 non-hydrogen atoms, which
 5 forms a π -complex with M when M is in the +2 formal oxidation state, whereupon n is 1 and p is 0;

X'' each occurrence is an anionic ligand group that is covalently bonded to M when M is in the +4 formal oxidation state, whereupon n is 0 and p is 2, and optionally two X'' groups together form a divalent anionic ligand group; and

10 R''' is hydrogen, hydrocarbyl, silyl, halo-, cyano, dialkylamino, halohydrocarbyl, halocarbyl, dialkylamino substituted-hydrocarbyl, or hydrocarbyl-substituted metalloid wherein the metalloid is selected from Group 14 of the Periodic Table of the Elements, said R''', when a multi-atomic ligand group, containing up to 20 nonhydrogen atoms.

15

5. A catalyst composition comprising an activating cocatalyst and one or more Group 3, 4 or Lanthanide metal complexes corresponding to the formula:



20 or a dimer, solvated adduct, chelated derivative or mixture thereof, wherein:

Y' is a boratabenzene group or a hydrocarbyl-, dihydrocarbylamino-, silyl- or germyl-substituted boratabenzene group containing up to 50 nonhydrogen atoms that is bonded via its delocalized π -electrons to M;

25 L' is Y' or a hydrocarbyl group that is bound to M by means of its delocalized π -electrons, or L' is an amido group, said L' group containing up to 50 nonhydrogen atoms;

L and Y are as previously defined in claim 1;

30 M is a metal of Group 3, 4 or the Lanthanide series of the Periodic Table of the Elements;

Z is a covalently bound, divalent substituent of up to 50 non-hydrogen atoms having the formula, $-(ER^2)_m-$, wherein E independently each occurrence is carbon, silicon or germanium, R^2 independently each occurrence is selected from the group consisting of hydrocarbyl, hydrocarbyloxy, silyl, and germyl of up to 20 atoms other than hydrogen, and m is an integer from 1 to 3;

X' is a neutral ligand having up to 20 non-hydrogen atoms;

X" independently each occurrence is a monovalent, anionic moiety selected from hydride, halo, hydrocarbyl, silyl, germyl, hydrocarbyloxy, amide, siloxy, halohydrocarbyl, halosilyl, silylhydrocarbyl, and dihydrocarbylaminohydrocarbyl having up to 20 non-hydrogen atoms, or two X" groups together form a divalent hydrocarbadiyl group;

n is a number from 0 to 3; and

p is an integer from 0 to 2,

provided that when two Y groups or two Y' groups are present in the complex, then the activating cocatalyst does not consist solely of an alumoxane.

6. A metal complex according to claim 1 which is [1,2-bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)ethane]zirconium dichloride, [(tert-butylamido)dimethyl(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)silane]zirconium dichloride, [2-(η^5 -cyclopentadienyl)-2-(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)propane]zirconium dichloride, or [bis(η^6 -1-N,N-diisopropylaminoboratabenzene-4-yl)dimethylsilane]zirconium dichloride.

7. A catalyst composition comprising an activating cocatalyst and a metal complex according to any one of claims 1-6.

8. A supported catalyst composition comprising a catalyst composition according to claim 7 and a substrate.

9. A process for polymerizing an α -olefin, comprising contacting an α -olefin or a mixture of α -olefins with a catalyst composition according to claim 7.

10. A process for polymerizing an α -olefin, comprising contacting an α -olefin or a mixture of α -olefins with a catalyst system according to claim 8.

INTERNATIONAL SEARCH REPORT

Int. onal Application No
PCT/US 97/04884

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F17/00 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 6 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 118, 6 March 1996, pages 2291-2292, XP002032885 ASHE, A.J. ET AL.: "aminoboratabenzene derivatives of zirconium: a new class of olefin polymerization catalysts" see the whole document ---	1-10
P,X	WO 96 23004 A (OCCIDENTAL CHEMICAL CORPORATION) 1 August 1996 see the whole document ---	1-10
P,X	WO 97 01566 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ BV) 16 January 1997 see the whole document ---	1-10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 June 1997

Date of mailing of the international search report

24- 06- 1997

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INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/US 97/04884

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 97 05143 A (ASAHI KASEI KOGYO KABUSHIKI KAISHA) 13 February 1997 see the whole document -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 97/04884

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9623004 A	01-08-96	US 5554775 A AU 4524396 A	10-09-96 14-08-96
WO 9701566 A	16-01-97	AU 6306196 A	30-01-97
WO 9705143 A	13-02-97	NONE	