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(54) Title: AZABOROLYL GROUP 4 METAL COMPLEXES, CATALYSTS AND OLEFIN POLYMERIZATION PROCESS

(57) Abstract: Metal complexes, catalysts derived therefrom, and polymerization processes using the same, characterized by the presence of one or more nitrogen and boron containing, anionic, 5-membered cyclic ligand groups, especially 1,2-azaborolyl groups, are disclosed.

**AZABOROLYL GROUP 4 METAL COMPLEXES, CATALYSTS AND OLEFIN
POLYMERIZATION PROCESS**

CROSS REFERENCE STATEMENT

This application claims the benefit of U.S. Provisional Application No. 60/372,462, filed April 12, 2002.

FIELD OF THE INVENTION

This invention relates to a class of metal complexes, the ligands used to prepare these metal complexes, polymerization catalysts derived therefrom, and the resulting polymerization processes using the same. More particularly, such metal complexes are characterized by the presence of one or more nitrogen and boron containing, anionic, 5-membered, cyclic ligand groups.

BACKGROUND

It is previously known in the art to use metallocene catalysts to polymerize olefins to form high molecular weight polyolefin products. Examples include Group 4 metal compounds containing one or more cyclopentadienyl ligands or derivatives thereof, as disclosed in US-A-4,530,914, US-A-4,871,705, US-A-4,937,299, US-A-5,017,714, US-A-5,055,438, US-A-5,096,867, US-A-5,120,867, US-A-5,124,418, US-A-5,198,401, US-A-5,210,352, US-A-5,229,478, US-A-5,264,405, US-A-5,278,264, US-A-5,278,119, US-A-5,304,614, US-A-5,324,800, US-A-5,347,025, US-A-5,350,723, US-A-5,384,299, US-A-5,391,790, US-A-5,391,789, US-A-5,399,636, US-A-5,408,017, US-A-5,470,993, US-A-5,491,207, US-A-5,455,366, US-A-5,534,473, US-A-5,539,124, US-A-5,554,775, US-A-5,621,126, US-A-5,684,098, US-A-5,693,730, US-A-5,698,634, 5,703,187, 5,710,297, US-A-5,712,354, US-A-5,714,427, US-A-5,714,555, 5,728,641, 5,728,839, 5,753, 577, 5,767,209, 5,770,753, 5,770,664, 5,972,020, 6,034,002, 6,040,041, 6,150,297, 6,376,406, and elsewhere.

Despite the advance in the art, particular higher use temperature, obtained by such prior art metal complexes as were disclosed in the foregoing references, there remains a desire for improved metal complexes capable of even further increase in use temperature that are still capable of forming catalyst compositions useful in producing polymers having high molecular weights and, for polymerization of ethylene/ higher α -olefin copolymers, high incorporation of comonomer. The subject compositions of this invention show unexpected improvement in these desirable features.

SUMMARY OF THE INVENTION

According to the present invention there is provided a compound corresponding to the formula, $CpM(Z)_z(X)_x(L)_t(X')_{x'} \quad (I)$,

where Cp is a nitrogen and boron containing, anionic, 5-membered cyclic ligand group or substituted derivative thereof, bound to at least M ;

M is a metal selected from Groups 3-10 or the Lanthanide series of the Periodic Table of the Elements;

Z is either:

a) a cyclic ligand group containing delocalized π -electrons (including a second or third anionic ligand, Cp) said Z being bonded to M by means of delocalized π -electrons and optionally also covalently bonded to Cp through a divalent bridging group, Z', or

b) a divalent moiety of the formula $-Z'Y-$, with Z' bonded to Cp and Y covalently or coordinate covalently bonded to M, wherein,

Z' is SiR^6_2 , CR^6_2 , $\text{SiR}^6_2\text{SiR}^6_2$, $\text{CR}^6_2\text{CR}^6_2$, $\text{CR}^6=\text{CR}^6$, $\text{CR}^6_2\text{SiR}^6_2$, BR^6 , $\text{BR}^6\text{L}''$, or GeR^6_2 ;

Y is $-\text{O}-$, $-\text{S}-$, $-\text{NR}^5-$, $-\text{PR}^5-$; $-\text{NR}^5_2$, or $-\text{PR}^5_2$;

R^5 , independently each occurrence, is hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl, said R^5 having up to 20 atoms other than hydrogen, and optionally two R^5 groups or R^5 together with Y form a ring system;

R^6 , independently each occurrence, is hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, $-\text{NR}^5_2$, and combinations thereof, said R^6 having up to 20 non-hydrogen atoms, and optionally, two R^6 groups form a ring system;

L'' is a monodentate or polydentate Lewis base optionally bonded to R^6 ;

X is hydrogen or a monovalent anionic ligand group having up to 60 atoms not counting hydrogen;

L independently each occurrence is a neutral ligating compound having up to 20 atoms, other than hydrogen, and optionally L and X are bonded together;

X' is a divalent anionic ligand group having up to 60 atoms other than hydrogen;

z is 0, 1 or 2;

x is 0, 1, 2, or 3;

t is a number from 0 to 2, and

x' is 0 or 1.

The above compounds may exist as isolated crystals, as a mixture with other compounds, in the form of a solvated adduct, dissolved in a solvent, especially an organic liquid solvent, in the form of a dimer, or as a chelated derivative, especially wherein the chelating agent is an organic material such as ethylenediaminetetraacetic acid (EDTA).

Also, according to the present invention, there is provided a catalyst for olefin polymerization comprising:

- A.
 - i) a metal compound of formula (I), and
 - ii) an activating cocatalyst,

the molar ratio of i) to ii) being from 1:10,000 to 100:1, or

B. the reaction product formed by converting a metal compound of formula (II) to an active catalyst by use of an activating technique.

Further according to the present invention there is provided a process for the polymerization of olefins comprising contacting one or more C₂₋₂₀ olefins, including cyclic olefins, under polymerization conditions with a catalyst comprising:

A. i) a metal compound of formula (I), and
ii) an activating cocatalyst,

the molar ratio of i) to ii) being from 1:10,000 to 100:1, or

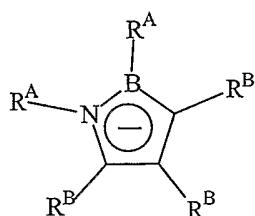
B. the reaction product formed by converting a metal compound of formula (I) to an active catalyst by use of an activating technique.

The catalysts of this invention may also be supported on a solid material and used in olefin polymerization processes in a slurry or in the gas phase. The catalyst may be prepolymerized with one or more olefin monomers *in situ* in a polymerization reactor or in a separate process with intermediate recovery of the prepolymerized catalyst prior to the primary polymerization process.

DETAILED DESCRIPTION

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., 2001. Also, any reference to a Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. As used herein the term "comprising" is not intended to exclude any additional component, additive or step. For purposes of United States patent practice, the contents of any patent, patent application or publication referenced herein are hereby incorporated by reference in their entirety, especially with respect to the disclosure of synthetic techniques and general knowledge in the art.

In a preferred embodiment, Cp is an 1,2-azaborolyl anionic ligand, corresponding to the formula:

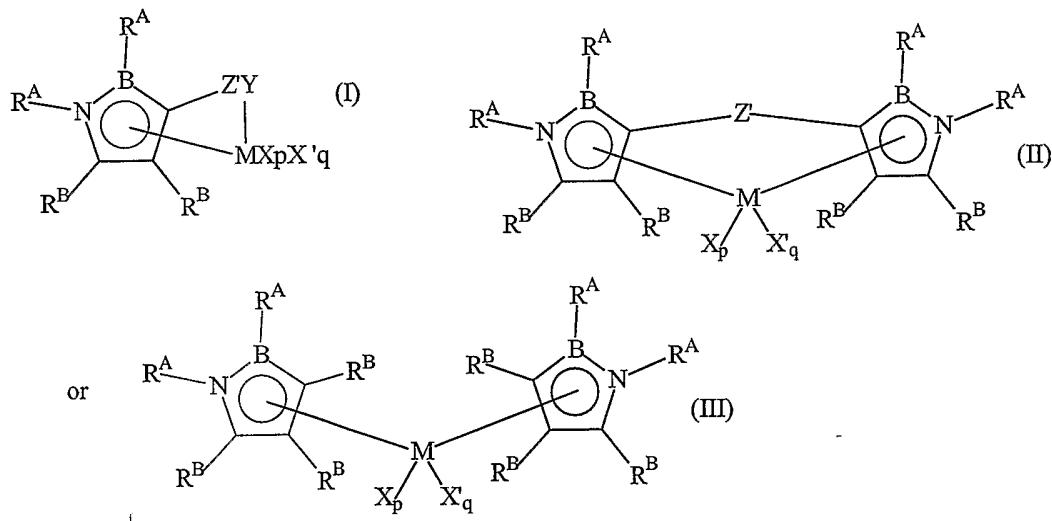


wherein,

R^A, independently each occurrence, is a group of from 1 to 40 atoms, not counting hydrogen, selected from the group consisting of hydrocarbyl, trihydrocarbysilyl, trihydrocarbysilylhydrocarbyl, dihydrocarbylamino, and hydrocarbyleneamino, and optionally two R^A groups may be joined together thereby forming a fused multi-ring ligand group;

R^B , independently each occurrence, is selected from the group consisting of hydrogen, Z' and R^A , where Z' is as previously defined.

Preferred metal complexes according to the present invention correspond to the formula:



where M is a Group 4 metal that is in the +2, +3 or +4 formal oxidation state;

R^A independently each occurrence is a hydrocarbyl, dihydrocarbylamino, or hydrocarbyleneamino group of from 1 to 40 atoms, not counting hydrogen, or two or more R^A groups may be covalently linked together;

R^B independently each occurrence is hydrogen or R^A ;

Z' is SiR^6_2 , CR^6_2 , $SiR^6_2SiR^6_2$, $CR^6_2CR^6_2$, $CR^6=CR^6$, or BR^6 ;

Y is $-NR^5-$, $-PR^5-$, $-NR^5_2$, or $-PR^5_2$;

R^5 , independently each occurrence, is C_{1-20} hydrocarbyl;

R^6 , independently each occurrence, is hydrogen, or C_{1-20} hydrocarbyl;

X is an anionic or dianionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' independently each occurrence is a neutral ligand having up to 40 atoms;

p is zero, 1 or 2, and is two less than the formal oxidation state of M when X is an anionic ligand, and when X is a dianionic ligand group, p is 1; and

q is zero, 1 or 2.

