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(54) Title: DIMERIC GROUP 4 METALLOCENES IN +3 OXIDATION STATE

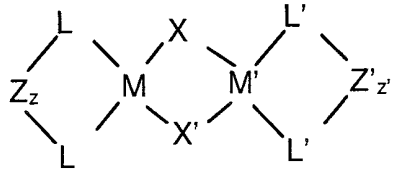
(57) Abstract: Dimeric Group 4 metal metallocene compounds wherein the metal is in the +3 formal oxidation state useful as components of catalysts for addition polymerizations.

DIMERIC GROUP 4 METALLOCENES IN +3 OXIDATION STATE

The present invention relates to compounds that are useful as catalysts or catalyst components. More particularly, the present invention relates to such compounds comprising two Group 4 metal atoms in the +3 formal oxidation state that are particularly adapted for use in the coordination polymerization of unsaturated compounds. Such compounds are particularly advantageous for use in a polymerization process wherein at least one polymerizable monomer is combined under polymerization conditions with a catalyst or catalyst composition to form a polymeric product. In addition, the complexes of the current invention are especially useful in the production of stereoregular polymers derived from α-olefins, especially isotactic polypropylene.

Group 4 metal complexes, especially metallocenes having utility as Ziegler-Natta polymerization catalysts, particularly when combined with an activator or cocatalyst are well known. In US-A-5,616,664, versions of such complexes wherein the metal is in the +2 formal oxidation state were disclosed. Stable dimeric metallocenes of Group 4 metals wherein the metal is in the +3 formal oxidation state have not been previously known much less disclosed for use in polymerization processes.

According to the present invention there are now provided dimeric Group 4 metal metallocene compounds corresponding to the formula:



(I)

wherein:

L and L' independently each occurrence are ligand groups containing delocalized electrons by means of which said L and L' are π-bond to M or M' respectively,

M and M' are the same or different and are Group 4 metals in the +3 formal oxidation state,

Z and Z' are the same or different and are optional divalent bridging groups,

X and X' are the same or different and are anionic ligand groups, and

z and z' independently are 0 or 1.

In the compounds of the invention, some or all of the bonds between the core elements M, M', X and X' may possess partial bond characteristics. The compounds may exist in the form of a solution in an aliphatic or aromatic solvent, as solvated adducts, such as an adduct with a Lewis base, particularly a trihydrocarbyl phosphine or dihydrocarbyl ether, or as a solid crystal.

The compounds of the invention may be formed by contacting the corresponding Group 4 metal monomeric or dimeric complex containing three X groups for each M and three X' groups for each M', two of each three such X or X' groups being good leaving groups, with a source of the ligand groups: L, L', L-Z_z-L, or L'-$Z'_{z'}$-L'.

The present invented compounds are stable at elevated temperatures of at least 0 °C, preferably at least 20 °C up to as high as 150 °C or higher. Generally, they require protection from oxidants and water. They are usefully employed in a process for polymerization of ethylenically unsaturated monomers under solution, slurry, high pressure, or gas phase polymerization conditions either homogeneously or supported on an inert support. Relatively high yields of polymers may be readily obtained by use of the present metal complexes in the foregoing polymerization processes. Particularly, when employed as a component of a catalyst composition in a solution, slurry or gas-phase olefin polymerization processes, the present invented complexes are suitable for producing ethylene homopolymers and copolymers of ethylene and a C_{2-8} α-olefin comonomer having high comonomer incorporation (low density) and additionally may provide polymers having enhanced long chain branch incorporation and increased molecular weights. The catalysts are also useful for preparing α-olefin homopolymers and copolymers of two or more α-olefins that are highly isotactic.

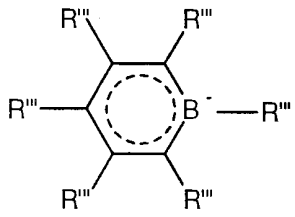
Accordingly, the present invention additionally provides a process for the polymerization of one or more ethylenically unsaturated, polymerizable monomers comprising contacting the same, optionally in the presence of an inert aliphatic, alicyclic or aromatic hydrocarbon, under polymerization conditions with the above metal complex and a cocatalyst.

All references herein to elements belonging to a certain Group refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 1995. Also any reference to the 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.

Preferably, L and L' independently each occurrence are cyclic or non-cyclic, aromatic or non-aromatic, anionic ligand groups containing delocalized π-electrons capable of forming a bond with the Group 4 metal and containing up to 50 atoms other than hydrogen. Exemplary of such π-bonded groups are conjugated or nonconjugated, cyclic or non-cyclic dienyl groups, allyl groups, boratabenzene groups, and phosphole groups. Each atom in the delocalized π-bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, substituted heteroatom groups wherein the heteroatom is selected from Group 13-17 of the Periodic Table of the Elements, and the substituents are hydrocarbyl, silyl, hydrocarbylene, or another Group 13-17 heteroatom containing moiety, and optionally any of the foregoing hydrocarbyl, silyl, or hydrocarbylene substituents may be further substituted with a Group 13-17 heteroatom group. In addition two or more such radicals may together form a fused ring system, including partially or fully hydrogenated fused ring systems. Included within the term "hydrocarbyl" are C_{1-20} straight, branched and cyclic alkyl or alkenyl radicals, C_{6-20} aromatic radicals, C_{7-20} alkyl-substituted aromatic radicals, and C_{7-20} aryl-substituted alkyl radicals. Suitable heteroatom groups include alkoxy, aryloxy, dialkylamino, alkanediylamino, dialkylphosphino, silyl, germyl, and siloxy groups containing from 1 to 20 atoms not counting hydrogen. Examples include N,N-dimethylamino, pyrrolidinyl, trimethylsilyl, triethylsilyl, t-butyldimethylsilyl, methyldi(t-butyl)silyl, triphenylgermyl, and trimethylgermyl groups.

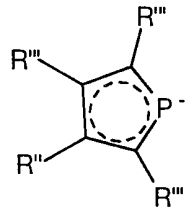
Examples of suitable anionic, delocalized π-bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups, indacenyl, s-indacenyl, gem-dimethylacenaphthalenyl, cyclopenta(*l*)phenanthrenyl, phosphole, and boratabenzene groups, as well as C_{1-20} hydrocarbyl-, C_{1-20} dihydrocarbylamido-, C_{1-20} hydrocarbyleneamido-, C_{1-20} halohydrocarbyl-, C_{1-20} amido-, or C_{1-20} hydrocarbylsilyl-substituted derivatives thereof.

The boratabenzenes are anionic ligands that are boron-containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in Organometallics, 14,1, 471-480 (1995). Preferred boratabenzenes correspond to the formula:



wherein R''' in one occurrence is a covalent bond to Z, and in each remaining occurrence R''' is independently, hydrogen or a hydrocarbyl, silyl, N,N-dihydrocarbylamino, hydrocarbadiylamino, or germyl group, said R''' having up to 20 atoms not counting hydrogen, and optionally one or more R''' groups may be bonded together forming a multicyclic fused ring system.

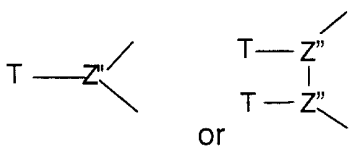
Phospholes are anionic ligands that are phosphorus- containing analogues to a cyclopentadienyl group. They are previously known in the art having been described by WO 98/50392, and elsewhere. Preferred phosphole ligands correspond to the formula:



wherein R''' is as previously defined.

Preferred L and L' groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydrofluorenyl and octahydrofluorenyl groups, optionally substituted with one or more hydrocarbyl, halo, halohydrocarbyl, dihydrocarbylamino, alkanediylamino, or silyl ligand groups and containing up to 30 atoms other than hydrogen. A particularly preferred L or L' group is the 2-methyl-4-phenylinden-1-yl group.

Suitable Z groups for use herein include carbon, silicon, germanium, aluminum, nitrogen, oxygen and/or boron containing divalent bridging groups containing up to 20 atoms other than hydrogen. Examples include divalent ligands corresponding to the following formulas:

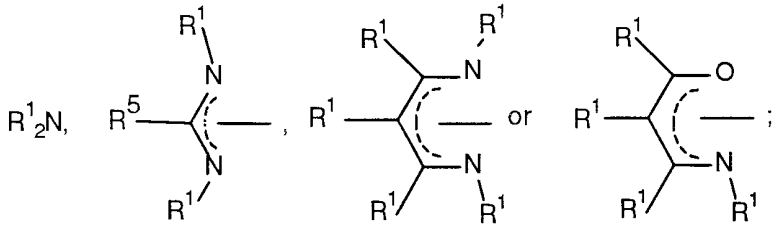


Formula 1 or Formula 2

wherein:

Z" is boron or aluminum;

T independently each occurrence is:



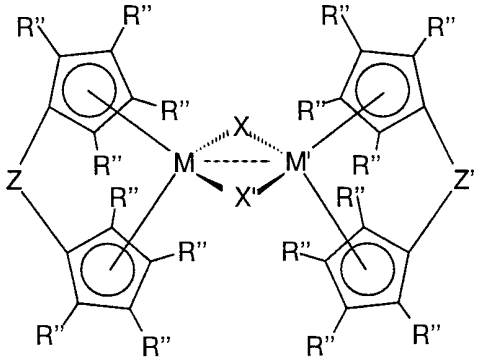
R^1 is independently each occurrence hydrogen, a hydrocarbyl group, a trihydrocarbylsilyl group, or a trihydrocarbylsilylhydrocarbyl group, said R^1 groups containing up to 20 atoms not counting hydrogen, and two such R^1 groups may optionally be joined together to form a ring structure; and

R^5 is R^1 or $N(R^1)_2$.

