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(54) Title: BRIDGED METALLOCENES FOR OLEFIN COPOLYMERIZATION

(57) Abstract

The invention is directed to bridged metallocene catalyst complexes that are sufficiently soluble in aliphatic solvents to be particularly suitable for solution olefin polymerization processes such that olefin copolymers can be prepared with high molecular weights and catalyst activities particularly at high polymerization reaction temperatures. More specifically, the invention particularly relates to a polymerization process for ethylene copolymers having a density of about 0.850 to about 0.940 comprising contacting, under solution polymerization conditions at a reaction temperature at or above 60 °C to 250 °C, ethylene and one or more comonomers capable of insertion polymerization with a bridged metallocene catalyst complex derived from two ancillary ligands, each of which independently may be substituted or unsubstituted, wherein the ligands are bonded by a covalent bridge containing a substituted single Group 14 atom, the substitution on said Group 14 atom comprising aryl groups at least one of which contains a hydrocarbylsilyl substituent; and B) an activating cocatalyst.

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TITLE: BRIDGED METALLOCENES FOR OLEFIN COPOLYMERIZATION

Technical Field

This invention relates to aryl-substituted-bridge containing organometallic catalyst compounds suitable for olefin polymerization processes.

BACKGROUND ART

Olefin polymers comprising ethylene and at least one or more α-olefin and optionally one or more diolefin make up a large segment of polyolefin polymers and will be addressed as "ethylene copolymers" herein. Such polymers range from crystalline polyethylene copolymers such as High Density Polyethylene with a density in excess of 0.94, to slightly crystalline polyethylene such as Linear Low Density Polyethylene with a density between 0.915 to 0.94, to largely amorphous elastomers with a density down to 0.85 and a relatively high molecular weight and with a new area of semi-crystalline "plastomers" with a density of between 0.915 and 0.86 and a moderate molecular weight. In particular, ethylene copolymer plastomers are now a well established class of industrial polymers having a variety of uses associated with their unique properties, such as elastomeric properties and their thermo-oxidative stability. Uses of the plastomers include general thermoplastic olefins, films, wire and cable coatings, polymer modification, injection molding, foams, footwear, sheeting, functionalized polymers and components in adhesive and sealant compounds.

Commercially prepared ethylene copolymers have been traditionally been made via Ziegler-Natta polymerization with catalyst systems largely based on vanadium or titanium. Newer metallocene catalyst compounds have received attention due to their ease of larger monomer incorporation and potential increases in polymerization activities. U.S. patent 5,324,800 describes metallocenes having substituted and unsubstituted cyclopentadienyl ligands which are suitable for producing high molecular weight olefin polymers, including linear, low density copolymers of ethylene with minor amounts of α-olefin.

The utility of bridged metallocene-based ionic catalysts in olefin polymerization is described in U.S. patents 5,408,017 and 5,767,208, EP 0 612 768, and EP 0 612 769. Each addresses suitable bridged metallocene catalysts for high temperature processes for olefin copolymerization. Substituted single carbon, or methylene, bridging groups for metallocenes suitable as olefin polymerization catalysts is described in U.S. patents 4,892,851, 5,155,080 and 5,132,381. Isopropylidene, mono- and diaryl methylene groups are identified as particularly suitable.

Olefin solution polymerization processes are generally conducted in aliphatic solvents that serve both to maintain reaction medium temperature profiles and solvate the polymer products prepared. However, aryl-group containing metallocenes, those having cyclopentadienyl derivatives and other fused or pendant aryl-group substituents, are at best sparingly soluble in such solvents and typically are introduced in aryl solvents such as toluene. Solution polymerization processes in aliphatic solvents thus can be contaminated with toluene that must be removed to maintain process efficiencies and to accommodate health-related concerns for both industrial manufacturing processes and polymer products from them. Alternatively, relatively insoluble catalysts can be introduced via slurry methods, but such methods required specialized handling and pumping procedures that complicate and add significant costs to industrial scale plant design and operation. Low solubility can also become disadvantageous should the process involve low temperature operation at some stage such as in typical adiabatic processes run in areas subject to low ambients temperatures. Additionally, separating or counteracting the build up in the recycle system of special catalyst solvents may become another problem. At the same time means of maintaining high molecular weights in olefin polymers while operating at economically preferable high polymerization reaction temperatures and high polymer production rates is highly desirable. It is therefore desirable to provide a metallocene catalyst which is active for polyethylene polymerization particularly at elevated temperatures which nevertheless has increased solubility in aliphatic solvents.