The above complexes may exist as isolated crystals optionally in pure, enantiomeric form or as a mixture, including a racemic mixture, with other complexes, in the form of a solvated adduct, optionally in a solvent, especially an organic liquid, in the form of a dimer or as a polymeric or crosslinked polymeric product, wherein one or more R^A groups are polymerized with one another or copolymerized with an ethylenically unsaturated comonomer.

Preferred compounds according to the invention are those compounds of formulas (I)-(III), wherein M is a Group 4, metal, preferably titanium for compounds of formula (I) and zirconium for compounds of formulas (II) or (III).

Preferred X groups are halo, C₁₋₁₀ hydrocarbyl or trialkylsilylalkyl groups of up to 20 carbons, or two such X groups together form a divalent ligand group. Most preferred X groups are chloro, methyl, benzyl, trimethylsilylmethyl, or two X groups together are (dimethylsilylene)bis-(methylene).

Preferred R^A groups are hydrocarbyl groups, more preferably alkyl, aryl or aralkyl groups of up to 10 carbons, or two adjacent R^A groups are joined together forming a fused ring.

Preferably R^B is C_{1,10} hydrocarbyl;

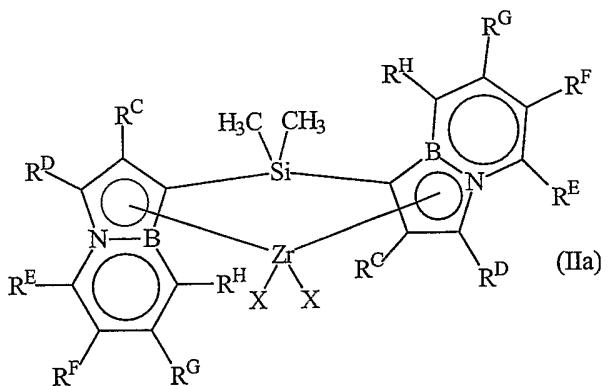
Preferably in all embodiments of the invention, Y is -NR^E— where R^E is C₁₋₆ alkyl or cycloalkyl, preferably isopropyl, cyclohexyl, or t-butyl.

Preferred Z groups are SiR⁶₂ where R⁶ is methyl, phenyl, or C₁₋₁₀ alkylphenyl.

Preferred X' groups in all of the foregoing embodiments of the invention are carbon monoxide; phosphines, especially trimethylphosphine, triethylphosphine, triphenylphosphine and bis(1,2-dimethylphosphino)ethane; P(OR^K)₃, wherein R^K, independently each occurrence, is hydrocarbyl, silyl or silylhydrocarbyl; ethers, especially tetrahydrofuran; amines, especially pyridine, bipyridine, tetramethylethylenediamine (TMEDA), or triethylamine; olefins; and conjugated dienes having from 4 to 40 carbon atoms. Complexes including the latter X' groups, especially terminally hydrocarbyl substituted-1,3-butadienes, include those wherein the metal is in the +2 formal oxidation state.

In the foregoing compounds when p is 2, q is zero, M is in the +3 or +4 formal oxidation state, and X independently each occurrence preferably is chloride, methyl, benzyl, trimethylsilylmethyl, allyl, pyrrolyl or two X groups together are 1,4-butane-diyl, 2-butene-1,4-diyl, 2,3-dimethyl-2-butene-1,4-diyl, 2-methyl-2-butene-1,4-diyl, xylyldiyl, or (dimethylsilylene)bis(methylene). Additionally, when p is 1, q is zero, M is in the +3 formal oxidation state, and X is preferably, 2-(N,N-dimethyl)aminobenzyl, 2-(N,N-dimethylaminomethyl)phenyl, allyl, or methallyl. Finally, when p is 0, q is 1, M is in the +2 formal oxidation state, and X' is 1,4-diphenyl-1,3-butadiene, 1,3-pentadiene or 2,4-hexadiene.

Highly desired metal complexes of formula (II) are ansa rac 4a,7a-azaborindenyl zirconium complexes corresponding to the formula:



wherein:

R^C , R^D , R^E , R^F , R^G , and R^H independently each occurrence are hydrogen, C₁₋₂₀ hydrocarbyl or N,N-di(C₁₋₄ hydrocarbyl)amino; and

X , independently each occurrence is chloride, methyl, benzyl, or trimethylsilylmethyl, or 2 X groups together are 1,3-pentadiene or 1,4-diphenyl-1,3-butadiene.

Preferably, R^C is C₁₋₄ alkyl, especially methyl, R^D , R^F , R^G and R^H are hydrogen, and R^E is phenyl or naphthyl.

The complexes can be prepared by use of well known synthetic techniques. The reactions are conducted in a suitable noninterfering solvent at a temperature from -100 to 300°C, preferably from -78 to 100°C, most preferably from 0 to 50°C. Suitable reaction media for the formation of the complexes include aliphatic and aromatic hydrocarbons, ethers, and cyclic ethers, particularly 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; aromatic and hydrocarbyl-substituted aromatic compounds such as benzene, toluene, and xylene, C₁₋₄ dialkyl ethers, C₁₋₄ dialkyl ether derivatives of (poly)alkylene glycols, and tetrahydrofuran. Mixtures of the foregoing are also suitable.

Optionally a reducing agent can be employed to produce the lower oxidation state complexes. By the term "reducing agent" herein is meant a metal or compound which, under reducing conditions causes the metal M, to be reduced from a higher to a lower oxidation state. Examples of suitable metal reducing agents are alkali metals, alkaline earth metals, aluminum and zinc, alloys of alkali metals or alkaline earth metals such as sodium/mercury amalgam and sodium/potassium alloy. Examples of suitable reducing agent compounds are sodium naphthalenide, potassium graphite, lithium alkyls, lithium or potassium alkadienyls; and Grignard reagents. Most preferred reducing agents are the alkali metals or alkaline earth metals, especially lithium and magnesium metal. Suitable techniques for preparing complexes of the present invention are well known to the skilled artisan and may be readily derived from techniques taught in the art.

The complexes are rendered catalytically active by combination with an activating cocatalyst or use of an activating technique, such as those that are previously known in the art for use with Group 4 metal olefin polymerization complexes. Suitable activating cocatalysts for use herein include polymeric or oligomeric alumoxanes, especially methylalumoxane, triisobutyl aluminum modified methylalumoxane, or isobutylalumoxane; neutral Lewis acids, such as C₁₋₃₀ hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluoro-phenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium- salts of compatible, noncoordinating anions, or ferrocenium salts of compatible, noncoordinating anions; bulk electrolysis (explained in more detail hereinafter); and combinations of the foregoing activating cocatalysts and techniques. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal complexes in the following references: EP-A-277,003, US-A-5,153,157, US-A-5,064,802, US-A-5,321,106, US-A-5,721,185, US-A-5,350,723, US-A-5,425,872, US-A-5,625,087, US-A-5,883,204, US-A-5,919,983, US-A-5,783,512, US-A-6,395,671, and WO 99/15534.

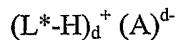
Combinations of neutral Lewis acids, especially the combination of a trialkylaluminum compound having from 1 to 4 carbons in each alkyl group and a halogenated tri(hydrocarbyl)boron compound having from 1 to 20 carbons in each hydrocarbyl group, especially tris(pentafluorophenyl)borane, further combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane are especially desirable activating cocatalysts. Preferred molar ratios of Group 4 metal complex:tris(pentafluoro-phenylborane):alumoxane are from 1:1:1 to 1:10:30, more preferably from 1:1:1.5 to 1:5:10.

Suitable ion forming compounds useful as cocatalysts in one embodiment of the present invention comprise a cation which is a Bronsted acid capable of donating a proton, and a compatible, noncoordinating anion, A⁻. As used herein, the term "noncoordinating" means an anion or substance which either does not coordinate to the Group 4 metal containing precursor complex and the catalytic derivative derived therefrom, or which is only weakly coordinated to such complexes thereby remaining sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating anion specifically refers to an anion which when functioning as a charge balancing anion in a cationic metal complex does not transfer an anionic substituent or fragment thereof to said cation thereby forming neutral complexes. "Compatible anions" are anions which are not degraded

to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gallium, niobium or tantalum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

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



wherein:

L^* is a neutral Lewis base;

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

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

d is an integer from 1 to 3.

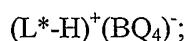
More preferably A^{d-} corresponds to the formula: $[M'Q_4]^-$;

wherein:

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

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloide, halo-substituted hydrocarbyl, halo-substituted hydrocarbyloxy, and halo- substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloide Q groups are disclosed in U. S. Patent 5,296,433.

In a more preferred embodiment, d is one, that is, the counter ion has a single negative charge and is A^- . Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:



wherein:

L^* is as previously defined;

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

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorohydrocarbyl-, fluorohydrocarbyloxy-, hydroxyfluorohydrocarbyl-, dihydrocarbylaluminumoxyfluorohydrocarbyl-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl. Most preferably, Q is each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Preferred Lewis base salts are ammonium salts, more preferably trialkylammonium salts containing one or more C₁₂₋₄₀ alkyl groups.

Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this invention are

tri-substituted ammonium salts such as:

trimethylammonium tetrakis(pentafluorophenyl) borate,
triethylammonium tetrakis(pentafluorophenyl) borate,
tripropylammonium tetrakis(pentafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate,
N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(4-(t-butyldimethylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(4-(trisopropylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate,
dimethyltetradecylammonium tetrakis(pentafluorophenyl) borate,
dimethylhexadecylammonium tetrakis(pentafluorophenyl) borate,
dimethyloctadecylammonium tetrakis(pentafluorophenyl) borate,
methylditetradecylammonium tetrakis(pentafluorophenyl) borate,
methylditetradecylammonium (hydroxyphenyl)tris(pentafluorophenyl) borate,
methylditetradecylammonium (diethylaluminioxyphenyl)tris(pentafluorophenyl) borate,
methyldihexadecylammonium tetrakis(pentafluorophenyl) borate,
methyldihexadecylammonium (hydroxyphenyl)tris(pentafluorophenyl) borate,
methyldihexadecylammonium (diethylaluminioxyphenyl)tris(pentafluorophenyl) borate,
methyldioctadecylammonium tetrakis(pentafluorophenyl) borate,
methyldioctadecylammonium (hydroxyphenyl)tris(pentafluorophenyl) borate,
methyldioctadecylammonium (diethylaluminioxyphenyl)tris(pentafluorophenyl) borate,
mixtures of the foregoing,

dialkyl ammonium salts such as:

di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate,
methyloctadecylammonium tetrakis(pentafluorophenyl) borate,
methyloctadodecylammonium tetrakis(pentafluorophenyl) borate, and
dioctadecylammonium tetrakis(pentafluorophenyl) borate;

tri-substituted phosphonium salts such as:

triphenylphosphonium tetrakis(pentafluorophenyl) borate,
methyldioctadecylphosphonium tetrakis(pentafluorophenyl) borate, and
tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate;

di-substituted oxonium salts such as:

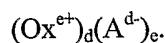
diphenyloxonium tetrakis(pentafluorophenyl) borate,
di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and
di(octadecyl)oxonium tetrakis(pentafluorophenyl) borate;

di-substituted sulfonium salts such as:

di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and
methylcotadecylsulfonium tetrakis(pentafluorophenyl) borate.