Preferred Z groups are those corresponding to the formula BNR'''_2 or $(ER'''_2)_r$ wherein E is carbon, silicon or germanium, R''' independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, or two R''' groups together form a ring system, said R''' having up to 30 atoms other than hydrogen, and r is an integer from 1 to 8. Preferably R''' independently each occurrence is hydrogen, methyl, methoxy, benzyl, tert-butyl or phenyl. Most highly preferred Z and Z' are both dimethylsilanediyl, dimethylamidoborane, or 1,2-ethanediyl. Preferably, z and z' are both 1.

Preferred Group 4 metals include zirconium and hafnium, most preferably zirconium. Preferred X groups are halide or C_{1-10} hydrocarbyl, most preferably X each occurrence is methyl or chloride.

A preferred class of Group 4 metal compounds according to the present invention corresponds to the formula:



wherein:

M and M' are both zirconium or hafnium;

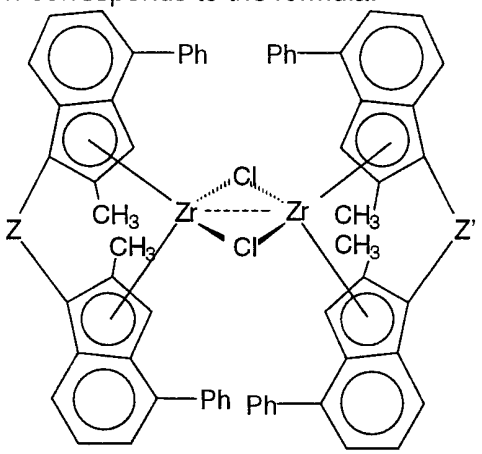
R" in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, halohydrocarbyl, N,N-dialkylamino, and alkanediylamino,

said R" having up to 20 atoms, not counting hydrogen, or adjacent R" groups are joined together thereby forming a fused ring system,

X and X' each occurrence are methyl or halide; and

Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^*{=}CR^*$, $CR^*_2SiR^*_2$, BNR^*_2, or GeR^*_2, wherein R* independently each occurrence is C_{1-6} alkyl or C_{6-10} aryl, or optionally two R* groups are joined together.

A most preferred class of Group 4 metal compounds according to the present invention corresponds to the formula:



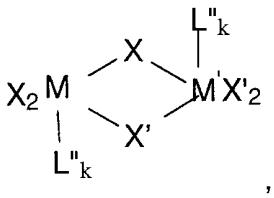
wherein:

Ph is phenyl, and

Z and Z' are each dimethylsilane, dimethylamidoborane or 1,2-ethanediyl.

The metal complexes exist as a mixture of two diastereomers and are suitably employed in an olefin polymerization in such form, or alternatively, the two isomers may be separated by standard techniques such as fractional crystallization.

The foregoing Group 4 metal complexes are readily prepared by reacting a dimeric compound corresponding to the formula:



,

wherein

M, M', X, and X' are as previously defined,

L" is a Lewis base, and

k is a number from 0 to 3

with two equivalents of a metallated ligand corresponding to the formula: MeL, MeL', MeL-Z-LMe, or MeL'-Z'-L'Me,

wherein,

L, L', Z, and Z' are as previously defined, and

Me is an alkali metal or Grignard.

The initial dimeric reagent for the process may be prepared by a process comprising contacting in any order, in an inert diluent, and optionally in the presence of a Lewis base, a Group 4 metal complex corresponding to the formula, MX_4, $MX_4(L)_k$ (or mixtures with compounds of the formula: $M'X'_4$ or $M'X'_4(L)_k$) with a reducing agent. Highly preferably, the reducing agent in the foregoing process is an alkali metal or alkali metal alkyl, most preferably lithium or lithium alkyl, such as n-butyl lithium, and the inert diluent is a hydrocarbon liquid, most preferably an aliphatic or aromatic hydrocarbon. Also, preferably, the reaction is conducted in the presence of a trihydrocarbyl phosphine as a Lewis base.

In general, both of the foregoing processes involve combining the respective reactants, preferably in a solution, optionally while agitating and/or heating above ambient temperature (25°C). Recovery and purification of the intermediate products when a multiple step reaction is employed may be desirable, but is not required. The process preferably is conducted in an inert, noninterfering solvent at a temperature from -100°C to 300°C, preferably from -78 to 130°C, most preferably from -40 to 120°C.

Suitable inert, noninterfering solvents for the formation of the complexes are aliphatic and aromatic hydrocarbons and halohydrocarbons, ethers, and cyclic ethers. 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; aromatic and hydrocarbyl-substituted aromatic compounds such as benzene, toluene, and xylene, C_{1-4} dialkyl ethers, C_{1-4} dialkyl ether derivatives of (poly)alkylene glycols, and tetrahydrofuran. Mixtures of solvents from the foregoing list are also suitable.

The recovery procedure involves separation of the resulting byproducts and devolatilization of the reaction medium. Extraction into a secondary solvent may be employed if desired. Alternatively, if the desired product is an insoluble precipitate, filtration or other separation technique may be employed.

The complexes are rendered catalytically active by combination with an activating cocatalyst or by use of an activating technique. Suitable activating cocatalysts for use herein include polymeric or oligomeric alumoxanes, especially methylalumoxane, triisobutyl aluminum modified methylalumoxane, or isobutylalumoxane. Other activators can generally be used, optionally after alkylation

or other technique is employed to produce a complex having an abstractable ligand group. Examples of other activators include neutral Lewis acids, such as C_{1-30} hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 20 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluorophenyl)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-, sulfonium-, 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: US-A-5,132,380, 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, and WO-97/04234, equivalent to USSN 08/818,530, filed March 14, 1997.

Combinations of neutral Lewis acids, especially the combination of a trialkyl aluminum 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 also suitable activating cocatalysts.

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

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

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

wherein:

L* is a neutral Lewis base;

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

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

d is an integer from 1 to 3.

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

wherein:

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

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, halohydrocarbyl, halocarbyl, hydrocarbyloxide, hydrocarbyloxy substituted-hydrocarbyl, organometal substituted-hydrocarbyl, organometalloid substituted-hydrocarbyl, halohydrocarbyloxy, halohydrocarbyloxy substituted hydrocarbyl, halocarbyl- substituted hydrocarbyl, 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 hydrocarbyloxide 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:

$(L^*\text{-}H)^+(BQ_4)^-$;

wherein:

L* is as previously defined;

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

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

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

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

tri-substituted ammonium salts such as:

trimethylammonium tetraphenylborate,

methyldioctadecylammonium tetraphenylborate,

triethylammonium tetraphenylborate,

tripropylammonium tetraphenylborate,

tri(n-butyl)ammonium tetraphenylborate,

methyltetradecyloctadecylammonium tetraphenylborate,

N,N-dimethylanilinium tetraphenylborate,

N,N-diethylanilinium tetraphenylborate,

N,N-dimethyl(2,4,6-trimethylanilinium) tetraphenylborate,

trimethylammonium tetrakis(pentafluorophenyl)borate,

methylditetradecylammonium tetrakis(pentafluorophenyl)borate,

methyldioctadecylammonium 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-diethylanilinium tetrakis(pentafluorophenyl)borate,

N,N-dimethyl(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate,

trimethylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate,

triethylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate,

tripropylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate,

tri(n-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate,

dimethyl(t-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate,
N,N-dimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl)borate,
N,N-diethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl)borate, and
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate;

dialkyl ammonium salts such as:
dioctadecylammonium tetrakis(pentafluorophenyl)borate,
ditetradecylammonium tetrakis(pentafluorophenyl)borate, and
dicyclohexylammonium 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.

Preferred are tetrakis(pentafluorophenyl)borate salts of long chain alkyl mono- and disubstituted ammonium complexes, especially C_{14}-C_{20} alkyl ammonium complexes, especially methyldi(octadecyl)ammonium tetrakis(pentafluorophenyl)borate and methyldi(tetradecyl)-ammonium tetrakis(pentafluorophenyl)borate, or mixtures including the same Such mixtures include protonated ammonium cations derived from amines comprising two C_{14}-, C_{16}- or C_{18}- alkyl groups and one methyl group. Such amines are available from Witco Corp., under the trade name Kemamine™ T9701, and from Akzo-Nobel under the trade name Armeen™ M2HT.

Another suitable ammonium salt, especially for use in heterogeneous catalyst systems is formed upon reaction of a organometal compound, especially a tri(C_{1-6}alkyl)aluminum compound with an ammonium salt of a hydroxyaryltris(fluoroaryl)borate compound. The resulting compound is an organometaloxyaryltris(fluoroaryl)borate compound which is generally insoluble in aliphatic liquids. Typically, such compounds are advantageously precipitated on support materials, such as silica, alumina or trialkylaluminum passivated silica, to form a supported cocatalyst mixture. Examples of suitable compounds include the reaction product of a tri(C_{1-6} alkyl)aluminum compound with the ammonium salt of hydroxyaryltris(aryl)borate. Suitable hydroxyaryltris(aryl)-borates include the ammonium salts, especially the foregoing long chain alkyl ammonium salts of:
(4-dimethylaluminumoxy-1-phenyl)tris(pentafluorophenyl)borate,
(4-dimethylaluminumoxy-3,5-di(trimethylsilyl)-1-phenyl)tris(pentafluorophenyl)borate,
(4-dimethylaluminumoxy-3,5-di(t-butyl)-1-phenyl)tris(pentafluorophenyl)borate,
(4-dimethylaluminumoxy-1-benzyl)tris(pentafluorophenyl)borate,