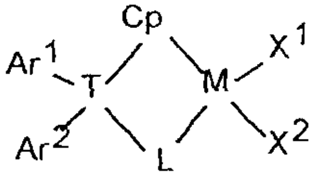
BRIEF SUMMARY OF THE INVENTION

The invention thus addresses specifically substituted, bridged metallocene catalyst complexes comprising a solubilizing covalent bridge comprising at least one hydrocarbylsilyl substitutent. It can be described as a Group 4 organometallic compound comprising two ancillary monanionic ligands, each of which independently may be substituted or unsubstituted, wherein the ligands are bonded by a covalent bridge containing a substituted single Group 14 atom, the substitution on said Group 14 atom comprising aryl groups at least one of which contains at least one hydrocarbylsilyl substituent group sufficient to provide increased solubility in aliphatic solvents. Additionally, the invention relates to solution polymerization processes for ethylene copolymers having a density of about 0.850 to about 0.940 comprising contacting, under supercritical or solution polymerization conditions at reaction temperatures of 40 °C to 300 °C, ethylene and one or more comonomers capable of insertion polymerization with a metallocene catalyst complex derived from A) a metallocene compound having a covalent bridge connecting a cyclopentadienyl ligand to another ancillary anionic metal ligand group, said bridge containing a substituted single Group 14 atom, the substitution on said Group 14 comprising aryl groups at least one of which contains at least one hydrocarbylsilyl substituent group of the formula $R^2{}_nSiR^1{}_{3-n}$, where each R^1 is independently a C_1-C_{20} hydrocarbyl, hydrocarbylsilyl, hydrofluorocarbyl substitutent, R^2 is a C_1-C_{10} linking group between Si and the aryl group, and $n = 0$, 1 or 2. Where n=0, the Si atom is covalently bound directly to an aryl group ring carbon atom.

DETAILED DESCRIPTION OF THE INVENTION

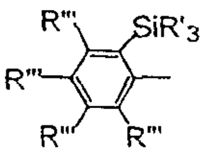
The bridged metallocene compounds of the invention are those having a single substituted carbon or silicon atom bridging two ancillary monanionic ligands, such as substituted or unsubstituted cyclopentadienyl-containing (Cp) ligands and/or substituted and unsubstituted Group 13-16 heteroatom ligands, of the metallocene metal centers. The bridge substituents are substituted aryl groups, the substituents including at least one solubilizing hydrocarbylsilyl substituent located on at least one of the aryl group bridge substituents. Substituents present on the cyclopentadienyl and/or heteroatom ligands include C_1-C_{30} hydrocarbyl, hydrocarbylsilyl or hydrofluorocarbyl groups as replacements for one or more of the hydrogen groups on those ligands, or those on fused aromatic rings on the cyclopentadienyl rings. Aromatic rings can be substituents on cyclopentadienyl ligand and are inclusive of the indenyl and fluorenyl derivatives of cyclopentadienyl groups, and their hydrogenated counterparts. Such typically may include one or more aromatic ring substituent selected from linear, branched, cyclic, aliphatic, aromatic or combined structure groups, including fused-ring or pendant configurations. Examples include methyl, isopropyl, n-propyl, n-butyl, isobutyl, tertiary butyl, neopentyl, phenyl, n-hexyl, cyclohexyl, benzyl, and adamantyl. For the purposes of this application the term "hydrocarbon" or "hydrocarbyl" is meant to include those compounds or groups that have essentially hydrocarbon characteristics but optionally contain not more than about 10 mol.% non-carbon heteroatoms, such as boron, silicon, oxygen, nitrogen, sulfur and phosphorous. Additionally, the term is meant to include hydrofluorocarbyl substitutent groups. "Hydrocarbylsilyl" is exemplified by, but not limited to, dihydrocarbyl- and trihydrocarbylsilyls, where the preferred hydrocarbyl groups are preferably C_1-C_{30} substituent hydrocarbyl, hydrocarbylsilyl or hydrofluorocarbyl substitutents for the bridging group phenyls. For heteroatom containing catalysts see WO 92/00333. Also, the use of hetero-atom containing rings or fused rings, where a non-carbon Group 13, 14, 15 or 16 atom replaces one of the ring carbons is considered for this specification to be within the terms "cyclopentadienyl", "indenyl", and "fluorenyl". See, for example, the background and teachings of WO 98/37106, having common priority with U.S. Ser. No. 08/999,214, filed 12/29/97, and WO 98/41530, having common priority with U.S. Ser. No. 09/042,378, filed 3/13/98, both incorporated by reference for purposes of U.S. patent practice.