Preferred (L*-H)⁺ cations are methyldioctadecylammonium and dimethyloctadecylammonium. The use of the above Bronsted acid salts as activating cocatalysts for addition polymerization catalysts is known in the art, having been disclosed in USP 5,064,802, 5,919,983, 5,783,512 and elsewhere.

Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:



wherein:

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

e is an integer from 1 to 3; and

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

Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^{+} or Pb^{+2} . Preferred embodiments of A^{d-} are those anions previously defined with respect to the Bronsted acid containing activating cocatalysts, especially tetrakis(pentafluorophenyl)borate. The use of the above salts as activating cocatalysts for addition polymerization catalysts is known in the art, having been disclosed in USP 5,321,106.

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

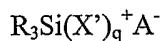


wherein:

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

A^- is as previously defined. A preferred carbenium ion is the trityl cation, that is triphenylmethyl cation. The use of the above carbenium salts as activating cocatalysts for addition polymerization catalysts is known in the art, having been disclosed in USP 5,350,723.

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



wherein:

R is C_{1-10} hydrocarbyl, and X' , q and A^- are as previously defined.

Preferred silylum salt activating cocatalysts are trimethylsilylum tetrakis(pentafluorophenyl)borate, triethylsilylum tetrakis(pentafluorophenyl)borate and ether substituted adducts thereof. The use of the above silylum salts as activating cocatalysts for addition polymerization catalysts is known in the art, having been disclosed in USP 5,625,087.

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

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

wherein:

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

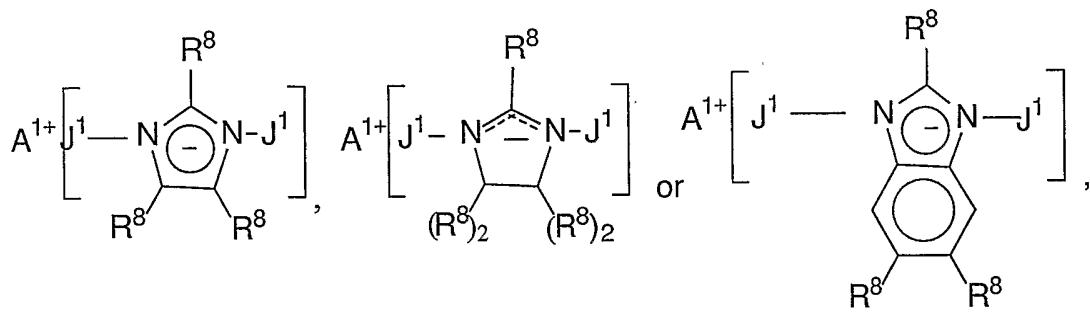
Z^1 is an anion group of from 1 to 50, preferably 1 to 30 atoms, not counting hydrogen atoms, further containing two or more Lewis base sites;

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

j^1 is a number from 2 to 12 and

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

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



wherein:

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

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

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

Examples of these catalyst activators include the trihydrocarbylammonium-, especially, methylbis(tetradecyl)ammonium- or methylbis(octadecyl)ammonium- salts of:

bis(tris(pentafluorophenyl)borane)imidazolide,

bis(tris(pentafluorophenyl)borane)-2-undecylimidazolide, bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolide, bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolide,

bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolide,

bis(tris(pentafluorophenyl)borane)imidazolinide,

bis(tris(pentafluorophenyl)borane)-2-undecylimidazolinide, bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolinide, bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolinide,

bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolinide,

bis(tris(pentafluorophenyl)borane)-5,6-dimethylbenzimidazolide,

bis(tris(pentafluorophenyl)borane)-5,6-bis(undecyl)benzimidazolide,

bis(tris(pentafluorophenyl)alumane)imidazolide,

bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolide, bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolide,

bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolide,

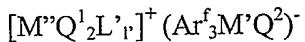
bis(tris(pentafluorophenyl)alumane)imidazolinide,

bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide, bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide,

bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide,

bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolide, and bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolide.

A further class of suitable activating cocatalysts include cationic Group 13 salts corresponding to the formula:



wherein:

M'' is aluminum, gallium, or indium;

M' is boron or aluminum;

Q^1 is C_{1-20} hydrocarbyl, optionally substituted with one or more groups which independently each occurrence are hydrocarbyloxy, hydrocarbysiloxy, hydrocarbysilylarnino, di(hydrocarbysilyl)arnino, hydrocarbylarnino, di(hydrocarbyl)arnino, di(hydrocarbyl)phosphino, or hydrocarbysulfido groups having from 1 to 20 atoms other than hydrogen, or, optionally, two or more Q^1 groups may be covalently linked with each other to form one or more fused rings or ring systems;

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

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

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

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

Examples of the foregoing Group 13 metal salts are alumicinium tris(fluoroaryl)borates or gallicinium tris(fluoroaryl)borates corresponding to the formula: $[M''Q^1_2L',]^+(Ar^f_3BQ^2)^-$, wherein M'' is aluminum or gallium; Q^1 is C_{1-20} hydrocarbyl, preferably C_{1-8} alkyl; Ar^f is perfluoroaryl, preferably pentafluorophenyl; and Q^2 is C_{1-8} alkyl, preferably C_{1-8} alkyl. More preferably, Q^1 and Q^2 are identical C_{1-8} alkyl groups, most preferably, methyl, ethyl or octyl.

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

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used

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

The catalysts, whether or not supported in any suitable manner, may be used to polymerize ethylenically unsaturated monomers having from 2 to 100,000 carbon atoms either alone or in combination. Preferred addition polymerizable monomers for use herein include olefins, diolefins and mixtures thereof. Preferred olefins are aliphatic or aromatic compounds containing vinylic unsaturation as well as cyclic compounds containing ethylenic unsaturation. Examples of the latter include cyclobutene, cyclopentene, norbornene, and norbornene derivatives that are substituted in the 5- and 6-positions with C₁-20 hydrocarbyl groups. Preferred diolefins are C₄-40 diolefin compounds, including ethyldene norbornene, 1,4-hexadiene, and norbornadiene. The catalysts and processes herein are especially suited for use in preparation of ethylene/ 1-butene, ethylene/1-hexene, ethylene/styrene, ethylene/propylene, ethylene/1-pentene, ethylene/4-methyl-1-pentene and ethylene/1-octene copolymers as well as terpolymers of ethylene, propylene and a nonconjugated diene, such as, for example, EPDM terpolymers.

Most preferred monomers include the C₂-20 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, C₁-4 alkyl substituted styrene, ethyldenenorbornene, 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.

Preferred monomers include a combination of ethylene and one or more comonomers selected from monovinyl aromatic monomers, 4-vinylcyclohexene, vinylcyclohexane, norbornadiene, ethyldene-norbornene, C₃-10 aliphatic α -olefins (especially propylene, isobutylene, 1-butene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, and 1-octene), and C₄-40 dienes. Most preferred monomers are mixtures of ethylene and styrene; mixtures of ethylene, propylene and styrene; mixtures of ethylene, styrene and a nonconjugated diene, especially ethyldenenorbornene or 1,4-hexadiene, and mixtures of ethylene, propylene and a nonconjugated diene, especially ethyldenenorbornene or 1,4-hexadiene.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0-250°C, preferably 30 to 200°C and pressures from atmospheric to 10,000 atmospheres. Suspension, solution, slurry, gas phase, solid state powder polymerization or other process condition may be employed if desired. A support, especially silica, alumina, or a polymer (especially poly(tetrafluoroethylene) or a polyolefin) may be employed, and desirably is employed when the catalysts are used in a gas phase polymerization process. The support is preferably employed in an amount to provide a weight ratio of catalyst (based on metal):support from 1:10⁶ to 1:10³, more preferably from 1:10⁶ to 1:10⁴.

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

Suitable solvents use for solution polymerization are liquids that are substantially inert under process conditions encountered in their usage. 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 alkyl-substituted aromatic compounds such as benzene, toluene, xylene, and ethylbenzene. Suitable solvents also include liquid olefins which may act as monomers or comonomers.

The catalysts may be utilized in combination with at least one additional homogeneous or heterogeneous polymerization catalyst in the same reactor 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.

The present catalyst compositions may be advantageously employed to prepare olefin polymers having improved processing properties by polymerizing ethylene alone or ethylene/α-olefin mixtures with low levels of a "H" branch inducing diene, such as norbornadiene, 1,7-octadiene, or 1,9-decadiene. The unique combination of elevated reactor temperatures, high molecular weight (or low melt indices) at high reactor temperatures and high comonomer reactivity advantageously allows for the economical production of polymers having excellent physical properties and processability. Preferably such polymers comprise ethylene, a C₃₋₂₀ α-olefin and a "H"-branching comonomer. Preferably, such polymers are produced in a solution process, most preferably a continuous solution process.

The catalyst composition may be prepared as a homogeneous catalyst by addition of the requisite components to a solvent or diluent in which polymerization will be conducted. The catalyst composition may also be prepared and employed as a heterogeneous catalyst by adsorbing, depositing or chemically attaching the requisite components on an inorganic or organic particulated

solid. Examples of such solids include, silica, silica gel, alumina, clays, expanded clays (aerogels), aluminosilicates, trialkylaluminum compounds, and organic or inorganic polymeric materials, especially polyolefins. In a preferred embodiment, a heterogeneous catalyst is prepared by reacting an inorganic compound, preferably a tri(C₁₋₄ alkyl)aluminum compound, with an activating cocatalyst, especially an ammonium salt of a hydroxyaryl(trispentafluoro-phenyl)borate, such as an ammonium salt of (4-hydroxy-3,5-ditertiarybutylphenyl)tris-(pentafluorophenyl)borate or (4-hydroxyphenyl)-tris(pentafluorophenyl)borate. This activating cocatalyst is deposited onto the support by coprecipitating, imbibing, spraying, or similar technique, and thereafter removing any solvent or diluent. The metal complex is added to the support, also by adsorbing, depositing or chemically attaching the same to the support, either subsequently, simultaneously or prior to addition of the activating cocatalyst.