(4-dimethylaluminumoxy-3-methyl-1-phenyl)tris(pentafluorophenyl)borate,
(4-dimethylaluminumoxy-tetrafluoro-1-phenyl)tris(pentafluorophenyl)borate,
(5-dimethylaluminumoxy-2-naphthyl)tris(pentafluorophenyl)borate,
4-(4-dimethylaluminumoxy-1-phenyl)phenyltris(pentafluorophenyl)borate,
4-(2-(4-(dimethylaluminumoxyphenyl)propane-2-yl)phenyloxy)tris(pentafluorophenyl)borate,
(4-diethylaluminumoxy-1-phenyl)tris(pentafluorophenyl)borate,
(4-diethylaluminumoxy-3,5-di(trimethylsilyl)-1-phenyl)tris(pentafluorophenyl)borate,
(4-diethylaluminumoxy-3,5-di(t-butyl)-1-phenyl)tris(pentafluorophenyl)borate,
(4-diethylaluminumoxy-1-benzyl)tris(pentafluorophenyl)borate,
(4-diethylaluminumoxy-3-methyl-1-phenyl)tris(pentafluorophenyl)borate,
(4-diethylaluminumoxy-tetrafluoro-1-phenyl)tris(pentafluorophenyl)borate,
(5-diethylaluminumoxy-2-naphthyl)tris(pentafluorophenyl)borate,
4-(4-diethylaluminumoxy-1-phenyl)phenyltris(pentafluorophenyl)borate,
4-(2-(4-(diethylaluminumoxyphenyl)propane-2-yl)phenyloxy)tris(pentafluorophenyl)borate,
(4-diisopropylaluminumoxy-1-phenyl)tris(pentafluorophenyl)borate,
(4-diisopropylaluminumoxy-3,5-di(trimethylsilyl)-1-phenyl)tris(pentafluorophenyl)borate,
(4-diisopropylaluminumoxy-3,5-di(t-butyl)-1-phenyl)tris(pentafluorophenyl)borate,
(4-diisopropylaluminumoxy-1-benzyl)tris(pentafluorophenyl)borate,
(4-diisopropylaluminumoxy-3-methyl-1-phenyl)tris(pentafluorophenyl)borate,
(4-diisopropylaluminumoxy-tetrafluoro-1-phenyl)tris(pentafluorophenyl)borate,
(5-diisopropylaluminumoxy-2-naphthyl)tris(pentafluorophenyl)borate,
4-(4-diisopropylaluminumoxy-1-phenyl)phenyltris(pentafluorophenyl)borate, and
4-(2-(4-(diisopropylaluminumoxyphenyl)propane-2-yl)phenyloxy)tris(pentafluorophenyl)borate.

An especially preferred ammonium compound is methylditetradecylammonium (4-diethylaluminumoxy-1-phenyl)tris(pentafluorophenyl)borate, methyldihexadecylammonium (4-diethylaluminumoxy-1-phenyl)tris(pentafluorophenyl)borate, methyldioctadecyl-ammonium (4-diethylaluminumoxy-1-phenyl)tris(pentafluorophenyl)borate, and mixtures thereof. The foregoing complexes are disclosed in US-A-5,834,393 and US-A-5,783,512.

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

$(Ox^{e+})_d (A'^{d-})_e$, wherein

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

e is an integer from 1 to 3; and

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

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

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

$$©^{+} A'^{-}$$

wherein:

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

A'^{-} is a noncoordinating, compatible anion having a charge of -1. A preferred carbenium ion is the trityl cation, especially triphenylmethylium.

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

$$R_3Si^{+}A'^{-}$$

wherein:

R is C_{1-10} hydrocarbyl; and

A'^{-} is as previously defined.

Preferred silylium salt activating cocatalysts are trimethylsilylium tetrakispentafluorophenylborate, triethylsilylium tetrakispentafluorophenylborate and ether substituted adducts thereof. Silylium salts have been previously generically disclosed in J. Chem Soc. Chem. Comm., 1993, 383-384, as well as Lambert, J. B., et al., Organometallics, 1994, 13, 2430-2443. The use of the above silylium salts as activating cocatalysts for addition polymerization catalysts is claimed in US-A-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 US-A-5,296,433.

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 10:1, 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 preferably employed in large molar ratio, generally at least 100 times the quantity of metal complex on a molar basis. Tris(pentafluorophenyl)borane, where used as an activating cocatalyst is preferably 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 preferably employed in approximately equimolar quantity with the metal complex of its alkylated derivative.

Suitable addition polymerizable monomers for use with the foregoing novel catalyst compositions include ethylenically unsaturated monomers, acetylenic compounds, conjugated or non-conjugated dienes, and polyenes. Preferred monomers include olefins, for example alpha-olefins having from 2 to 20,000, preferably from 2 to 20, more preferably from 2 to 8 carbon atoms and combinations of two or more of such alpha-olefins. Particularly suitable alpha-olefins include, for example, ethylene, propylene, 1-butene, isobutylene, 1-pentene, 4-methylpentene-1, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, or combinations thereof, as well as long chain vinyl terminated oligomeric or polymeric reaction products formed during the polymerization, and C_{10-30} α-olefins specifically added to the reaction mixture in order to produce relatively long chain branches in the resulting polymers. Preferably, the alpha-olefins are ethylene, propylene, 1-butene, 1-pentene, 4-methyl-pentene-1, 1-hexene, 1-octene, and combinations of ethylene and/or propene with one or more other alpha-olefins. Other preferred monomers include styrene, halo- or alkyl substituted styrenes, vinylbenzocyclobutene, 1,4-hexadiene, dicyclopentadiene, ethylidene norbornene, and 1,7-octadiene. Mixtures of the above-mentioned monomers may also be employed.

In general, the polymerization may be accomplished under conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions. Suspension, solution, slurry, gas phase or high pressure, whether employed in batch or continuous form or other process conditions, may be employed if desired. Examples of such well known polymerization processes are depicted in WO 88/02009, US-A-5,084,534, US-A-5,405,922, US-A-4,588,790, US-A-5,032,652, US-A-4,543,399, US-A-4,564,647, US-A-4,522,987, and elsewhere. Preferred polymerization temperatures are from 0-250°C. Preferred polymerization pressures are from atmospheric to 3000 atmospheres.

Preferred processing conditions include solution polymerization, more preferably continuous solution polymerization processes, conducted in the presence of an aliphatic or alicyclic liquid diluent. By the term "continuous polymerization" is meant that at least the products of the polymerization are continuously removed from the reaction mixture. Preferably one or more reactants are also continuously added to the polymerization mixture during the polymerization. Examples of suitable aliphatic or alicyclic liquid diluents include straight and branched-chain C_{4-12} hydrocarbons and mixtures thereof; alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; and perfluorinated hydrocarbons such as perfluorinated C_{4-10} alkanes. Suitable diluents also include aromatic hydrocarbons (particularly for use with aromatic α-olefins such as styrene or ring alkyl-substituted styrenes) including toluene, ethylbenzene or xylene, as well as liquid olefins (which may act as monomers or comonomers) including ethylene, propylene, 1-butene, isobutylene, butadiene, 1-pentene, cyclopentene, 1-hexene, cyclohexene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, vinyltoluene (including all isomers alone or in admixture). Mixtures of the foregoing are also suitable. The foregoing diluents may also be advantageously employed during the synthesis of the metal complexes and catalyst activators of the present invention.

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.

Molecular weight control agents can be used in combination with the present cocatalysts. Examples of such molecular weight control agents include hydrogen, trialkyl aluminum compounds or other known chain transfer agents. A particular benefit of the use of the present cocatalysts is the ability (depending on reaction conditions) to produce narrow molecular weight distribution α-olefin homopolymers and copolymers in greatly improved catalyst efficiencies. Preferred polymers have Mw/Mn of less than 2.5, more preferably less than 2.3. Such narrow molecular weight distribution polymer products are highly desirable due to improved tensile strength properties.

The catalyst composition of the present invention can also be employed to advantage in the gas phase polymerization and copolymerization of olefins, preferably by supporting the catalyst composition by any suitable technique. Gas phase processes for the polymerization of olefins, especially the homopolymerization and copolymerization of ethylene and propylene, and the copolymerization of ethylene with higher alpha olefins such as, for example, 1-butene, 1-hexene, 4-methyl-1-

pentene are well known in the art. Such processes are used commercially on a large scale for the manufacture of high density polyethylene (HDPE), medium density polyethylene (MDPE), linear low density polyethylene (LLDPE) and polypropylene.

The gas phase process employed can be, for example, of the type which employs a mechanically stirred bed or a gas fluidized bed as the polymerization reaction zone. Preferred is the process wherein the polymerization reaction is carried out in a vertical cylindrical polymerization reactor containing a fluidized bed of polymer particles supported above a perforated plate, the fluidization grid, by a flow of fluidization gas.

The gas employed to fluidize the bed comprises the monomer or monomers to be polymerized, and also serves as a heat exchange medium to remove the heat of reaction from the bed. The hot gases emerge from the top of the reactor, normally via a tranquilization zone, also known as a velocity reduction zone, having a wider diameter than the fluidized bed and wherein fine particles entrained in the gas stream have an opportunity to gravitate back into the bed. It can also be advantageous to use a cyclone to remove ultra-fine particles from the hot gas stream. The gas is then normally recycled to the bed by means of a blower or compressor and one or more heat exchangers to strip the gas of the heat of polymerization.