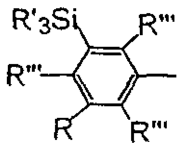
These compounds can be generically represented as illustrated below:

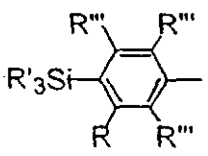


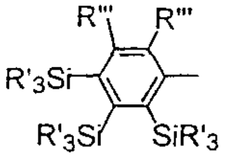
where Cp is a substituted or unsubstituted cyclopentadienyl-containing ancillary ligand, L is independently selected from Cp ligands as previously defined, or is a substituted or unsubstituted Group 13-16 heteroatom ligand, T is a Group 14 element-containing bridging group, Ar^1 and Ar^2 are the substituted aryl groups which may be the same or different, M is a Group 3-6 metal, and X^1 and X^2 are the same or different labile ligands capable of being abstracted for activation and suitable for olefin insertion, or capable of alkylation so as to be abstractable and suitable for olefin insertion. The term "ancillary ligand" is being used to refer to bulky monoanioic ligands that stabilize the metal center to which bonded against oxidative reaction (i.e., debonding of the ligand by chemical reaction) and the term "labile ligand" refers to ligands which may be readily replaced, abstracted, or removed from the metal center to which bonded.

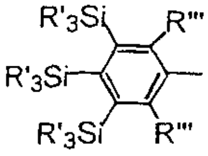
For illustration purposes Ar^1 and Ar^2 may be independently selected from the groups below:

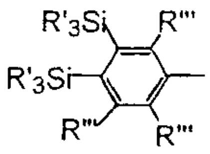


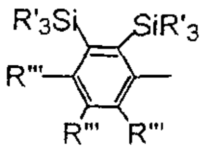


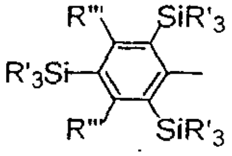


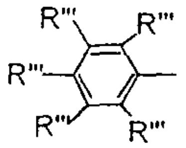


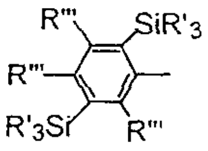


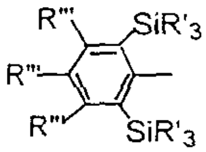


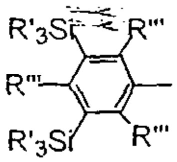


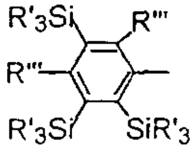


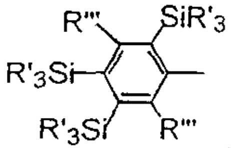












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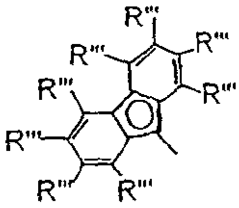
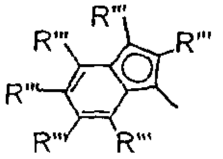
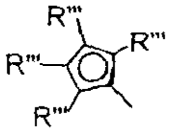
where any R' is independently any of the groups below except H and any R''' is independently any of the groups below:

H
CH_3
CH_2CH_3
$CH_2CH_2CH_3$
$CH_2(CH_2)_2CH_3$
$CH_2(CH_2)_{3-30}CH_3$
$CH_2C(CH_3)_3$
$CH=CH_2$
$CH(CH_3)_2$
$CH_2CH(CH_3)_2$
$CH_2CH_2CH(CH_3)_2$
$C(CH_3)_2CH(CH_3)_2$
$CH(C(CH_3)_3)CH(CH_3)_2$
$C(CH_3)_3$
$CH_2Si(CH_3)_3$
CH_2Ph
C_4H_7
C_5H_9
C_6H_{11}
C_7H_{13}
C_8H_{15}
C_9H_{17}
C_6H_5
CH_2SiR_3
$CH_2CH=CH_2$
$CH_2CH_2CH=CH_2$
$CH_2CH_2(CF_2)_7CF_3$
CF_3
$N(CH_3)_2$
$N(C_2H_5)_2$
$OC(CH_3)_3$

Cp and L, independently, may be any of ligands below where R''' is as shown above.