When prepared in heterogeneous or supported form, the catalyst composition is employed in a slurry or gas phase polymerization. As a practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization is one or more hydrocarbons with less than 5 carbon atoms. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. Likewise, the α -olefin monomer or a mixture of different α -olefin monomers may be used in whole or part as the diluent. Most preferably, at least a major part of the diluent comprises the α -olefin monomer or monomers to be polymerized. A dispersant, particularly an elastomer, may be dissolved in the diluent utilizing techniques known in the art, if desired.

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

The polymerization may be carried out as a batchwise or a continuous polymerization process. A continuous process is preferred, in which event catalyst, ethylene, comonomer, and optionally solvent, are continuously supplied to the reaction zone, and polymer product continuously removed therefrom.

Without limiting in any way the scope of the invention, one means for carrying out such a polymerization process is as follows: In a stirred-tank reactor, the monomers to be polymerized are introduced continuously, together with solvent and an optional chain transfer agent. The reactor contains a liquid phase composed substantially of monomers, together with any solvent or additional diluent and dissolved polymer. Catalyst and cocatalyst are continuously introduced in the reactor liquid phase. The reactor temperature and pressure may be controlled by adjusting the solvent/monomer ratio, the catalyst addition rate, as well as by cooling or heating coils, jackets or both. The polymerization rate is controlled by the rate of catalyst addition. The ethylene content of

the polymer product is determined by the ratio of ethylene to comonomer in the reactor, which is controlled by manipulating the respective feed rates of these components to the reactor. The polymer product molecular weight is controlled, optionally, by controlling other polymerization variables such as the temperature, monomer concentration, or by the previously mentioned chain transfer agent, such as a stream of hydrogen introduced to the reactor, as is well known in the art. The reactor effluent is contacted with a catalyst kill agent such as water. The polymer solution is optionally heated, and the polymer product is recovered by flashing off gaseous monomers as well as residual solvent or diluent at reduced pressure, and, if necessary, conducting further devolatilization in equipment such as a devolatilizing extruder. In a continuous process the mean residence time of the catalyst and polymer in the reactor generally is from 5 minutes to 8 hours, and preferably from 10 minutes to 6 hours.

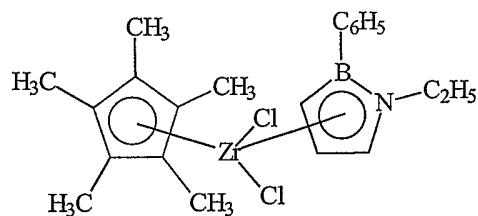
Ethylene homopolymers and ethylene/α-olefin copolymers are particularly suited for preparation according to the invention. Generally such polymers have densities from 0.85 to 0.96 g/ml. Typically the molar ratio of α-olefin comonomer to ethylene used in the polymerization may be varied in order to adjust the density of the resulting polymer. When producing materials with a density range of from 0.91 to 0.93 the comonomer to monomer ratio is less than 0.2, preferably less than 0.05, even more preferably less than 0.02, and may even be less than 0.01. In the above polymerization process hydrogen has been found to effectively control the molecular weight of the resulting polymer. Typically, the molar ratio of hydrogen to monomer is less than 0.5, preferably less than 0.2, more preferably less than 0.05, even more preferably less than 0.02 and may even be less than 0.01.

EXAMPLES

It is understood that the present invention is operable in the absence of any component which has not been specifically disclosed. The following examples are provided in order to further illustrate the invention and are not to be construed as limiting. Unless stated to the contrary, all parts and percentages are expressed on a weight basis. The term "overnight", if used, refers to a time of approximately 16-18 hours, "room temperature", if used, refers to a temperature of 20-25 °C, and "mixed alkanes" refers to a mixture of hydrogenated propylene oligomers, mostly C₆-C₁₂ isoalkanes, available commercially under the trademark Isopar E™ from Exxon Chemicals Inc. HRMS refers to high resolution mass spectroscopy.

All solvents were purified using the technique disclosed by Pangborn et al, Organometallics, 15, 1518-1520, (1996). All compounds, solutions, and reactions were handled under an inert atmosphere (dry box). ¹H and ¹³C NMR shifts were referenced to internal solvent resonances and are reported relative to TMS.

Example 1 Preparation of (η -1-Ethyl-2-phenyl-1H-1,2-azaborolyl)(η -pentamethyl-cyclopentadienyl)zirconium(IV)dichloride



A) (N-Allyl-N-ethylamino)vinylphenylborane

The title product was obtained by reaction of N-allyl-N-ethylamine with vinylphenylboron in the presence of triethylamine substantially according to the procedure of *Org. Lett.*, 2, p2089 (2000). The product was obtained by vacuum distillation as a clear colorless liquid (84 percent), bp 67-70 °C at 0.05 torr.

B) 1,5-Dihydro-1-ethyl-2-phenyl-1,2-azaborole

A solution of (N-Allyl-N-ethylamino)vinylphenylborane (17.2 g, 86.4 mmol) in 120 mL of CH₂Cl₂ was added to a solution of bis(tricyclohexylphosphine)benzylidene ruthenium (IV) dichloride (Grubbs' catalyst) (3.55 g, 4.31 mmol) in 40 mL of CH₂Cl₂ at 25°C. The mixture was stirred at 25°C for 10 hours after which the color had changed from purple-red to dark brown. The solvent was removed *in vacuo* and the product (12.6 g, 85 percent) as a clear colorless liquid, bp 60°C at 0.05 torr.

¹H NMR (C₆D₆, 400 MHz): δ 7.75 (d, 2H, J= 8.0 Hz, ArH), 7.33 (t, 2H, J= 8.0 Hz, ArH), 7.25 (t, 1H, J= 8.0 Hz, ArH), 6.93 (d, 1H, J= 8.1 Hz, vinyl), 6.60 (d, 1H, J= 8.1 Hz, vinyl), 3.51 (m, 2H, NCH₂CH=), 3.26 (q, 2H, J= 7.0 Hz, Et), 0.94 (t, 3H, J= 7.0 Hz, Et).

¹³C NMR (C₆D₆, 100.6 MHz): δ 148.5, 134.1, 132.3, 132.1, 128.9, 128.1, 127.6, 60.3 (NCH₂C=), 41.4 (Et), 16.7 (Et).

¹¹B NMR (C₆D₆, 115.5 MHz): δ 39.4.

HRMS (EI, m/z): calculated for C₁₂H₁₄¹¹BN (M⁺), 171.1219; found, 171.1224.

Analysis: Calculated for C₁₁H₁₄BN: C, 77.24; H, 8.25; N, 8.19. Found: C, 77.83; H, 8.45; N, 7.68.

C) Lithium 1-ethyl-2-phenyl-1,2-azaborolide

1,5-Dihydro-1-ethyl-2-phenyl-1,2-azaborole (5.0 g, 29.2 mmol) was dissolved in 15 mL of ether at -78°C. To this was added a solution of lithiumdiisopropylamide (3.13 g, 29.2 mmol) in 15 mL of ether. The mixture was stirred at -78°C for 2 hours and at 25°C for 10 hours. After removal of the solvent the residue was washed with 3x 20 mL of pentane. The residue was dried under vacuum to give the product as a light yellow powder (3.9 g, 77 percent).

¹H NMR (THF-d8, 400 MHz): δ 7.51 (d, 2H, J = 8.0 Hz, ArH), 7.05 (t, 2H, J = 8.0 Hz, ArH), 6.87 (t, 1H, J = 8.0 Hz, ArH), 5.91 (m, 1H, H₄), 5.86 (m, 1H, H₅), 4.16 (m, 1H, H₃), 3.78 (q, 2H, J = 7.0 Hz, Et), 1.27 (t, 3H, J = 7.0 Hz, Et).

¹³C NMR (THF-d8, 100.6 MHz): δ 133.9, 127.2, 123.8, 112.8, 111.9, 86.5 (br), 43.2 (Et), 19.6 (Et).

¹¹B NMR (THF-d8, 115.5 MHz): δ 29.4.

D) (η -1-ethyl-2-phenyl-1H-1,2-azaborolyl)(η -pentamethylcyclopentadienyl)zirconium(IV) dichloride

A solution of lithium 1-ethyl-2-phenyl-1,2-azaborolide (0.42 g, 2.37 mmol) in 10 mL of ether was added to a suspension of pentamethylcyclopentadienylzirconium trichloride (0.78 g, 2.34 mmol) in 10 mL of ether at -78 °C. Stirring was maintained for 12 h as the mixture was slowly warmed to 25 °C. The solvent was removed *in vacuo* and residue was washed with pentane and dried, affording the product (0.54 g, 56 percent) as a yellow powder.

¹H NMR (400 MHz, C₆D₆): δ 7.79 (dd, J =8.2, 1.4 Hz, 2H, ArH); 7.29 (t, J =7.3 Hz, 2H, ArH); 7.19 (t, J =7.4 Hz, 1H, ArH); 6.24 (t, J =2.6 Hz, 1H, ring CH); 5.33 (dd, J =4.5, 2.7 Hz, 1H, ring CH); 4.62 (dd, J =4.9, 2.7 Hz, H, ring CH); 4.06 (dq, J = 14.0, 7.0 Hz, 1H, NCH); 3.86 (dq, J =14.0, 7.0 Hz, 1H, NCH'); 1.77 (s, 15H, CpMe) 0.89 (t, J =7.3 Hz, 3H, NCH₂CH₃).

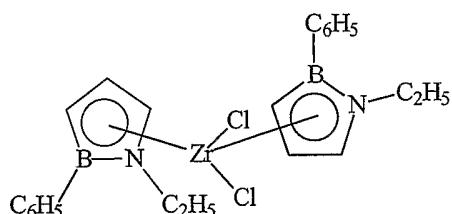
¹³C NMR (100.6 MHz, C₆D₆): δ 134.5, 128.5, 127.7, 127.5, 123.5, 114.1, 44.1, 16.8, 12.2.

¹¹B NMR (115.6 MHz, C₆D₆): δ 33.7.

HRMS: Calculated for C₂₁H₂₈¹¹B³⁵Cl₂NZr, 465.0740. Found: 465.0740.

Analysis: Calculated for C₂₁H₂₈BCl₂NZr: C, 53.96; H, 6.05; N, 3.00. Found: C, 52.52; H, 6.41; N, 2.79.