A preferred method of cooling of the bed, in addition to the cooling provided by the cooled recycle gas, is to feed a volatile liquid to the bed to provide an evaporative cooling effect. The volatile liquid employed in this case can be, for example, a volatile inert liquid, for example, a saturated hydrocarbon having about 3 to about 8, preferably 4 to 6, carbon atoms. In the case that the monomer or comonomer itself is a volatile liquid or can be condensed to provide such a liquid, this can be suitably be fed to the bed to provide an evaporative cooling effect. Examples of olefin monomers which can be employed in this manner are olefins containing from about 3 to about eight, preferably from 3 to six carbon atoms. The volatile liquid evaporates in the hot fluidized bed to form gas which mixes with the fluidizing gas. If the volatile liquid is a monomer or comonomer, it may undergo some polymerization in the bed. The evaporated liquid then emerges from the reactor as part of the hot recycle gas, and enters the compression/heat exchange part of the recycle loop. The recycle gas is cooled in the heat exchanger and, if the temperature to which the gas is cooled is below the dew point, liquid will precipitate from the gas. This liquid is desirably recycled continuously to the fluidized bed. It is possible to recycle the precipitated liquid to the bed as liquid droplets carried in the recycle gas stream, as described, for example, in EP-A-89691, US-A-4543399, WO 94/25495 and US-A-5352749. A

particularly preferred method of recycling the liquid to the bed is to separate the liquid from the recycle gas stream and to reinject this liquid directly into the bed, preferably using a method which generates fine droplets of the liquid within the bed. This type of process is described in WO 94/28032.

The polymerization reaction occurring in the gas fluidized bed is catalyzed by the continuous or semi-continuous addition of catalyst. Such catalyst can be supported on an inorganic or organic support material if desired. The catalyst can also be subjected to a prepolymerization step, for example, by polymerizing a small quantity of olefin monomer in a liquid inert diluent, to provide a catalyst composite comprising catalyst particles embedded in olefin polymer particles.

The polymer is produced directly in the fluidized bed by catalyzed (co)polymerization of the monomer(s) on the fluidized particles of catalyst, supported catalyst or prepolymer within the bed. Start-up of the polymerization reaction is achieved using a bed of preformed polymer particles, which, preferably, is similar to the target polyolefin, and conditioning the bed by drying with a dry inert gas such as nitrogen prior to introducing the catalyst, the monomer(s) and any other gases which it is desired to have in the recycle gas stream, such as a diluent gas, hydrogen chain transfer agent, or an inert condensable gas when operating in gas phase condensing mode. The produced polymer is discharged continuously or discontinuously from the fluidized bed as desired, optionally exposed to a catalyst kill and optionally pelletized.

For polymerization of higher olefins such as propylene to produce polypropylene slightly different reaction conditions may be employed. The polymerization is generally conducted under continuous or semicontinuous slurry polymerization conditions in hydrocarbons such as propylene, propane, butene, butane, pentane, butene-2, isobutane, hexane, heptane, and mixtures of the foregoing, generally at temperatures from 50 to 100 °C, and pressures from atmospheric to 1MPa. The polymerization may be conducted in one or more continuous stirred tank tubular reactors or fluidized bed, gas phase reactors, connected in series or parallel. Condensed monomer or solvent may be added to the gas phase reactor as is well known in the art. The catalyst may also be supported and/or prepolymerized prior to use.

In a continuous reaction system, the reaction mixture is typically maintained at conditions at which the polymer is produced as a slurry of powder in the reaction mixture. Use of highly active and highly stereospecific catalyst systems in propylene polymerization substantially eliminates the need to remove catalyst components or atactic polymer from the polymer product. The mixture of reaction components is fed

continuously or at frequent intervals into the reactor system and is continuously monitored so as to ensure an efficient reaction and the desired product. For example, it is well known that supported coordination catalysts and catalyst systems of the type described above are highly sensitive, in varying degrees, to catalyst poisons such as water, oxygen, carbon oxides, acetylenic compounds and sulfur compounds. Introduction of such compounds may result in reactor upset and production of off-grade product. Typically, computer control systems are used to maintain process variables within acceptable limits, often by measuring polymer variables such as viscosity, density and tacticity, or catalyst productivity.

In the process, reactants and diluents, which may be a mixture of propylene, hydrogen, nitrogen, unreacted comonomers and inert hydrocarbons, are continuously recycled through the reactor, optionally with scavenging to remove impurities and condensation to remove the heat of polymerization. Catalyst and cocatalysts, fresh monomer or comonomer(s) and selectivity control agents, branching agents or chain transfer agents, if desired, are likewise continuously fed to the reactor. The polymer product is continuously or semi-continuously removed and volatile components removed and recycled. Suitable processes for preparing polypropylene polymers are known in the art and illustrated by those taught in US-A-4,767,735, US-A-4,975,403, and US-A-5,084,513, among others.

Utilizing the catalysts of the present invention, copolymers having high comonomer incorporation and correspondingly low density, yet having a low melt index, may be readily prepared. That is, high molecular weight polymers are readily attained by use of the present catalysts, even at elevated reactor temperatures. This result is highly desirable because the molecular weight of α-olefin copolymers can be readily reduced by the use of hydrogen or similar chain transfer agent, however increasing the molecular weight of α-olefin copolymers is usually only attainable by reducing the polymerization temperature of the reactor. Disadvantageously, operation of a polymerization reactor at reduced temperatures significantly increases the cost of operation since heat must be removed from the reactor to maintain the reduced reaction temperature, while at the same time heat must be added to the reactor effluent to vaporize the solvent. In addition, productivity is increased due to improved polymer solubility, decreased solution viscosity, and a higher polymer concentration. Utilizing the present catalysts, α-olefin homopolymers and copolymers having densities from 0.85 g/cm^3 to 0.96 g/cm^3, and melt flow rates from 0.001 to 1000 dg/min are readily attained in a high temperature process.

The catalyst system may be prepared as a homogeneous catalyst by addition of the requisite components to a solvent in which polymerization will be carried out by solution polymerization procedures. The catalyst system may also be prepared and employed as a heterogeneous catalyst by adsorbing the requisite components on a catalyst support material such as silica, alumina, aluminosilicates, or other suitable inorganic support material, or a polymer, such as preformed olefin polymer. A preferred support material is silica that has been heated (calcined) to 200 to 800 °C for a time sufficient to remove substantially all surface water and thereafter reacted with a Lewis acid, especially a C_{1-6} trialkylaluminum compound to react substantially all available hydroxyl groups. The heterogeneous form of the catalyst system is employed in a slurry polymerization. As a practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization is one or more hydrocarbons with less than 5 carbon atoms. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. Likewise the α-olefin monomer or a mixture of different α-olefin monomers may be used in whole or part as the diluent. Most preferably the diluent comprises in at least major part the α-olefin monomer or monomers to be polymerized.

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

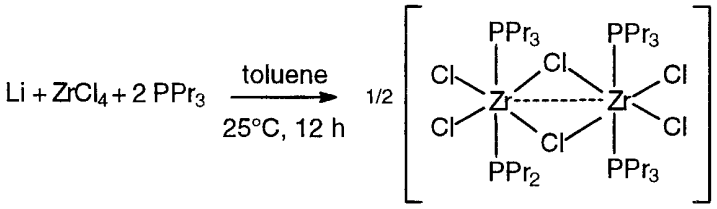
It is understood that the present invention is operable in the absence of any component which has not been specifically disclosed. The following examples are provided in order to further illustrate the invention and are not to be construed as limiting. Unless stated to the contrary, all parts and percentages 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 about 20-25 °C, and "mixed alkanes" refers to a mixture of hydrogenated propylene oligomers, mostly C_6-C_{12} isoalkanes, available commercially under the trademark Isopar E™ from Exxon Chemicals Inc.

Tetrahydrofuran (THF), diethylether, toluene, and other solvents were used following passage through double columns charged with activated alumina and alumina supported mixed metal oxide catalyst (Q-5® catalyst, available from Engelhard Corp.) Grignard reagents, n-BuLi, MAO, and metal halides, if recited, were

all used as purchased from the supplier. All syntheses were performed under dry nitrogen or argon atmosphere using a combination of glove box and high vacuum techniques. All chemical shifts for ^{31}P NMR spectra were relative to a fixed external standard (H_3PO_4) in benzene-d_6 or toluene-d_8, both of which were dried over Na/K alloy and filtered or distilled prior to use. ^{1}H and ^{13}C NMR shifts were referenced to internal solvent resonances and are reported relative to TMS.

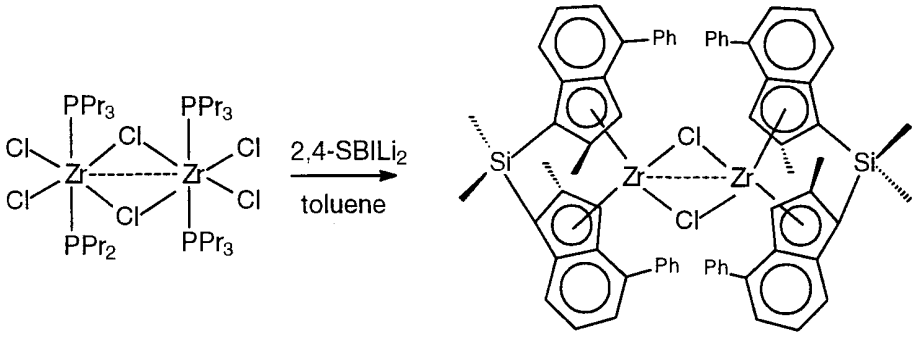
Example 1 dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro zirconium (III) dimer

Step A Preparation of zirconium (III) trichloride bis(tri-n-propylphosphine) dimer



In a glove box, lithium powder (0.309 g, 44.47 mmol, low sodium) was added to a toluene solution of zirconium tetrachloride·(tri-n-propylphosphine)$_2$ adduct (prepared from a dropwise addition of 8.9 mL (44.47 mmol) tri-n-propylphosphine to a suspension of 5.18 g (22.24 mmol) $ZrCl_4$ in 100 mL of toluene) and the mixture was then stirred for 12 h at room temperature. The resulting dark green suspension was filtered through a glass frit using diatomaceous earth filter aid. The volatile components were removed under reduced pressure to afford 10.53 g of the product as a green solid. Both ^{1}H and ^{31}P NMR spectra indicated the desired pure product without any further purification. Yield: 91.4 percent. ^{1}H NMR (C_6D_6): δ 2.06 (s, br, 12 H, CH_2), 1.69 (s, br, 12 H, CH_2), 0.97 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 18 H, CH_3). ^{31}P NMR (C_6D_6): δ -9.66 (s).