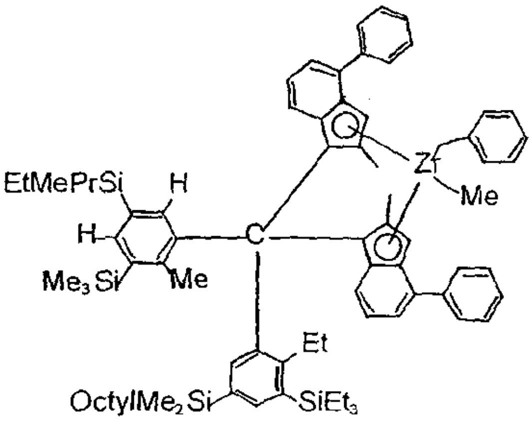






X^1 and X^2 may independently be any of the groups listed for R''' plus any of Cl, Br, I, -NHR''', $-N(R''')_2$, or -OR'''. X^1 and X^2 may additionally be linked together so as to form a bidentate ligand such as cycloaliphatic hydrocarbyl bidentate ligand or cycloalkenyl hydrocarbyl ligand.

An illustrative representative is



where Me is methyl, Et is ethyl and Octyl is octyl.

Specific exemplary bridged hafnium catalysts include those derived from: indenyl-based complexes such as the isomers, or mixtures, of di(para-triethylsilyl-phenyl) methylene bis(indenyl) hafnium dimethyl, di(para-trimethylsilyl-phenyl) methylene bis(indenyl) hafnium dimethyl, of di(para-tri-n-propylsilyl-phenyl) methylene bis(indenyl) hafnium dimethyl, (para-triethylsilyl-phenyl) (para-t-butylphenyl)methylene (fluorenyl) (indenyl) hafnium dimethyl,. (para-triethylsilyl-phenyl) (para-methylphenyl)methylene (fluorenyl) (indenyl) hafnium dimethyl, di(para-triethylsilyl-phenyl) methylene (2,7-di tertbutyl fluorenyl) (indenyl) hafnium dimethyl, (para-trimethylsilyl-phenyl) (para-n-butylphenyl) methylene (2,7-di tertbutyl fluorenyl) (indenyl) hafnium dimethyl, (para-triethylsilyl-phenyl) (para-n-butylphenyl) methylene bis(tetrahydroindenyl) hafnium dibenzyl and di(para-triethylsilyl-phenyl) methylene bis(tetrahydroindenyl) hafnium dimethyl.

Similarly, exemplary zirconium compounds include di(para-triethylsilyl-phenyl) methylene bis(indenyl) zirconium dimethyl, di(para-trimethylsilyl-phenyl) methylene bis(indenyl) zirconium dimethyl, of di(para-tri-n-propylsilyl-phenyl) methylene bis(indenyl) zirconium dimethyl, (para-triethylsilyl-phenyl) (para-t-butylphenyl)methylene (fluorenyl) (indenyl) zirconium dimethyl, (para-triethylsilyl-phenyl) (para-methylphenyl)methylene (fluorenyl) (indenyl) zirconium dimethyl, di(para-triethylsilyl-phenyl) methylene (2,7-di tertbutyl fluorenyl) (indenyl) zirconium dimethyl, (para-trimethylsilyl-phenyl) (para-n-butylphenyl) methylene (2,7-di tertbutyl fluorenyl) (indenyl) zirconium dimethyl, (para-triethylsilyl-phenyl) (para-n-butylphenyl) methylene bis(tetrahydroindenyl) zirconium dibenzyl and di(para-triethylsilyl-phenyl) methylene bis(tetrahydroindenyl) zirconium dimethyl. Additional preferred zirconium metallocenes useful when prepared with the solubilizing bridging groups in accordance with this invention are those described in copending U.S. application Ser. No. 09/251,819, filed February 17, 1999, and equivalent WO 99/41294, these catalyst structures and the solution polymerization process described with them are particularly suited for this invention, and are incorporated by reference for purposes of U.S. patent practice.