Example 2 Preparation of bis(1-ethyl-2-phenyl-1,2-azaborolyl)zirconium dichloride



A suspension of lithium (1-ethyl-2-phenyl-1,2-azaborolide) (1C), 0.80 g, 4.52 mmol) in 25 mL of ether was added to a suspension of ZrCl₄ (0.51 g, 2.19 mmol) in 25 mL of ether at -50 °C. The mixture was stirred for 8 h, during which time the mixture warmed to 25 °C. The mixture was filtered through diatomaceous earth and the solvent was removed *in vacuo*. The residue was washed with ether and dried to obtain the desired product (0.65 g, 59 percent). The ¹H NMR spectra indicated that the product is a mixture of two diasteromers in the ratio of 4:1. Spectral signals for the major isomer are reported.

¹H NMR (400 MHz, C₆D₆): δ 7.76 (d, J=8.1 Hz, 4H, ArH), 7.21 (m, 6H, ArH); 6.25 (m, 2H, ring CH); 6.07 (m, 2H, ring CH), 4.80 (m, 2H, ring CH), 3.75 (dq, J=14.2, 7.1 Hz, 2H, NCH); 3.57 (dq, J=14.2, 7.1 Hz, 2H, NCH), 0.75 (t, J=7.31 Hz, 6H).

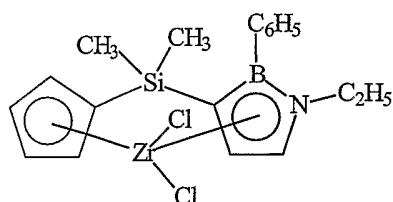
¹³C NMR (100.5 MHz, CDCl₃): δ 134.4; 128.9, 128.1, 123.3, 120.1, 98 (br), 45.5, 17.6.

¹¹B NMR (115.6 MHz, C₆D₆): δ 3.7.

HRMS: Calculated for C₂₂H₂₆¹¹B₂³⁵Cl₂N₂Zr: 500.0606. Found: 500.0604.

Analysis: Calculated for C₂₂H₂₆B₂Cl₂N₂Zr: C, 52.61; H, 5.23; N, 5.58. Found: C, 51.36; H, 5.18; N, 5.32.

Example 3 Preparation of [(η^5 -cyclopentadien-1-yl)(η^5 -1-ethyl-2-phenyl-1H-1,2-azaborol-3-yl)dimethylsilane]zirconium dichloride



A) 1-Ethyl-3-chlorodimethylsilyl-2,3-dihydro-2-phenyl-1H-1,2-azaborole

A solution of Me₂SiCl₂ (0.69 mL, 0.73 g, 5.65 mmol) in 15 mL of ether was added dropwise to a solution of lithium (1-ethyl-2-phenyl-1,2-azaborolide) (Ex. 1C), 1.0 g, 5.65 mmol) in 25 mL of ether at -78 °C. When the addition was complete, the mixture was warmed slowly to 25 °C and stirred for 10 h. The solvent was removed under reduced pressure and the residue was extracted with pentane. The extracts were filtered through diatomaceous earth and the solvent was removed *in vacuo* leaving the product as an orange oil (1.38 g, 92 percent).

¹H NMR (400 MHz, CDCl₃): δ 7.40 (dd, J=7.7, 1.8 Hz, 2H, ArH), 7.23 (m, 3H, ArH); 6.34 (dd, J=3.8, 1.3 Hz, 1H, ViH); 5.70 (dd, J=3.8, 2.4 Hz, 1H, ViH); 3.30 (m, 1H, NCH); 3.12 (m, 1H, NCH'); 2.64 (br s, 1H, BCH); 0.94 (t, J=7.1 Hz, 3H, CMe), 0.14 (s, 3H, SiMe'), 0.09 (s, 3H, SiMe')

¹³C NMR (100.6 MHz, C₆D₆): δ 139.1, 133.5 (Ph), 128.8 (Ph), 127.9 (Ph), 112.2, 41.1. (NCH₂), 39 (br, BCH), 17.3 (CMe), 2.4 (SiMe), 0.2 (SiMe').

¹¹B NMR (115.5 MHz, C₆D₆): δ 44.6.

HRMS. Calculated for C₁₃H₁₉¹¹B³⁵ClNSi: 263.1068. Found: 263.1078.

Analysis: calculated for C₁₃H₁₉BClNSi: C, 59.21; H, 7.28; N, 5.31. Found: C, 59.04; H, 7.12; N, 5.46.

B) 1-Ethyl-3-[cyclopentadienyl]dimethylsilyl-2,3-dihydro-2-phenyl-1H-1,2-azaborole

A solution of cyclopentadienyl lithium (0.16 g, 2.27 mmol) in 10 mL of THF was added slowly to a solution of 1-ethyl-3-chlorodimethylsilyl-2,3-dihydro-2-phenyl-1H-1,2-azaborole (0.60 g, 2.27 mmol) in 10 mL of THF at -50 °C. The reaction mixture was slowly warmed to 25 °C and

stirred for 12 h. The solvent was removed in *vacuo* and the residue was extracted with pentane. Solvent was removed from the extracts leaving the desired product as a brown oil (0.58 g, 87 percent).

¹H NMR (400 MHz, C₆D₆): δ 7.40 (dd, J=7.9, 1.2 Hz, 2H, ArH); 7.16 (t, J=7.0 Hz, 2H, ArH); 7.10 (t, J=7.0 Hz, IR, ArH); 6.54 (br s, 2H, Cp); 6.50 (br s, 2H, Cp), 6.28 (dd, J=4.0, 1.1 Hz, 1H, ViH); 5.54 (dd, J=3.9, 2.8 Hz, 1H, ViH); 3.30 (m, 1H, NCH); 3.22 (br s, 1H, Cp); 3.10 (m, 1H, N CH'), 2.45 (dd, J=2.6, 1.1 Hz, 1H, BCH); 0.92 (t, J=7.1 Hz, 3H, CMe); -0.13 (s, 3H, SiMe); -0.35 (s, 3H, SiMe').

¹³C NMR (C₆D₆, 100.6 mHz): δ 137.8, 133.5, 133.0, 130.4, 128.6, 128.0, 127.7, 113.4, 67.5, 41.1, 37.4 (bn), 25.6, 17.5, -4.8, -4.9.

¹¹B NMR (115.5 Hz, C₆D₆): δ 45.0.

HRMS: Calculated for C₁₈H₂₄¹¹BNSi: 293.1771. Found: 293.1774.

C) [(η⁵-cyclopentadien-1-yl)(η⁵-1-ethyl-2-phenyl-1H-1,2-azaborol-3-yl)dimethylsilane]zirconium dichloride

A solution of lithiumdiisopropylamide (0.66 g, 6.20 mmol) in THF (20 mL) was added to a solution of 1-ethyl-3-[cyclopentadienyldimethylsilyl]-2,3-dihydro-2-phenyl-1H-1,2-azaborole (0.91 g, 3.10 mmol) in 20 mL of THF at -78 °C. The mixture was slowly warmed to 25 °C and allowed to stir for 12 h. After removal of the solvent *in vacuo* the residue was washed with pentane. The solid was dissolved in 20 mL of toluene and added to a suspension of ZrCl₄ (0.69 g, 3.00 mmol) in 10 mL of toluene at -50 °C. When the addition was complete, the mixture was allowed to warm to 25 °C with stirring for 12 h. The solvent was removed under reduced pressure and the product was extracted with ether, which was then filtered through diatomaceous earth. Removal of solvent left a yellow solid, which was washed with pentane. The yield was 0.80 g (59 percent).

¹H NMR (300 MHz, CDCl₃): δ 7.57 (m, 2H, ArH); 7.38 (d, J=2.5 Hz, 1H, C₃H₂BN), 7.26 (m, 3H, ArH), 6.98 (m, 1H, Cp); 6.87 (m, 1H, Cp); 6.00 (m, 1H, Cp); 5.92 (d, J=2.5 Hz, 1H, C₃H₂BN); 5.88 (m, 1H, Cp); 4.08 (dq, J=13.7, 7.1 Hz, 1H, NCH); 3.75 (dq, J=13.7, 7.1 Hz, NCH); 1.21 (t, J=7.3 Hz, 3H, CH₃C); 0.62 (s, 3H, SiMe); 0.37 (s, 3H, SiMe').

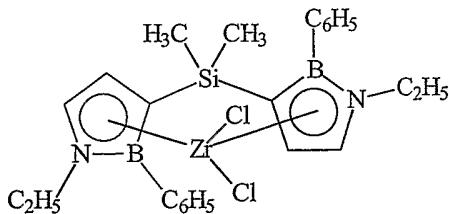
¹³C NMR (100.6 MHz, CDCl₃): δ 140.4; 135.6; 129.5; 128.6; 127.3; 120.9; 120.6; 112.5; 110.4; 44.1; 16.8; -2.3; -3.5.

¹¹B NMR (115.6 MHz, CDCl₃): δ 34.6.

HRMS: Calculated for C₁₈H₂₂¹¹BCl₂NSiZr: 451.0039. Found: 451.0016.

Analysis: Calculated for C₁₈H₂₂B¹¹Cl₂NSiZr: C, 47.68; H, 4.90; N, 3.09. Found: C, 47.92; H, 5.17; N, 3.11.

Example 4 Preparation of Rac-[bis(η^5 -1-ethyl-2-phenyl-1H-1,2-azaborol-3-yl)-dimethylsilane]zirconium dichloride



A) Bis[1-ethyl-2,3-dihydro-2-phenyl-1H-1,2-azaborol-3-yl]dimethylsilane

The title compound was prepared in the same manner as Example 3B) from lithium (1-ethyl-2-phenyl-1,2-azaborolide) (1C), 0.41 g, 2.31 mmol) in 15 mL of THF and 1-ethyl-3-chlorodimethylsilyl-2,3-dihydro-2-phenyl-1H-1,2-azaborole (Ex. 3A), 0.01g, 2.31 mmol) in 15 mL of THF. The product was obtained as a yellow oil (0.85 g, 92 percent).

¹H NMR (400 MHz, C₆D₆): δ 7.40 (dd, J=8.0, 1.5 Hz, 4H, ArH); 7.18 (t, J=7.3 Hz, 4H, ArH); 7.12 (t, J=7.3 Hz, 2H, ArH); 6.29 (dd, J=4.0, 1.1 Hz, 2H, ViH); 5.58 (dd, J=3.6, 1.1 Hz, 2H, ViH); 3.26 (m, 2H, NCH); 3.11 (m, 2H, NCH); 2.43 (dd, J=2.6, 1.1 Hz, 2H, BCH); 0.89 (t, J=7.0 Hz, 6H, CMe); -0.18 (s, 3H, SiMe); -0.42 (s, 3H, SiMe).