Step B Preparation of dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro zirconium (III) dimer



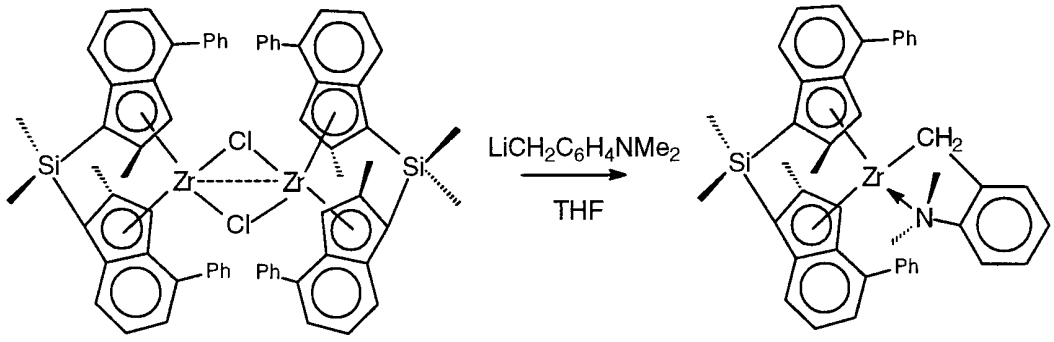
In a glove box, dimethylsilanebis(2-methyl-4-phenylindenyl)dilithium salt (2,4-SBILi$_2$) (1.922 g, 4.00 mmol) was suspended in 80 mL toluene in a flask and the

mixture was cooled to -35°C in the freezer. To this suspension was added solid $[ZrCl_3(n\text{-}Pr_3P)_2]_2$ (2.07 g, 2.00 mmol) in small portions and the mixture was stirred at room temperature for 4 h. The resulting dark red suspension was filtered through a glass frit using diatomaceous earth filter aid and the volatile components were removed under reduced pressure. Hexane (20 mL) was added to the resulting sticky red residue and stirred for 10 min, and then filtered. The solid which collected by filtration was washed with hexane (2 x 5 mL) and dried under vacuum for overnight to produce a greenish brown solid (1.88 g, 80 percent yield). NMR spectra of this crude product indicated the formation of a mixture of two diastereomers with a 1:1.2 molar ratio. There was some residual $n\text{-}Pr_3P$ present in the product based on ^{31}P NMR. The crude material was then redissolved in toluene and filtered. The solvent was removed under reduced pressure and the residue was taken up hexane. The resulting slurry was filtered and the brown solid which collected was dried at 40°C for few hours. The corresponding NMR spectra indicated a clean product (a mixture of diastereomers believed to be rac-rac and meso-meso in a molar ratio of 1:1.5) with interaction between zirconium atoms. There was no phosphine residue detected by ^{31}P NMR.

^1H NMR (C_6D_6, 23°C) for diastereomer A (40 percent): δ 7.84 (d, $J_{H\text{-}H}$ = 7.8 Hz, 8 H, C_6-ring H), 7.30 (d, $J_{H\text{-}H}$ = 8.7 Hz, 4 H, C_6-ring H), 7.23-6.95 (m, 20 H, C_6-ring H), 6.86 (t, $J_{H\text{-}H}$ = 6.9 Hz, 4 H, C_5-ring H), 2.01 (s, 12 H, Cp-Me), 0.77 (s, 12 H, $SiMe_2$). Diastereomer B (60 percent): δ 7.79 (d, $J_{H\text{-}H}$ = 7.8 Hz, 8 H, C_6-ring H), 7.42 (d, $J_{H\text{-}H}$ = 8.7 Hz, 4 H, C_6-ring H), 7.23-6.95 (m, 20 H, C_6-ring H), 6.72 (t, $J_{H\text{-}H}$ = 6.9 Hz, 4 H, C_5-ring H), 2.13 (s, 12 H, Cp-Me), 0.93 (s, 6 H, $SiMe_2$), 0.68 (s, 6 H, $SiMe_2$). ESR in toluene, g value= 1.973.

Further syntheses

1. Preparation of dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)(α-dimethylamino)benzyl zirconium

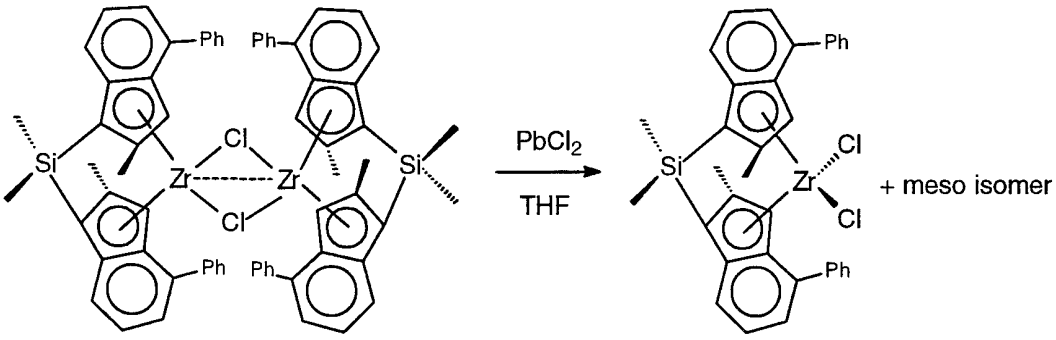


two diastereomers

two diastereomers

In a glove box, dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro zirconium dimer (0.355 g, 0.30 mmol) was dissolved in 20 mL THF in a flask and α-dimethylamino benzyl lithium (0.085, 0.60 mmol) was added in solid. The mixture was stirred at room temperature for overnight. The solvent of the resulting dark red suspension was removed under reduced pressure and the residue was extracted with 20 mL of toluene. The slurry was filtered through a glass frit using diatomaceous earth filter aid and the volatile components were removed under reduced pressure. Hexane (20 mL) was added to the resulting residue and stirred for 10 min, and then filtered. The solid which collected by filtration was washed with hexane (2 x 5 mL) and dried under vacuum for overnight to produce a brown solid (0.18 g, 44 percent yield). NMR spectra showed only broad peaks.

2) Oxidation of dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro zirconium dimer



two diastereomers

In a glove box, dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro zirconium dimer (0.355 g, 0.30 mmol) was dissolved in 20 mL THF in a flask and lead dichloride (0.10 g, 0.36 mmol) was added in solid. The mixture was stirred at room temperature for 2 h and the formation of lead metal was gradually visible. The solvent of the resulting yellow suspension was removed under reduced pressure and the residue was extracted with 20 mL of toluene. The slurry was filtered through a glass frit using diatomaceous earth filter aid and the volatile components were removed under reduced pressure. Hexane (20 mL) was added to the resulting residue and stirred for 10 min, and then filtered. The solid which collected by filtration was washed with hexane (2 x 5 mL) and dried under vacuum to 0.31 g of the product as an orange solid (84 percent yield). NMR spectra indicated formation of a mixture of racemic and meso isomers in a 1:1.2 ratio.

Polymerizations

All 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 and cocatalysts are handled in a glovebox containing an atmosphere of argon or nitrogen. A stirred 2.0 liter reactor is charged with about 740 g of mixed alkanes solvent and 119 g of 1-octene comonomer. Hydrogen is added as a molecular weight control agent by differential pressure expansion from a 75 ml addition tank at 25 psi (2070 kPa). The reactor is heated to the polymerization temperature of 140 °C and saturated with ethylene at 500 psig (3.4 MPa). Catalysts and activator (methylalumoxane, MAO), as dilute solutions in toluene, were mixed and transferred to a catalyst addition tank and injected into the reactor. 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 10 ml of a toluene solution containing approximately 67 mg of a hindered phenol antioxidant (Irganox™ 1010 from Ciba Geigy Corporation) and 133 mg of a phosphorus stabilizer (Irgafos™ 168 from Ciba Geigy Corporation.

Between polymerization runs a wash cycle in which 850 g of mixed alkanes is added to the reactor and the reactor heated to 150 °C was conducted. 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 about 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	μmoles catalyst/ activator	Exo-therm (°C)	Yield (g)	Efficiency (g polymer/ μmole metal)	Den-sity (g/cm^3)	MMI** (dg/min)	Tm, Tc (°C)
A*	CGC-$TiCl_2$	2.5/ 2500	8.7	64.1	25.6	0.910	4.5	
1	Ex. 1	2.5/ 2500	39.1	197.7	79.1	0.876	37.1	
2	"	1/ 1000	19.3	169.8	169.8	0.878	14.2	
3	"	0.5/ 500	5.3	125.1	250.2	0.884	8.0	86.8, 69.6
B*	CGC-$TiCl_2$	2.5/ 2500	7.6	64.8	25.9	0.910	11.0	104.4, 85.5

• ((t-butylamido)(tetramethylcyclopentadienyl)titanium dichloride, comparative, not an example of the invention

** melt index, determined by comparison to known standards using micromelt index technique

Propylene Homopolymerization

The previous polymerization conditions were substantially repeated using the 2-liter Parr reactor charged with about 600 g of Isopar-E™ mixed alkanes solvent and 150 g of propylene. Hydrogen was added as a molecular weight control agent by differential pressure expansion form a 75 ml addition tank at 25 psi. The reactor was heated to the indicated polymerization temperature (70 or 90 °C) and catalyst and cocatalyst (MAO) mixed and transferred to a catalyst addition tank and injected into the reactor.