Particularly suitable cyclopentadienyl-based complexes are the compounds, isomers, or mixtures, of (para-trimethylsilylphenyl)(para-n-butylphenyl)methylene (fluorenyl) (cyclopentadienyl) hafnium dimethyl, di(para-trimethylsilylphenyl)methylene (2,7-di-tertbutyl fluorenyl) (cyclopentadienyl) hafnium dimethyl, di(para-triethylsilylphenyl)methylene (2,7-di-tertbutyl-fluorenyl) (cyclopentadienyl) hafnium dimethyl, (para-triethylsilylphenyl) (para-t-butylphenyl) methylene (2,7-di tertbutyl fluorenyl) (cyclopentadienyl) hafnium dimethyl or dibenzyl, and di(para-triethylsilyl-phenyl)methylene (2,7-dimethylfluorenyl)(cyclopentadienyl) hafnium dimethyl or dibenzyl. The zirconocene analogues are (para-trimethylsilylphenyl)(para-n-butylphenyl)methylene (fluorenyl) (cyclopentadienyl) zirconium dimethyl, di(para-trimethylsilylphenyl)methylene (2,7-di-tertbutyl fluorenyl) (cyclopentadienyl) zirconium dimethyl, di(para-triethylsilylphenyl)methylene (2,7-di-tertbutyl-fluorenyl) (cyclopentadienyl) zirconium dimethyl, (para-triethylsilylphenyl) (para-t-butylphenyl) methylene (2,7-di tertbutyl fluorenyl) (cyclopentadienyl) zirconium dimethyl or dibenzyl, and di(para-triethylsilyl-phenyl)methylene (2,7-dimethylfluorenyl)(cyclopentadienyl) zirconium dimethyl or dibenzyl. It has been found that the substituted bridge-containing compounds, such as those asymmetric compounds listed above, are particularly useful in accordance with the invention.

In particular, for the bridged metallocene compounds, increasing the degree of substitution on an aromatic fused-ring substituted ligand Cp can be effective for increased molecular weight, e.g., 2,7-dimethyl-fluorenyl, 2,7-di-tert-butyl-fluorenyl and 2,7-methyl-phenyl-fluorenyl groups are exemplary of such. Preferably substitution on fluorenyl or indenyl radicals (ii) in the metallocene compounds will generally comprise two or more C_1 to C_{30} hydrocarbyl or hydrocarbylsilyl replacements, or substitutions, for a ring hydrogen of at least one 6-member fused-ring, preferably both where a fluorenyl radical.

The bridged metallocene compounds according to the invention may be activated for polymerization catalysis in any manner sufficient to allow coordination or cationic polymerization. This can be achieved for coordination polymerization when one ligand can be abstracted and another will either allow insertion of the unsaturated monomers or will be similarly abstractable for replacement with a ligand that allows insertion of the unsaturated monomer (labile ligands), e.g., alkyl, silyl, or hydride. The traditional activators of coordination polymerization art are suitable, those typically include Lewis acids such as alumoxane compounds, and ionizing, anion precursor compounds that abstract one so as to ionize the bridged metallocene metal center into a cation and provide a counter-balancing noncoordinating anion.

Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly for the invention metal compounds comprising halide ligands. The alumoxane component useful as catalyst activator typically is an oligomeric aluminum compound represented by the general formula $(R''\text{-Al-O})_n$, which is a cyclic compound, or $R''(R''\text{-Al-O})_nAlR''_2$, which is a linear compound. In the general alumoxane formula R'' is independently a C_1 to C_{10} alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "n" is an integer from 1 to about 50. Most preferably, R'' is methyl and "n" is at least 4. Alumoxanes can be prepared by various procedures known in the art. For example, an aluminum alkyl may be treated with water dissolved in an inert organic solvent, or it may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of an aluminum alkyl with a limited amount of water yields a mixture of the linear and cyclic species of the alumoxane. Methylalumoxane and modified methylalumoxanes are preferred. For further descriptions see, U.S. patents No. 4,665,208, 4,952,540, 5,041,584, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and EP 0 561 476 A1, EP 0 279 586 B1, EP 0 516 476 A, EP 0 594 218 A1 and WO 94/10180, each being incorporated by reference for purposes of U.S. patent practice.

When the activator is an alumoxane, the preferred transition metal compound to activator molar ratio is from 1:2000 to 10:1, more preferably from about 1:500 to 10:1, even more preferably from about 1:250 to 1:1 and most preferably from about 1:100 to 1:1.

The term "noncoordinating anion" is recognized to mean an anion which either does not coordinate to the metal cation or which is only weakly coordinated to it thereby remaining sufficiently labile to be displaced by a neutral Lewis base, such as an olefinically or acetylenically unsaturated monomer. Any complex capable of counterbalancing a cationic charge without impeding or interfering with olefin polymerization, including both being incapable of reacting with metallocene cations so as to render them neutral and remaining sufficiently labile so as to be replaceable at the polymerization site by olefin monomers, will be suitable in accordance with the invention. Typically such complexes are based on ionic salts or neutral Lewis acids of the Group 8-14 metalloid or metal elements, particularly boron or aluminum having substituted aryl groups that are substituted so as to present steric or electronic impediments to oxidation of the complexes by reaction of the transition metal center with the aryl groups bonded to the Group 13 atoms. Zwitterionic complexes of Group 13 elements comprising both catonic and anionic charges where meeting the functional requisites above are additionally suitable.