¹³C NMR (100.6 MHz, CDCl₃): δ 137.4, 133.5 (Ph); 128.3 (Ph); 127.7 (Ph), 113.7, 41.2 (NCH₂), 37.2 (br, BCH), 17.9 (CMe), -4.3 (SiMe), -4.4 (SiMe).

¹¹B (CDCl₃, 115.5 MHz): δ 4.52.

HRMS: Calculated for C₂₉H₃₂¹¹B₂N₂Si: 398.2520. Found: 398.2516.

B) Rac-[bis(η^5 -1-ethyl-2-phenyl-1H-1,2-azaborol-3-yl)dimethylsilane]zirconium dichloride

A solution of lithium diisopropylamide (0.46 g, 4.26 mmol) in 10 mL of THF was added to a solution of bis[1-ethyl-2,3-dihydro-2-phenyl-1H-1,2-azaborol-3-yl]dimethylsilane (0.85 g, 2.13 mmol) in 10 mL of THF at -78 °C. The mixture was slowly warmed to 25 °C and stirred for 8 h. The solvent was removed *in vacuo* and the residue was washed with 3 x 10 mL of pentane. This solid was dissolved in 10 mL of toluene and the resulting solution was added to a suspension of ZrCl₄ (0.49 g, 2.13 mmol) in 10 mL of toluene at -50 °C. Stirring was continued for 12 h and the mixture was warmed slowly to 25 °C. The solvent was removed *in vacuo* and the product was dissolved in ether which was filtered through diatomaceous earth. Removal of the solvent under reduced pressure gave the product as an orange solid. The yield was 0.80 g (68 percent).

¹H NMR (300 MHz, C₆D₆): δ 7.70 (dd, J=8.1, 1.5 Hz, 4H, ArH); 7.25 (t, J=7.6 Hz, 4H, ArH); 7.15 (t, J=7.4 Hz, 2H, ArH); 6.83 (d, J=2.5 Hz, 2H, C₃H₂BN); 5.86 (d, J=2.5 Hz, 2H, C₃H₂BN); 3.75 (dq, J=13.4, 6.9 Hz, 2H, NCH); 3.38 (dq, J=13.4, 6.9 Hz, 2H, NCH'); 0.64 (t, J=7.2 Hz, 6H, CH₃), 0.32 (s, 6H, SiMe).

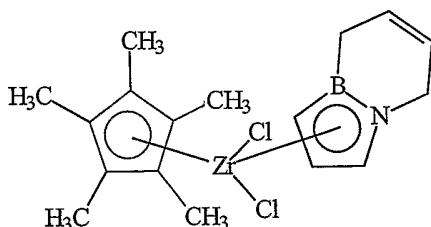
¹³C NMR (100.6 MHz, CDCl₃): δ 135.6, 131.4, 128.5, 127.6, 119.7, 44.7, 17.2, -1.0.

¹¹B (115.6 MHz, CDCl₃): δ 31.8.

HRMS: Calculated for C₂₄H₃₀¹¹B₂³⁵Cl₂N₂SiZr: 556.0788. Found: 556.0770.

Analysis: calculated for C₂₄H₃₀B₂Cl₂N₂SiZr: C, 51.62; H, 5.43; N, 5.02. Found: C, 51.32; H, 5.39; N, 5.08.

Example 5 Preparation of (4,7-Dihydro-3e,7a-azaborindenyl)(pentamethyl-cyclopentadienyl)zirconium dichloride



A) Allyl(N,N-diallylamino)boron chloride

A solution of allyltributyltin (62.2g, 0.19 mol) in 50 mL of hexane was added dropwise to a solution of BCl₃ (24.8 g, 0.21 mol) in 120 mL of hexane at -78°C. After the reaction mixture was stirred at -78°C for 1 hour, it was allowed to warm to 25°C for 2 hours followed by recooling to -78°C. Then diallylamine (23.5 mL, 0.19 mol) was added dropwise followed by triethylamine (26.7 mL, 0.19 mol). The mixture was stirred for 12 hours while it slowly warmed to 25°C. The solvent was removed under reduced pressure and the product (33.1g, 95 percent) was obtained by distillation (bp=38°C at 0.1 torr).

HRMS: Calculated for C₉H₁₅¹¹B³⁵ClN: 183.0986. Found: 183.0984.

¹H NMR (C₆D₆, 300 MHz): δ 1.90(d, J = 7.1 Hz, 2H, CH₂B), 3.32(d, J = 5.2 Hz, 2H, CH₂N), 3.65(d, J = 5.5Hz, 2H, CH₂N¹), 4.8-5.0(m, 6H, 3ViH), 5.3(m, 1H, ViH), 5.5 (m, 1H, ViH), 5.9(m, 1H, ViH).

¹¹B NMR (C₆D₆, 115.5 MHz): δ 38.1

¹³C NMR (C₆D₆, 75.5 MHz): δ 50.5, 51.3, 115.0, 116.0, 116.2, 134.9, 135.0

B) Allyl(N,N-diallylamino)vinyl borine

A solution of vinylmagnesium bromide, which had been prepared from vinylbromide (23.5g, 0.22 mol) and magnesium (5.3g, 0.2 mol) in 250 mL of THF, was added to a solution of allyl(N,N-diallylamino)boron chloride (33.1g, 0.18 mol) in 100mL of THF at -78°C. The reaction mixture was stirred for 10 hours and allowed to warm slowly to 25°C. The solvent was removed under reduced pressure and the residue was extracted with pentane. The solvent was removed from the extracts and the product (26.5g, 84 percent) was distilled (bp = 36°C at 0.1 torr).

HRMS: Calculated for C₁₁H₁₈¹¹BN: 175.1532. Found 175.1529.

¹H NMR (C₆D₆, 400 MHz): δ 1.94(d, J=7.3Hz, 2H, BCH₂), 3.48 (broad s, 4H, 2NCH₂), 4.88 (m, 6H, ViCH₂), 5.46 (m, 2H, ViH), 5.8-6.0 (m, 3H, ViH), 6.26 (dd, J=19.6, 13.7 Hz, 1H BCH).

¹¹B NMR (C₆D₆, 115 MHz): δ 39.7

¹³C NMR (CH₂D₂, 125.7 MHz): δ 24 (broad), 51, 51.4, 113.3, 115.2, 115.5, 131.4, 135.1, 136.5, 137.6, 139(broad)

C) 4,7-Dihydro-4a,7a-azaborindene

A solution of allyl(N, N-diallylamino)vinyl borine (26.5, 0.15mol) in 50 mL of CH₂Cl₂ was added to a solution of (Cy₃P)₂ (PhCH)RuCl₂ (6.23g, 75 Mmol) in 150 mL of CH₂Cl₂ and the resulting mixture was heated to reflux for 24 hours. The solvent was removed under reduced pressure and the residue was distilled to obtain the product (13.9g, 78 percent) bp = 27°C at 0.1 torr.

HRMS Calculated for C₇H₁₀¹¹BN: 119.0906. Found 119.0906.

¹H NMR (C₆D₆, 400 MHz): δ 1.68 (broad, s, 2H, CH₂B), 3.19(d, J= 3Hz, 2H, CH₂N), 3.46 (m, 2H, CH₂N¹), 5.50 (d,m,J=10.3 Hz, 1H, ViH), 5.84 (d,m,J=10.3Hz, 1H, ViH), 6.22 (d, J=7.7Hz, 1H, ViH), 6.78 (d, J=8.1 Hz, 1H, ViH).

¹¹B NMR(C₆D₆, 115.5 MHz): δ 37.7.

¹³C NMR (C₆D₆, 100.5 MHz): δ 13.0 (broad), 45.6, 60.0, 124.8, 125.8, 133 (broad), 148.

D) (4,7-Dihydro-3a,7a-azaborindenyl)(pentamethylcyclopentadienyl)zirconium dichloride

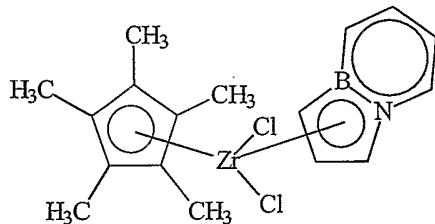
A 0.5M solution of KN(SiMe₃)₂ (6.80mL, 3.40mmol) in toluene was added dropwise to a solution of 4,7-dihydro-4a,7a-azaborindene in 10 mL toluene at -78°C. The mixture was stirred 10 hours and allowed to slowly warm to 25°C. The solution was filtered and the solid was washed successively with 3x5 mL of toluene and 3x10 mL of pentane. Ethyl ether (15mL) was added to the solid and the resulting suspension was added to a solution of pentamethylcyclopentadienyl zirconium trichloride (1.12g, 3.36mmol) in 10mL of ether at -50°C. The resulting orange suspension was stirred 10 hours and allowed to warm slowly to 25°C. After removal of the volatiles in vacuum the product was extracted with ether. The extracts were slowly concentrated by partial removal of solvent and the resulting solution was stored at -20°C until yellow crystals (0.71g, 51 percent) were obtained. The structure was confirmed by X-ray crystallography.

¹H NMR (CDCl₃, 400 MHz): δ 1.70(dm, J=20Hz, 1H, C(7)H), 2.00(dm, J=20Hz, 1H, C(7)H¹), 2.00(s, 15H, CpMe), 4.04(dm, J=17.9Hz, 1H, C(4)H), 4.14(dd, J=4.9, 2.4Hz, 1H, C(1)H), 4.62(dm, J=17.9Hz, 1H, C(4)H¹), 5.54 (dm, J=10.6 Hz, 1H, ViH), 5.82(dd, J=5.1, 2.5Hz, 1H, C(2)H), 5.89(dm, J=10.6Hz, 1H, ViH), 6.32(t, J=2.5Hz, 1H, C(3)H).

¹¹B NMR (CDCl₃, 115.5 MHz): δ 32.3

¹³C NMR (CDCl₃, 100.6 MHz): δ 12.7, 13.0(broad), 45.9, 93.0(broad), 117.3, 121.6, 122.7, 124.0, 126.9.

Example 6 Preparation of (3a,7a-azaborindenyl)(pentamethylcyclopentadienyl) zirconium dichloride



A) 3a,7a-Azaborindene

A solution of 4,7-Dihydro-4a,7a-azaborindene (Ex. 5C), 4.5g, 37.8mol) in 25mL pentane was added to a suspension of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (10.4g, 45.6mol) in 50mL of pentane. The mixture was stirred at 25°C for 10 hours after which the solid was removed by filtration. The filtrate was distilled affording the desired product (1.3g, 30 percent) bp=26°C at 0.1 torr.