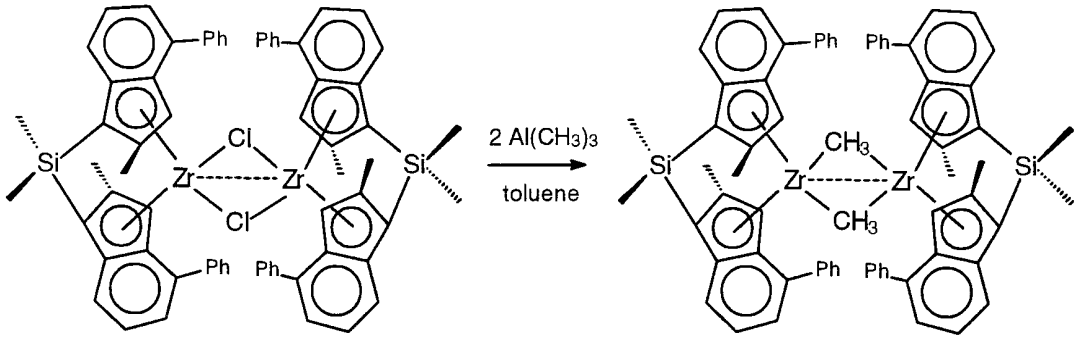
The polymerization conditions were maintained for 10 min. The resulting solution is removed from the reactor, quenched with isopropyl alcohol, and stabilized by addition of 10 mL of a toluene solution containing approximately 67 mg of a hindered phenol antioxidant (Irganox™ 1010 from Ciba Geigy Corporation) and 133 mg of a phosphorus stabilizer (Irgafos™ 168 from Ciba Geigy Corporation) were then added. The polymers were recovered by devolatilization at 120 °C for approximately 20 hours. Results are contained in Table 2.

Table 2

run	Catalyst	μmoles catalyst/ activator	Temp. (°C)	Yield (g)	Efficiency (g polymer/ μmole metal)	Tm (°C)
4	Ex. 1	0.5/ 500	70	65.0	130	157.1
5	Ex. 1	0.5/ 500	90	74.0	148	156.4
6	Ex. 1	0.5/ 500	70	60.2	121	157.3
D*	CE*	2.0/ 2.0	70	32.2	16.1	159.1

* comparative, not an example of the invention; catalyst = (rac-dimethylsilane bis(2-methyl-4-phenylindenyl)zirconium 1,4-diphenylbutadiene, prepared according to US-A-5,616,664 and activator dioctadecylmethylammonium 1,3-bis(tris(pentafluorophenyl) alumane)-2-undecylimidazolide, prepared according to U.S.S.N. 09/234831, filed January 21, 1999 (WO99/42467).

Example 2 Preparation of dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)methyl zirconium dimer ((2,4-SBI)ZrMe dimer)

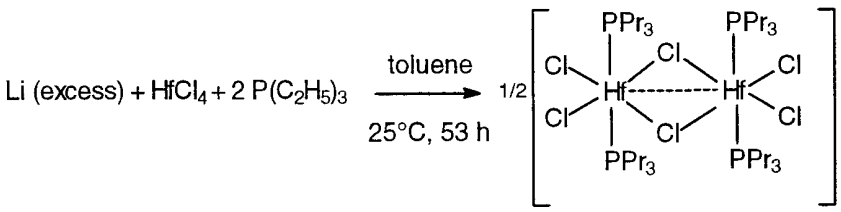


two diastereomers two diastereomers

In a glove box, dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro zirconium dimer (0.353 g, 0.30 mmol) was dissolved in 15 mL toluene in a flask and trimethyl aluminum (2.0 M in toluene, 0.3 mL, 0.60 mmol) was added via syringe. The mixture was stirred at room temperature for 2 h and filtered through a glass frit using diatomaceous earth filter aid. The solvent was removed under reduced pressure and the residue was extracted with 20 mL of hexane and filtered after stirring for 0.5 h. The solvent of the resulting green solution was reduced and cooled to –40 °C, affording a brown solid. ^{1}H- and ^{13}C-NMR analyses of this solid indicated a mixture of species. This product was discarded. The green solid that remained after filtration and solvent removal was dried under reduced pressure. Examination by ^{1}H NMR indicated the substance was the desired product. Yield: 0.232 g, 68.2 percent. Further recrystallization was carried out by layering hexane onto a toluene solution of the product which was retained in a freezer at –40 °C for several days. Dark green crystals were recovered. Analysis by ^{1}H NMR spectroscopy showed the product to be a mixture of two diastereomers.

Example 3 Dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro hafnium (III) dimer

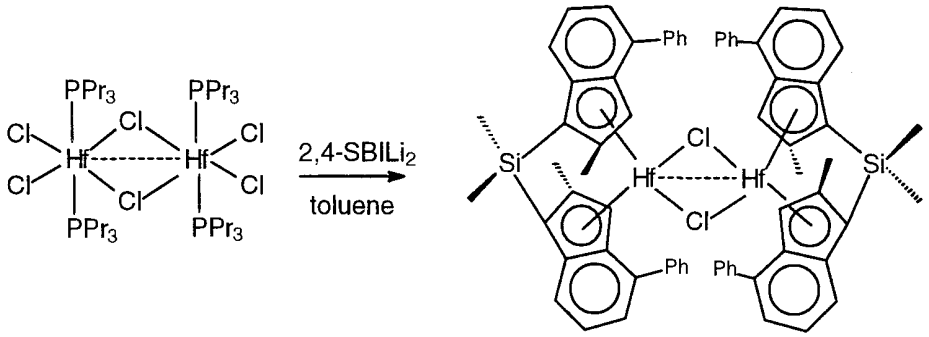
Step A Preparation of hafnium (III) trichloride bis(triethylphosphine) dimer



In a glove box, lithium powder (0.309 g, 44.47 mmol, low sodium) was added to a toluene solution of zirconium tetrachloride·(triethylphosphine)$_2$ adduct (prepared

from a dropwise addition of 6.57 mL (44.48 mmol) triethyllphosphine to a suspension of 7.12 g (22.24 mmol) $HfCl_4$ in 100 mL of toluene) and the mixture was then stirred for 22 h at room temperature. NMR spectra of a reaction aliquot indicated incomplete reaction. Another two equivalents of Li was added and the mixture was stirred for another 23 h. The reaction was still not complete, and another 2 equiv. of Li was then added and the mixture was stirred for 7 h (total 6 equiv. of Li, stirring for 53 h). The resulting dark suspension was filtered through a glass frit using diatomaceous earth filter aid and the volatile components were removed under reduced pressure. After washing with cold hexane and further drying under reduced pressure, 4.67 g of the product as a dark green solid was recovered. The crude product was further recrystallized from hexane at –40 °C to afford dark green crystals suitable for X-ray diffraction studies. ^1H NMR (C_6D_6): δ 2.05 (s, br, 24 H, CH_2), 1.13 (s, br, 36 H, CH_3). ^{31}P NMR (C_6D_6): δ -3.97 (s).

Step B Preparation of dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro hafnium (III) dimer



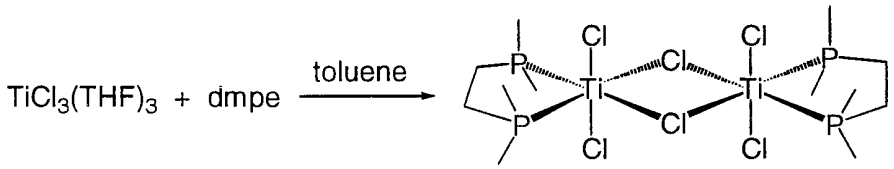
In a glove box, to a toluene (20 mL) suspension of dimethylsilanebis(2-methyl-4-phenylindenyl)dilithium salt (2,4-$SBILi_2$) (0.148 g, 0.31 mmol) in a flask was added solid $[ZrCl_3(Et_3P)_2]_2$ (0.16 g, 0.15 mmol) in small portions and the mixture was stirred at room temperature for 4 h. The resulting dark red suspension was filtered through a glass frit using diatomaceous earth filter aid and the volatile components were removed under reduced pressure. The residue was washed with 5 mL cold hexane and dried in vacuo to give 0.17 g of the product as a black solid (81.7 percent). Analysis by NMR spectroscopy indicated formation of a mixture of two diastereomers in a 1:1 ratio.

Spectroscopic data for $[Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}\eta^5\text{-}Ind)_2HfCl]_2$ are as follows. ^1H NMR (C_6D_6, 23 °C) for two diastereomers exhibiting metal center interaction: δ 7.85, 7.82 (d, $J_{H\text{-}H}$ = 7.8 Hz, 8 H, C_6-ring H), 7.42, 7.30 (d, $J_{H\text{-}H}$ = 8.7 Hz, 4 H, C_6-ring H),

7.23-6.95 (m, 20 H, C_6-ring H), 6.86, 6.71 (t, J_{H-H} = 6.9 Hz, 4 H, C_5-ring H), 2.25, 2.12 (s, 12 H, Cp-Me), 0.94, 0.79, 0.65 (s, 12 H, $SiMe_2$).