Additional suitable anions are known in the art and will be suitable for use with the metallocene catalysts of the invention. See in particular, U.S. patent 5,278,119 and the review articles by S. H. Strauss, "The Search for Larger and More Weakly Coordinating Anions", *Chem. Rev.*, *93*, 927-942 (1993) and C. A. Reed, "Carboranes: A New Class of Weakly Coordinating Anions for Strong Electrophiles, Oxidants and Superacids", *Acc. Chem. Res.*, *31*, 133 -139 (1998).

Specific descriptions of ionic catalysts, those comprising a transition metal cation and a noncoordinating anion, suitable for coordination polymerization appear in the U.S. patents 5,064,802, 5,132,380, 5,198,401, 5,278,119, 5,321,106, 5,347,024, 5,408,017, 5,599,671, and international publications WO 92/00333, WO 93/14132 and WO 97/35893. These teach a preferred method of preparation wherein metallocenes are protonated by noncoordinating anion precursors such that an alkyl, alkenyl or hydride group is abstracted by protonation from a transition metal to make it both cationic and charge-balanced by the noncoordinating anion.

The use of ionizing ionic compounds not containing an active proton but capable of producing both the metallocene cation and an noncoordinating anion is also useful. See, EP-A-0 426 637, EP-A-0 573 403 and U.S. patent 5,387,568 for instructive ionic compounds. Reactive cations of the ionizing ionic compounds, other than the Bronsted acids, include ferrocenium, silver, tropylium, triphenylcarbenium and triethylsilylium, or alkali metal or alkaline earth metal cations such as sodium, magnesium or lithium cations. A further class of noncoordinating anion precursors suitable in accordance with this invention are hydrated salts comprising the alkali metal or alkaline earth metal cations and a non-coordinating anion as described above. The hydrated salts can be prepared by reaction of the metal cation-noncoordinating anion salt with water, for example, by hydrolysis of the commercially available or readily synthesized $LiB(pfp)_4$ which yields $[Li \bullet xH_2O]$ $[B(pfp)_4]$, where (pfp) is pentafluorophenyl or perfluorophenyl.

Any metal or metalloid capable of forming a coordination complex which is resistant to degradation by water (or other Bronsted or Lewis Acids) may be used or contained in the noncoordinating anion. Suitable metals include, but are not limited to, aluminum, gold, platinum and the like. Suitable metalloids include, but are not limited to, boron, phosphorus, silicon and the like. The description of noncoordinating anions and precursors thereto of the documents of the foregoing paragraphs are incorporated by reference for purposes of U.S. patent practice.

An additional method of making the active polymerization catalysts of this invention uses ionizing anion pre-cursors which are initially neutral Lewis acids but form a metallocene cation and the noncoordinating anion upon ionizing reaction with the invention compounds, for example tris(pentafluorophenyl) boron acts to abstract a hydrocarbyl, hydride or silyl ligand to yield a metallocene cation and stabilizing noncoordinating anion, see EP-A-0 427 697 and EP-A-0 520 732 for illustration. See also the methods and compounds of EP-A-0 495 375. The description of noncoordinating anions and precursors thereto of these documents are similarly incorporated by reference for purposes of U.S. patent practice.

When the X_1 and X_2 labile ligands are not hydride, hydrocarbyl or silylhydrocarbyl, such as chloride, amido or alkoxy ligands and are not capable of discrete ionizing abstraction with the ionizing, anion pre-cursor compounds, these X ligands can be converted via known alkylation reactions with organometallic compounds such as lithium or aluminum hydrides or alkyls, alkylalumoxanes, Grignard reagents, etc. See EP-A-0 500 944, EP-A1-0 570 982 and EP-A1-0 612 768 for analogous processes describing the reaction of alkyl aluminum compounds with dihalide substituted metallocene compounds prior to or with the addition of activating noncoordinating anion precursor compounds.

Preferred invention activating cocatalyst, precursor ionizing compounds comprise Group 13 element complexes having at least two halogenated aromatic ligands such as the halogenated tetraphenyl boron and aluminum compounds exemplified in the identified prior art. Preferred aromatic ligands consist of the readily available phenyl, and polycyclic aromatic hydrocarbons and aromatic ring assemblies in which two or more rings (or fused ring systems) are joined directly to one another or together. These ligands, which may be the same or different, are covalently bonded directly to the metal/metalloid center. In a preferred embodiment the aryl groups are halogenated, preferably fluorinated, tetraaryl Group 13 element anionic complexes comprising at least one fused polycyclic aromatic hydrocarbon or pendant aromatic ring. The halogenated ligands are also represented by those aryl ligands having flourinated alkyl groups. Indenyl, napthyl, anthracyl, heptalenyl and biphenyl ligands are exemplary aryl ligands. See co-pending application U.S. Ser. No. 09/261,627, filed 3 March 1999, and equivalent WO 99/45042, incorporated by reference for the purposes of U.S. patent practice.