HRMS: Calculated for $C_7H_{10}^{11}BN$: 117.0750. Found 117.0752.

1H NMR (C_6D_6 , 400 MHz): δ 3.52 (broad, s, 2H, CH₂N), 6.11 (t, $J=6.3$ Hz, 1H, C(5)H), 6.52 (m, 2H, C(1)HC(2)H), 6.94(d, $J=6.3$, 1H, C(4)H), 7.06(d, $J=11.1$ Hz, 1H, BCH), 7.61(dd, $J=11.1$, 6.3Hz, 1H, C(6)H).

^{11}B NMR (C_6D_6 , 115.5 MHz): δ 34.2

^{13}C NMR (C_6D_6 , 100.5 MHz): δ 58.8, 109.5, 124(broad), 133.6(broad), 135.3, 143.2, 144.2.

B) (3a,7a-azaborindenyl)(pentamethylcyclopentadienyl) zirconium dichloride

In substantially the same manner as for Example 5, step D), 3a,7a-azaborindene (0.30g, 2.56 mmol) and pentamethylcyclopentadienylzirconium trichloride (0.85g, 2.56mmol) were contacted to give the desired product (0.63g, 60 percent). The structure was confirmed by X-ray crystallography.

1H NMR (CD_2Cl_2 , 400 MHz): δ 2.00(s, 15H, CpMe), 4.85(dd, $J=5.1$, 1.8Hz, 1H, C(1)H), 6.27 (dd, $J=5.3$, 2.4Hz, 1H, C(2)H), 6.58 (td, $J=6.6$, 1.1Hz, 1H, C(5)H), 6.82(t, $J=2.4$ Hz, 1H, C(3)H), 7.15(d, $J=11.7$ Hz, 1H, C(7)H), 7.36(dd, $J=11.7$, 6.4Hz, 1H, C(6)H), 7.64 (dd, $J=6.0$, 1.0Hz, 1H, C(4)H).

^{11}B NMR (CD_2Cl_2 , 115.5 MHz): δ 23.8

^{13}C NMR (CD_2Cl_2 , 100.5 MHz): δ 12.6, 115.4, 115.8, 121.5, 129.6, 136.9.

Ethylene/ 1-Octene Polymerization Conditions

All liquid and gas feeds were passed through columns of alumina and a decontaminant (Q-5™ catalyst available from Englehardt Chemicals Inc.) prior to introduction into the reactor. Catalyst components are handled in a glovebox containing an atmosphere of argon or nitrogen. A stirred 2.0 liter reactor is charged with 740 g of mixed alkanes solvent and 118 g of 1-octene

comonomer. Hydrogen (25 psi, 170 kPa) is added as a molecular weight control agent by differential pressure expansion from a 75 mL addition tank. The reactor is heated to 140 °C and saturated with ethylene at 500 psig (3.4 MPa). Metal complex as dilute toluene solution and cocatalyst as dilute solutions in hexane, were mixed and transferred to a catalyst addition tank and injected into the reactor. The cocatalyst was methylalumoxane used in a 1000:1 molar ratio to the catalyst. The polymerization conditions were maintained for 15 minutes with ethylene added on demand. The resulting solution was removed from the reactor, quenched with isopropyl alcohol, and stabilized by addition of a toluene solution containing 67 mg/100g polymer of a hindered phenol antioxidant (Irganox™ 1010 from Ciba Geigy Corporation) and 133 mg/100g polymer of a phosphorus stabilizer (Irgafos 168 from Ciba Geigy Corporation).

Between sequential polymerization runs, a wash cycle was conducted in which 850 g of mixed alkanes was added to the reactor and the reactor was heated to 150 °C. The reactor was then emptied of the heated solvent immediately before beginning a new polymerization run.

Polymers were recovered by drying in a vacuum oven set at 140 °C for 20 hours. Density values are derived by determining the polymer's mass when in air and when immersed in methylethyl ketone. Micro melt index values (MMI) are obtained using a Custom Scientific Instrument Inc. Model CS-127MF-015 apparatus at 190 °C, and are unit less values calculated as follows: $MMI = 1/(0.00343 t - 0.00251)$, where t = time in seconds as measured by the instrument. Results are contained in Table 1.

Table 1

Run	Catalyst (μmol)	Time (minutes)	Yield (g)	Efficiency ¹	Tm (°C)	MMI ²
1	Ex. 1 (0.75)	15	58.4	78	-	70
2	Ex. 2 (1.0)	17	90.79	91	131.5	60
3	Ex. 3 (1.0)	15	22.0	22	126.5	>100
4	Ex. 4 (1.0)	16	41.8	42	129.3	>100
5	Ex. 5 (2.0)	16	45.1	22	133.2	>100
6	Ex. 6 (1.0)	15	40.0	40	132	72

¹. efficiency, g polymer/ μmole zirconium

². micro melt index 190 °C, (comparative technique of melt index determination)

Propylene Conditions

Batch reactor polymerizations were conducted in a two liter Parr reactor equipped with an electrical heating jacket, internal serpentine coil for cooling, and a bottom drain valve. Pressures, temperatures and block valves were computer monitored and controlled. Mixed alkanes (650 g) was measured in a solvent shot tank fitted with a differential pressure transducer or weigh cell. It was then added to the reactor from the solvent shot tank. Propylene, 150 g, was measured using a mass flow meter. The contents of the reactor was stirred at 1200 rpm. Hydrogen was added by differential expansion (Δ 25 psi, 170 kPa) from a 75 ml shot tank initially at 300 psig (2.2 MPa).

The contents of the reactor were then heated to the desired run temperature. The catalyst (as 0.0050 M solution in toluene) and MAO cocatalyst were combined in a one to one thousand molar ratio in the glove box and transferred from the glove box to the catalyst shot tank through 1/16 in (0.16 cm) tubing using toluene to aid in the transfer. The catalyst tank was then pressurized to 350 psig (2.5 MPa) using nitrogen. After the contents of the reactor had stabilized at the desired run temperature of 70°C, 18 μ mol of the catalyst was injected into the reactor via a dip tube. The temperature was maintained by allowing cold glycol to pass through the internal cooling coils. The reaction was allowed to proceed for 46 minutes. The contents of the reactor were then expelled into a 4 liter nitrogen purged vessel and quenched with isopropyl alcohol and 100 mg of Irganox 1010 in toluene was added as an antioxidant. Volatile materials were removed from the polymer in a vacuum oven up to 140°C overnight and cooled to at least 50°C prior to removal from the oven. The yield of isotactic polypropylene was 41.9 g, giving an efficiency of 2.3 g/ μ mol Zr.

CLAIMS

1. A metal complex corresponding to the formula, $CpM(Z)_z(X)_x(L)_t(X')_{x'}$ (I), where Cp is a nitrogen and boron containing, anionic, 5-membered cyclic ligand group or substituted derivative thereof, bound to at least M; M is a metal selected from Groups 3-10 or the Lanthanide series of the Periodic Table of the Elements;

Z is either:

- a) a cyclic ligand group containing delocalized π -electrons (including a second or third anionic ligand, Cp) said Z being bonded to M by means of delocalized π -electrons and optionally also covalently bonded to Cp through a divalent bridging group, Z', or
- b) a divalent moiety of the formula $-Z'Y-$, with Z' bonded to Cp and Y covalently or coordinate covalently bonded to M, wherein,

Z' is SiR^6_2 , CR^6_2 , $SiR^6_2SiR^6_2$, $CR^6_2CR^6_2$, $CR^6=CR^6$, $CR^6_2SiR^6_2$, BR^6 , BR^6L'' , or GeR^6_2 ;

Y is $-O-$, $-S-$, $-NR^5-$, $-PR^5-$; $-NR^5_2$, or $-PR^5_2$;

R^5 , independently each occurrence, is hydrocarbyl, trihydrocarbysilyl, or trihydrocarbysilylhydrocarbyl, said R^5 having up to 20 atoms other than hydrogen, and optionally two R^5 groups or R^5 together with Y form a ring system;

R^6 , independently each occurrence, is hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, $-NR^5_2$, and combinations thereof, said R^6 having up to 20 non-hydrogen atoms, and optionally, two R^6 groups form a ring system;

L'' is a monodentate or polydentate Lewis base optionally bonded to R^6 ;

X is hydrogen or a monovalent anionic ligand group having up to 60 atoms not counting hydrogen;

L independently each occurrence is a neutral ligating compound having up to 20 atoms, other than hydrogen, and optionally L and X are bonded together;

X' is a divalent anionic ligand group having up to 60 atoms other than hydrogen;

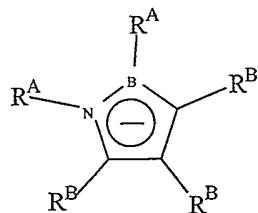
z is 0, 1 or 2;

x is 0, 1, 2, or 3;

t is a number from 0 to 2, and

x' is 0 or 1.

2. A metal complex according to claim 1 wherein Cp is an 1,2-azaborolyl anionic ligand, corresponding to the formula:

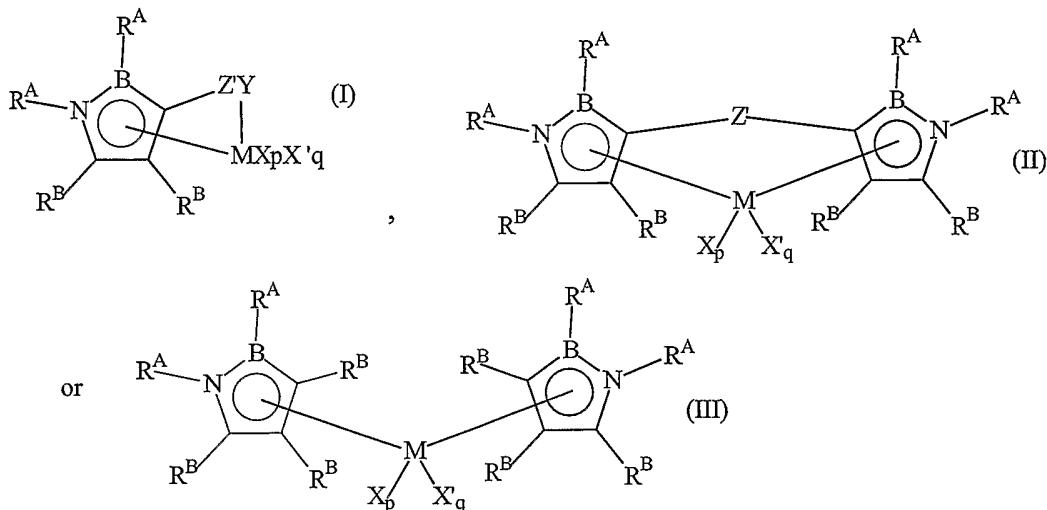


wherein,

R^A , independently each occurrence, is a group of from 1 to 40 atoms, not counting hydrogen, selected from the group consisting of hydrocarbyl, trihydrocarbysilyl, trihydrocarbysilylhydrocarbyl, dihydrocarbylamino, and hydrocarbyleneamino, and optionally two R^A groups may be joined together thereby forming a fused multi-ring ligand group;

R^B , independently each occurrence, is selected from the group consisting of hydrogen, Z' and R^A , where Z' is as previously defined in claim 1.