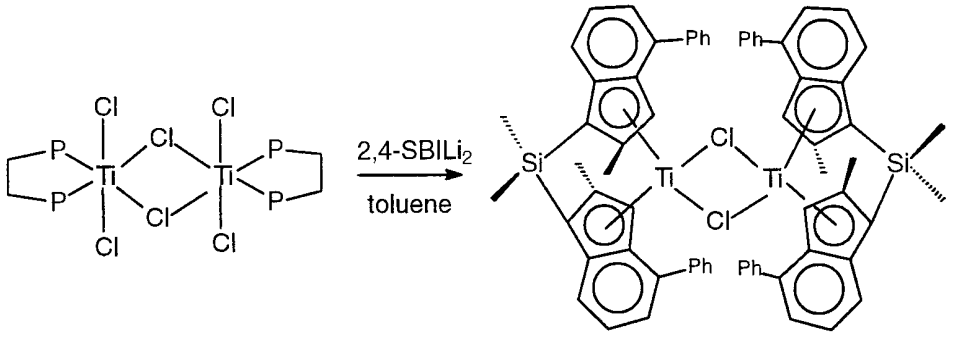
Example 4 Dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro titanium (III) dimer

Step A Preparation of titanium (III) trichloride bis(dmpe) dimer



In a glove box, $TiCl_3(THF)_3$ (0.342 g, 0.92 mmol) was suspended in 25 mL toluene and 1,2-ethanebis(dimethylphosphine) (dmpe) (0.269 mL, 1.61 mmol) was added. The resulting blue suspension was stirred at room temperature for 2 h and the mixture was then filtered through a glass frit using diatomaceous earth filter aid to afford a blue solution. Hexane (10 mL) was layered onto the solution and the mixture was cooled to -35 °C. Blue crystals were collected after filtration and drying under vacuum. Yield, 0.25 g (89 percent).

Step B Preparation of dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro titanium (III) dimer



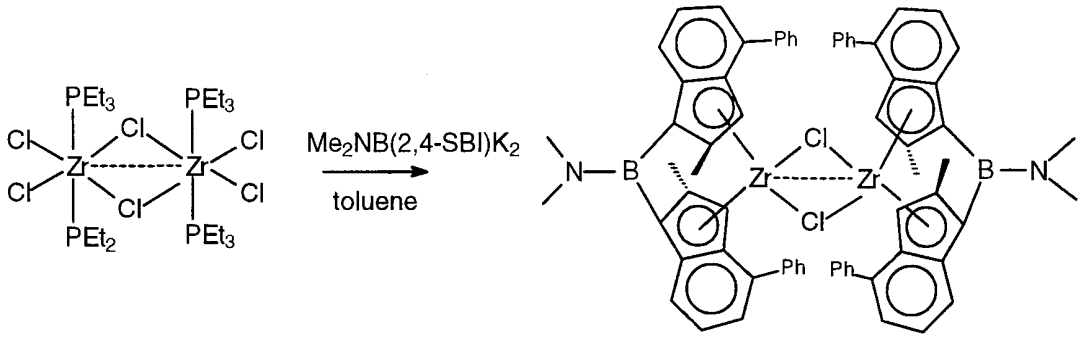
In a glove box, dimethylsilanebis(2-methyl-4-phenylindenyl)dilithium salt (2,4-$SBILi_2$) (0.395 g, 0.82 mmol) and $[TiCl_3(dmpe)]_2$ dimer (0.25 g, 0.41 mmol) were slurried in 30 mL toluene and the mixture was stirred at room temperature for 4 h. The resulting dark brown suspension was filtered through a glass frit using diatomaceous earth filter aid and the solvent of the filtrate was removed under reduced pressure. The residue was washed with 3 mL cold hexane and dried in vacuo to give 0.39 g of the product as a brown solid (87 percent). NMR spectra of the

product showed only very broad peaks. Oxidizing this Ti(III) dimer to the Ti(IV) monomer with $PbCl_2$ in THF and analyzing the product by NMR indicated formation of a mixture of two diastereomers in a 1:1.2 ratio.

Example 5 Alternate preparation of dimethylsilanebis(2-methyl-4-phenylindenyl-1-yl)chloro titanium (III) dimer

The reaction conditions of Example 4, step b were substantially repeated excepting that $TiCl_3(THF)_3$ was reacted with dimethylsilanebis(2-methyl-4-phenylindenyl)dilithium salt (2,4-SBILi$_2$) in toluene. Yield was 90.4 percent.

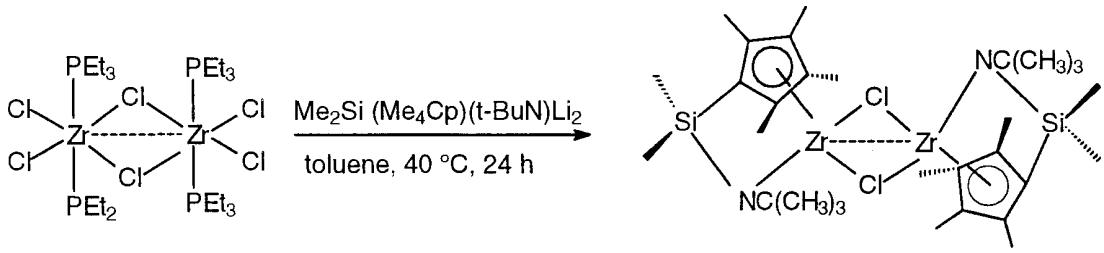
Example 6 Preparation of dimethylaminoboraneyldiyl-bis(2-methyl-4-phenylindenyl-1-yl)chloro zirconium (III) dimer



In a glove box, dimethylaminoboranediyl-bis(2-methyl-4-phenylindenyl) dipotassium salt (Me_2NB-2,4-SBIK_2) (0.542 g, 1.00 mmol) and $[ZrCl_3(Et_3P)_2]_2$ dimer (0.434 g, 0.50 mmol) were mixed in 30 mL toluene and stirred at room temperature for 4 h. The resulting dark red suspension was filtered through a glass frit using diatomaceous earth filter aid and the volatile components were removed under reduced pressure to give 0.52 g (88 percent) of the crude product. The product was further washed with 10 mL cold hexane and filtered and dried in vacuo for 2 h, affording 0.2 g of the dark solid as a mixture of two diastereomers in a 1:1.2 ratio.

Spectroscopic data for $[Me_2NB(2\text{-}Me\text{-}4\text{-}Ph\text{-}\eta^5\text{-}Ind)_2ZrCl]_2$ are as follows. ^1H NMR (C_6D_6, 23 °C) for diastereomer A (54 percent): δ 7.90 (d, $J_{H\text{-}H}$ = 7.8 Hz, 8 H, C_6-ring H), 7.30 (d, $J_{H\text{-}H}$ = 8.7 Hz, 4 H, C_6-ring H), 7.23-6.95 (m, 20 H, C_6-ring H), 6.80 (t, $J_{H\text{-}H}$ = 6.9 Hz, 4 H, C_5-ring H), 2.81 (s, 12 H, Me_2N), 1.94 (s, 12 H, Cp-Me). Diastereomer B (45 percent): δ 7.82 (d, $J_{H\text{-}H}$ = 7.8 Hz, 8 H, C_6-ring H), 7.25 (d, $J_{H\text{-}H}$ = 8.7 Hz, 4 H, C_6-ring H), 7.23-6.95 (m, 20 H, C_6-ring H), 6.69 (t, $J_{H\text{-}H}$ = 6.9 Hz, 4 H, C_5-ring H), 2.83 (s, 12 H, Me_2N), 2.04 (s, 12 H, Cp-Me).

Example 7 Preparation of dimethylsilane(t-butylamido)(tetramethyl-cyclopentadienyl)chloro zirconium dimer



In a glove box, dimethylsilyl(t-butylamido)(tetramethylcyclopentadieneyl) dilithium salt (Me_2Si (Me_4Cp)(t-BuN)Li_2) (0.263 g, 1.00 mmol) and $[ZrCl_3(Et_3P)_2]_2$ dimer (0.434 g, 0.50 mmol) were mixed in 20 mL toluene and stirred at room temperature overnight. NMR spectra of aliquots taken from the reaction mixture indicated incomplete reaction. The mixture was then heated to 40 °C and stirred at this temperature for 24 h. The resulting dark suspension was filtered through a glass frit using diatomaceous earth filter aid and the volatile components were removed under reduced pressure to give 0.33 g (89 percent) of the product as a dark gray solid. NMR spectra of the material indicated the clean product as a mixture of two diastereomers in a 2.5:1 ratio.

Spectroscopic data for $[Me_2Si(Me_4Cp)(t\text{-}BuN)ZrCl]_2$ are as follows. ^1H NMR (C_6D_6, 23 °C) for two diastereomers: δ 2.02, 2.01, 1.95, 1.72 (s, 24 H, Cp-Me), 1.33 (s, 18 H, *t*-Bu), 0.42 (s, 12 H, $SiMe_2$).

Propylene Homopolymerization

A 2-liter Parr reactor was charged with about 600 g of Isopar-E™ mixed alkanes solvent and 150 g of propylene. Hydrogen was added as a molecular weight control agent by differential pressure expansion form a 75 ml addition tank at 25 psi (170 kPa). The reactor was heated to 70 °C and catalyst and methylalumoxane cocatalyst (MAO) were mixed, transferred to a catalyst addition tank, and injected into the reactor.

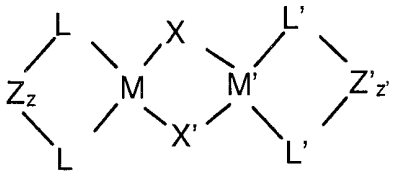
The polymerization conditions were maintained for 10 min. The resulting solution is removed from the reactor, quenched with isopropyl alcohol, and stabilized by addition of 10 mL of a toluene solution containing approximately 67 mg of a hindered phenol antioxidant (Irganox™ 1010 from Ciba Geigy Corporation) and 133 mg of a phosphorus stabilizer (Irgafos™ 168 from Ciba Geigy Corporation. The polymers were recovered by devolatilization at 120 °C for approximately 20 hours. Results are contained in Table 3.