Particularly preferred cocatalyst complexes for solution polymerization processes are those which are soluble in aliphatic solvents, whether by virtue of substitution on the Group 13 element ligands or substitution on precursor cations, see for example U.S. patent 5,502,017 and WO 97/35893. When the cation portion of an ionic noncoordinating anion precursor is a Bronsted acid such as protons or protonated Lewis bases (excluding water), or a reducible Lewis acid such as ferrocenium or silver cations, or alkaline metal or alkaline earth metal cations such as those of sodium, magnesium or lithium cations, the transition metal to activator molar ratio may be any ratio, but preferably from about 10:1 to 1:10, more preferably from about 5:1 to 1:5, even more preferably from about 2:1 to 1:2 and most preferably from about 1.2:1 to 1:1.2 with the ratio of about 1:1 being the most preferred.

Thus suitable active catalyst complexes for coordination and carbocationic polymerization can be prepared by activation with the traditional metallocene activators, typically alkylalumoxanes and ionizing haloaryl boron or aluminum compounds known in the art. The active catalysts thus are catalytically active components comprising complexes derived from the invention metallocene compounds containing the solubilizing bridge binding together the ancillary ligands according to the invention, and activating cocatalyst compounds.

The catalyst complexes of the invention are useful in polymerization of unsaturated monomers conventionally known to be polymerizable under either coordination polymerization conditions or cationic polymerization conditions. Such conditions are well known and include solution polymerization, supercritical phase polymerization, slurry polymerization, and low, medium and high pressure gas-phase polymerization. The catalyst of the invention may be supported and as such will be particularly useful in the known operating modes employing fixed-bed, moving-bed, fluid-bed, or slurry processes conducted in single, series or parallel reactors, with the added benefit that increased solubility will be useful in catalyst synthesis processes where the introduction of toluene is to be reduced. or slurry pump introduction means to be avoided.

When using the catalysts of the invention, the total catalyst system will generally additionally comprise one or more organometallic compound. Such compounds as used in this application and its claims is meant to include those compounds effective for removing polar impurities from the reaction environment and for increasing catalyst activity. Impurities can be inadvertently introduced with any of the polymerization reaction components, particularly with solvent, monomer and catalyst feed, and adversely affect catalyst activity and stability. It can result in decreasing or even elimination of catalytic activity, particularly when ionizing anion pre-cursors activate the catalyst system. The polar impurities, or catalyst poisons include water, oxygen, metal impurities, etc. Preferably steps are taken before provision of such into the reaction vessel, for example by chemical treatment or careful separation techniques after or during the synthesis or preparation of the various components, but some minor amounts of organometallic compound will still normally be used in the polymerization process itself.

Typically these compounds will be organometallic compounds such as the Group 13 organometallic compounds of U.S. patents 5,153,157, 5,241,025 and WO-A-91/09882, WO-A-94/03506, WO-A-93/14132, and that of WO 95/07941. Exemplary compounds include triethyl aluminum, triethyl borane, triisobutyl aluminum, methylalumoxane, and isobutyl aluminumoxane. Those compounds having bulky or C_6-C_{20} linear hydrocarbyl substituents covalently bound to the metal or metalloid center being preferred to minimize adverse interaction with the active catalyst. Examples include triethylaluminum, but more preferably, bulky compounds such as triisobutylaluminum, trisoprenylaluminum, and long-chain linear alkyl-substituted aluminum compounds, such as tri-n-hexylaluminum, tri-n-octylaluminum, or tri-n-dodecylaluminum. When alumoxane is used as activator, any excess over the amount needed to activate the catalysts present can act as a poison scavenger compound and additional organometallic compounds may not be necessary. Alumoxanes also may be used in scavenging amounts with other means of activation, e.g., methylalumoxane and trisobutyl-aluminoxane with boron-based activators. The amount of such compounds to be used with catalyst compounds of the inventions is minimized during polymerization reactions to that amount effective to enhance activity (and with that amount necessary for activation of the catalyst compounds if used in a dual role) since excess amounts may act as catalyst poisons.