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



where M is a Group 4 metal that is in the +2, +3 or +4 formal oxidation state;

R^A independently each occurrence is a hydrocarbyl, dihydrocarbylamino, or hydrocarbyleneamino group of from 1 to 40 atoms, not counting hydrogen, or two or more R^A groups may be covalently linked together;

R^B independently each occurrence is hydrogen or R^A ;

Z' is SiR^6_2 , CR^6_2 , $SiR^6_2SiR^6_2$, $CR^6_2CR^6_2$, $CR^6=CR^6$, or BR^6 ;

Y is $-NR^5-$, $-PR^5-$; $-NR^5_2$, or $-PR^5_2$;

R^5 , independently each occurrence, is C_{1-20} hydrocarbyl;

R^6 , independently each occurrence, is hydrogen, or C_{1-20} hydrocarbyl;

X is an anionic or dianionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups;

X' independently each occurrence is a neutral ligand having up to 40 atoms;

p is zero, 1 or 2, and is two less than the formal oxidation state of M when X is an anionic ligand, and when X is a dianionic ligand group, p is 1; and
q is zero, 1 or 2.

4. A metal complex according to claim 3 wherein:

X is halo, C₁₋₁₀ hydrocarbyl or trialkylsilylalkyl of up to 20 carbons, or two such X groups together form a divalent ligand group;

R^A independently each occurrence is hydrocarbyl or two adjacent R^A groups are joined together forming a fused ring;

R^B is C₁₋₁₀ hydrocarbyl;

Y is -NR^E- where R^E is C₁₋₆ alkyl or cycloalkyl; and

Z is SiR⁶₂ where R⁶ is methyl, phenyl, or C₁₋₁₀ alkylphenyl.

5. A metal complex according to claim 1 selected from the group consisting of:

(η -1-ethyl-2-phenyl-1H-1,2-azaborolyl)(η -pentamethylcyclopentadienyl)zirconium (IV)dichloride, bis(1-ethyl-2-phenyl-1,2-azaborolyl)zirconium dichloride, [(η ⁵-cyclopentadien-1-yl)(η ⁵-1-ethyl-2-phenyl-1H-1,2-azaborol-3-yl)dimethylsilane]zirconium dichloride, rac-[bis(η ⁵-1-ethyl-2-phenyl-1H-1,2-azaborol-3-yl)dimethylsilane]zirconium dichloride, (4,7-Dihydro-3a,7a-azaborindenyl)(pentamethyl-cyclopentadienyl)zirconium dichloride, and (3a,7a-azaborindenyl)(pentamethylcyclopentadienyl) zirconium dichloride.

6. A catalyst composition comprising (A) the metal complex of claims 1-5 and (B) an activating cocatalyst, or a reaction product thereof, wherein the molar ratio of (A) to (B) is from 1:10,000 to 100:1.

7. A process for polymerizing one or more addition polymerizable monomers, comprising contacting said monomer or a mixture of such monomers under polymerization conditions with a catalyst composition according to claim 6.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/09071

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C07F17/00 C08F10/00 C07F5/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C08F

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

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

CHEM ABS Data, EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category [°]	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SCHMID, GUENTER ET AL: "1,2-Azaborolyl complexes. XVIII. (.eta.5-1-tert-Butyl-2-methyl-1,2- azaborolyl)carbonylphosphine and -olefin cobalt complexes" retrieved from STN Database accession no. 119:139480 XP002245609 abstract & CHEMISCHE BERICHTE (1993), 126(4), 899-906 ,</p> <p>----- -/-</p>	1,2

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

26 June 2003

Date of mailing of the international search report

11/07/2003

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online!' CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SCHMID, GUENTER ET AL: "Azaborolyl complexes. 27. The 1-tert-butyl-2-methyl-1H-1,2-azaborolyl ring as a bifunctional ligand in rhodium complexes" retrieved from STN Database accession no. 117:70007 XP002245610 abstract & ZEITSCHRIFT FUER NATURFORSCHUNG, B: CHEMICAL SCIENCES (1992), 47(5), 635-9 ,</p> <p>---</p> <p>DATABASE CA 'Online!' CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SCHMID, GUENTER ET AL: "Azaboroliny1 complexes. VII. Preparative and structural studies on.eta.-1,2-azaboroliny1 complexes of titanium, vanadium, iron, and cobalt" retrieved from STN Database accession no. 98:54184 XP002245611 abstract & CHEMISCHE BERICHTE (1982), 115(12), 3830-41 ,</p> <p>---</p> <p>DATABASE CA 'Online!' CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; ASHE, ARTHUR J., III ET AL: "A Synthesis of Aromatic Five- and Six-Membered B-N Heterocycles via Ring Closing Metathesis" retrieved from STN Database accession no. 133:150606 XP002245612 abstract & ORGANIC LETTERS (2000), 2(14), 2089-2091 ,</p> <p>---</p> <p>---</p>	1,2
X		1,2
X		1,2

INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SCHMID, GUENTER ET AL: "1,2-Azaborolyl complexes. XXXI. Cyclooligomerization of alkynes at the 1,2-azaborolylcobalt moiety" retrieved from STN Database accession no. 123:144208 XP002245613 abstract & JOURNAL OF ORGANOMETALLIC CHEMISTRY (1995), 492(2), 185-9 ,</p> <p>---</p> <p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SCHMID, GUENTER ET AL: "Azaboroliny1 complexes. XVII. Titanium and vanadium chloride complexes with diazadiboretidine and 1,2-azaboroliny1 ligands" retrieved from STN Database accession no. 103:105033 XP002245615 abstract & CHEMISCHE BERICHTE (1985), 118(6), 2418-28 ,</p> <p>---</p> <p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SCHMID, GUENTER ET AL: "Azaboroliny1 complexes, XV. Bis(.eta.5-1,2-azaboroliny1)ruthenium sandwich complexes - synthesis and structure study" retrieved from STN Database accession no. 102:24787 XP002245616 abstract & ZEITSCHRIFT FUER NATURFORSCHUNG, TEIL B: ANORGANISCHE CHEMIE, ORGANISCHE CHEMIE (1984), 39B(8), 1082-7 ,</p> <p>---</p> <p>-/-</p>	1,2
X		1,2
X		1,2

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International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; SCHMID, GUENTER ET AL: "Azaborolinyl complexes. XVIII..eta.5-1,2-Azaborolinyl-.eta.6-arene sandwich complexes of iron" retrieved from STN Database accession no. 104:88778 XP002245617 abstract & ZEITSCHRIFT FUER NATURFORSCHUNG, TEIL B: ANORGANISCHE CHEMIE, ORGANISCHE CHEMIE (1985), 40B(6), 787-93 ,</p> <p>---</p>	1,2
X,P	<p>DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; ASHE, ARTHUR J., III ET AL: "Synthesis and Coordination Chemistry of 3a,7a-Azaborindenyl, a New Isoelectronic Analogue of the Indenyl Ligand" retrieved from STN Database accession no. 137:384931 XP002245618 abstract & ORGANOMETALLICS (2002), 21(22), 4578-4580 , 14 October 2002 (2002-10-14),</p> <p>---</p>	1,2
X	<p>US 6 228 958 B1 (KRISHNAMURTI RAMESH ET AL) 8 May 2001 (2001-05-08) the whole document</p> <p>---</p>	1-3,6,7
X	<p>EP 0 590 486 A (IDEMITSU KOSAN CO) 6 April 1994 (1994-04-06) page 2, line 31-37 page 3, line 1-28 page 4, line 55 -page 5, line 3</p> <p>---</p>	1-3,6,7
X	<p>PATENT ABSTRACTS OF JAPAN vol. 1997, no. 08, 29 August 1997 (1997-08-29) & JP 09 110917 A (UBE IND LTD), 28 April 1997 (1997-04-28) abstract</p> <p>---</p>	1-3,6,7
X	<p>PATENT ABSTRACTS OF JAPAN vol. 1996, no. 02, 29 February 1996 (1996-02-29) & JP 07 258322 A (IDEMITSU KOSAN CO LTD), 9 October 1995 (1995-10-09) abstract</p> <p>---</p> <p>-/-</p>	1-3,6,7

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/09071

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 75146 A (DOW CHEMICAL CO) 14 December 2000 (2000-12-14) page 3, line 3 -page 4, line 26; claims 2-7 -----	1-7

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 03 A9071

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1,2,6,7: partially

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claim(s) is impossible. Consequently, the search has been restricted to the compounds according to claim 3.

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

INTERNATIONAL SEARCH REPORT

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

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

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

2. Claims Nos.: 1, 2, 6, 7: partially because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

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

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

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

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

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

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

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

Remark on Protest

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

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/09071

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 6228958	B1	08-05-2001	US WO AU BR CA CN DE DE EP ES JP RU TW WO	5902866 A 0064705 A1 5314796 A 9608010 A 2219816 A1 1185787 A 69621796 D1 69621796 T2 0822946 A1 2178704 T3 11504361 T 2167879 C2 434270 B 9634021 A1		11-05-1999 02-11-2000 18-11-1996 05-01-1999 31-10-1996 24-06-1998 18-07-2002 02-01-2003 11-02-1998 01-01-2003 20-04-1999 27-05-2001 16-05-2001 31-10-1996
EP 0590486	A	06-04-1994	EP JP JP	0590486 A2 3308359 B2 6340704 A		06-04-1994 29-07-2002 13-12-1994
JP 09110917	A	28-04-1997	NONE			
JP 07258322	A	09-10-1995	NONE			
WO 0075146	A	14-12-2000	AU CA EP JP WO US	4996900 A 2368112 A1 1194431 A1 2003501433 T 0075146 A1 6420299 B1		28-12-2000 14-12-2000 10-04-2002 14-01-2003 14-12-2000 16-07-2002