Table 3

Catalyst	μmoles catalyst/ activator	Yield (g)	Efficiency (g polymer/ μmole metal)	Tm (°C)	Mw (10^4)
Ex. 3	6.0/ 6000	10.9	1.82	158.4	12.0
Ex. 4	7.0/ 7000	11.6	1.66	157.2	2.77
Ex. 6	0.5/ 500	40.6	81.2	156.0	26.7
Ex. 7	6.0/6000	5.6	0.93	145.3	2.12

CLAIMS:

1. A dimeric Group 4 metal metallocene compound corresponding to the formula:



(I)

wherein:

L and L' independently each occurrence are ligand groups containing delocalized electrons by means of which said L and L' are π-bond to M or M' respectively,

M and M' are the same or different and are Group 4 metals in the +3 formal oxidation state,

Z and Z' are the same or different and are optional divalent bridging groups,

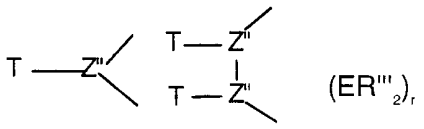
X and X' are the same or different and are anionic ligand groups, and

z and z' independently are 0 or 1.

2. A metal complex according to claim 1 wherein L and L' are a cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl, indacenyl, s-indacenyl, gem-dimethylacenaphthalenyl, cyclopenta(*l*)phenanthrenyl, phosphole, or boratabenzene group, or a C_{1-20} hydrocarbyl-, C_{1-20} dihydrocarbylamido-, C_{1-20} hydrocarbyleneamido-, C_{1-20} halohydrocarbyl-, C_{1-20} amido-, or C_{1-20} hydrocarbylsilyl- substituted derivative thereof.

3. A metal complex according to claim 2 wherein both L and L' are 2-methyl-4-phenylinden-1-yl.

4. A metal complex according to claim 1 wherein z and z' are both 1 and Z and Z' are divalent groups corresponding to the following formulas:

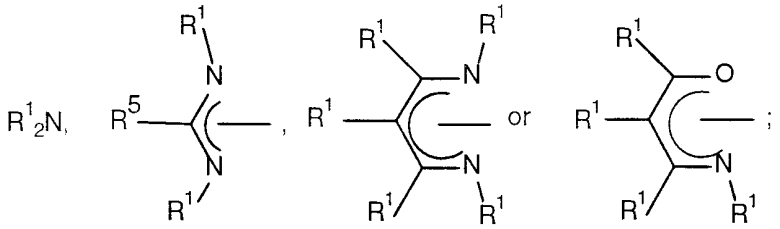


Formula ', Formula or

wherein:

Z" is boron or aluminum;

T independently each occurrence is:



R^1 is independently each occurrence hydrogen, a hydrocarbyl group, a trihydrocarbylsilyl group, or a trihydrocarbylsilylhydrocarbyl group, said R^1 groups containing up to 20 atoms not counting hydrogen, and two such R^1 groups may optionally be joined together to form a ring structure; and

R^5 is R^1 or $N(R^1)_2$.

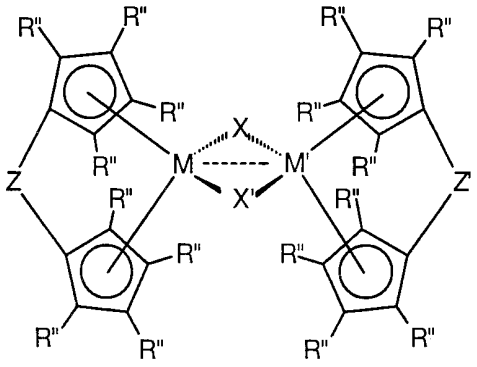
E is carbon, silicon or germanium,

R''' independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, or two R''' groups together form a ring system, said R''' having up to 30 atoms other than hydrogen,

and r is an integer from 1 to 8.

5. A metal complex according to claim 4 wherein Z and Z' each occurrence are both dimethylsilanediyl, dimethylamidoborane or 1,2-ethanediyl.

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



wherein:

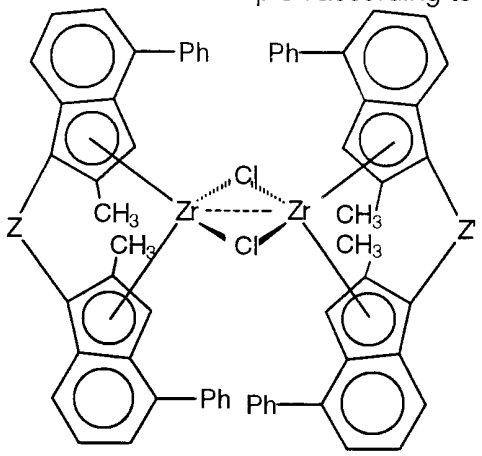
M and M' are both zirconium or hafnium;

R" in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, halohydrocarbyl, N,N-dialkylamino, and alkanediylamino, said R" having up to 20 atoms, not counting hydrogen, or adjacent R" groups are joined together thereby forming a fused ring system,

X and X' each occurrence are C_{1-10} hydrocarbyl or halide; and

Z is SiR^*_2, CR^*_2, $SiR^*_2SiR^*_2$, $CR^*_2CR^*_2$, $CR^*{=}CR^*$, $CR^*_2SiR^*_2$, BNR^*_2, or GeR^*_2, wherein R* independently each occurrence is C_{1-4} alkyl or C_{6-10} aryl, or optionally two R* groups are joined together.

7. A metal complex according to claim 6 corresponding to the formula:

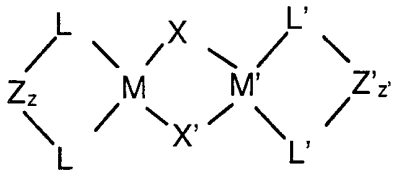


wherein:

Ph is phenyl, and

Z and Z' are each dimethylsilane or 1,2-ethanediyl.

8. A process for preparing a metal complex corresponding to the formula:



(I)

wherein:

L and L' independently each occurrence are ligand groups containing delocalized electrons by means of which said L and L' are π-bond to M or M' respectively,

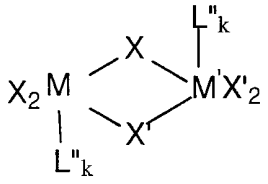
M and M' are the same or different and are Group 4 metals in the +3 formal oxidation state,

Z and Z' are the same or different and are optional divalent bridging groups,

X and X' are the same or different and are anionic ligand groups, and

z and z' independently are 0 or 1;

the steps of the process comprising reacting a dimeric reagent compound corresponding to the formula:



,

wherein

M, M', X, and X' are as previously defined,

L" is a Lewis base, and

k is a number from 0 to 3

with two equivalents of a metallated ligand corresponding to the formula: MeL, MeL', MeL-Z-LMe, or MeL'-Z'-L'Me,

wherein,

L, L', Z, and Z' are as previously defined, and

Me is an alkali metal or Grignard.

9. A process according to claim 7 wherein dimeric reagent compound is prepared by a process comprising contacting in any order, in an inert diluent, and optionally in the presence of a Lewis base, a Group 4 metal complex corresponding to the formula, MX_4, $MX_4(L)_k$ (or mixtures with compounds of the formula: $M'X'_4$ or $M'X'_4(L)_k$) with a reducing agent.

10. An addition polymerization process wherein an addition polymerizable monomer is contacted under polymerization conditions with a catalyst characterized in that the catalyst comprises a metal complex according to claim 1 and a cocatalyst.

11. The polymerization process according to claim 10 wherein the cocatalyst is an alumoxane.

INTERNATIONAL SEARCH REPORT

Int ional Application No
PCT/US 00/12680

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 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 7 C07F C08F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 70, no. 14, 7 April 1969 (1969-04-07) Columbus, Ohio, US; abstract no. 58391, AZUMA, KEIICHI ET AL: ".alpha.- Olefin catalytic polymerization or copolymerization" XP002143579 abstract & JP 43 013048 B (TOKUYAMA SODA CO., LTD.) 3 June 1968 (1968-06-03) --- -/--	1,10

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 July 2000	10/08/2000

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

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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte .ional Application No
PCT/US 00/12680

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	HITCHCOCK, PETER B. ET AL: "Lipophilic halozirconocene(III) complexes: '{Zr'.eta.-C5H3(SiMe3)2-1,3!2(.mu.-Cl)}2!, 'NBun4!'Zr{.eta.-C5H3(SiMe3)2-1,3}2Cl2! and 'Zr{.eta.-C5H3(SiMe3)2-1,3}2Cl2!" J. CHEM. SOC., CHEM. COMMUN. (1992), (6), 474-6 , 1992, XP002143578 the whole document ---	1
X	CHEMICAL ABSTRACTS, vol. 112, no. 15, 9 April 1990 (1990-04-09) Columbus, Ohio, US; abstract no. 139280, ANTINOLO, ANTONIO ET AL: "Aspects of the chemistry of a bulky zirconocene(III) chloride" XP002143580 abstract & POLYHEDRON (1989), 8(13-14), 1882 , 1989, ---	1
X	CHEMICAL ABSTRACTS, vol. 111, no. 22, 27 November 1989 (1989-11-27) Columbus, Ohio, US; abstract no. 203858, KUCHARENKO, S. V. ET AL: "Low-temperature voltammetric study of the mechanism of reduction of metallocene dichloride complex of Group IVB metals with formation of metastable metallocenes" XP002143581 abstract & METALLOORG. KHIM. (1989), 2(2), 395-403 , 1989, ---	1
A	US 5 616 748 A (NEWMAN, T.H.) 1 April 1997 (1997-04-01) column 3, line 43-45 -----	1,10

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte ional Application No
PCT/US 00/12680

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 43013048 B		NONE	
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