In preferred embodiments of the process for this invention, the catalyst system is employed in liquid phase (solution, slurry, suspension, bulk phase or combinations thereof), in high pressure liquid or supercritical fluid phase. Each of these processes may be employed in singular, parallel or series reactors. The liquid processes comprise contacting olefin monomers with the above described catalyst system in a suitable diluent or solvent and allowing said monomers to react for a sufficient time to produce the invention copolymers. Aliphatic solvents and mixed aliphatic solvents are industrially suitable for solution processes, and are particularly preferred.

The process of the invention is especially applicable to homogeneous solution polymerization which is also substantially adiabatic, that is to say the heat of polymerization is accommodated by a rise in temperature of the polymerization reactor contents, here principally solvent. This adiabatic process typically has no internal cooling and suitably no external cooling. The reactor outlet stream removes the heat of polymerization from the reactor. The productivity of such adiabatic processes can be improved by cooling the inlet solvent and/or monomer stream(s) prior to introduction into the reactor to permit a greater polymerization exotherm. Thus the catalyst, cocatalyst and scavenger selections disclosed in this application can be advantageously practiced in a continuous, solution process operated at or above 140 °C, above 150 °C or above 160 °C, up to about 250 °C. Typically this process is conducted in an inert hydrocarbon solvent, linear, cyclic or branched aliphatic, or aromatic, at a pressure of from 20 to 200 bar. These catalysts' ability to provide a commercially desirable polymer at elevated temperatures contributes to a greater exotherm, to high polymer contents in the reactor because of lower viscosity, and to reduced energy consumption in evaporating and recycling solvent, and better monomer and comonomer conversions. See, for example, U.S. 5,767,208, and co-pending U.S. application Serial No. 09/261,637, filed 3 March 1999, and its equivalent WO 99/45041, all of which are incorporated by reference for purposes of U.S. patent practice.

The catalyst according to the invention may be supported for use in gas phase, bulk, slurry polymerization processes, or otherwise as needed. Numerous methods of support are known in the art for copolymerization processes for olefins, any is suitable for the invention process in its broadest scope. See, for example, alumoxane activated catalysts of U.S. patents 5,057,475 and 5,227,440. An example of supported ionic catalysts appears in WO 94/03056. Particularly effective methods for ionic catalysts are that described in U.S. patents 5,427,991, 5,647,847 and WO 98/55518. A bulk, or slurry, process utilizing supported, invention metallocene compounds activated with alumoxane co-catalysts can be utilized as described for ethylene-propylene rubber in U.S. patents 5,001,205 and 5,229,478, these processes will additionally be suitable with the catalyst systems of this application. Both inorganic oxide and polymeric supports may be utilized in accordance with the knowledge in the field. See U.S. patents 5,422,325, 5,427,991, 5,498,582, 5,466,649, copending U.S. patent applications 08/265,532 and 08/265,533, both filed 6/24/95, and international publications WO 93/11172 and WO 94/07928. Each of the foregoing documents is incorporated by reference for purposes of U.S. patent practice.

Bulk and slurry processes are typically done by contacting the catalysts with a slurry of liquid monomer or diluent, the catalyst system being supported. Gas phase processes typically use a supported catalyst and are conducted in any manner known to be suitable for ethylene homopolymers or copolymers prepared by coordination polymerization. Illustrative examples may be found in U.S. patents 4,543,399, 4,588,790, 5,028,670, 5,382,638, 5,352,749, 5,436,304, 5,453,471, and 5,463,999, and WO 95/07942. Each is incorporated by reference for purposes of U.S. patent practice.

Generally speaking the polymerization reaction temperature can vary from about -50°C to about 300°C. Preferably the reaction temperature conditions will be from -20°C to 250°, and most advantageously in high temperature, adiabatic solution processes from and including about 120°C to including and about 230°C. The pressure can vary from about 1 mm Hg to 2500 bar, preferably from 0.1 bar to 1600 bar, most preferably from 1.0 to 500 bar.

Ethylene-α-olefin (including ethylene-cyclic olefin and ethylene-α-olefin-diolefin) elastomers of high molecular weight and low crystallinity can be prepared utilizing the catalysts of the invention under traditional solution polymerization processes (above) or by introducing ethylene gas into a slurry utilizing the α-olefin or cyclic olefin or mixture thereof with other monomers, polymerizable and not, as a polymerization diluent in which the invention catalyst is suspended. Typical ethylene pressures will be between 10 and 1000 psig (69-6895 kPa) and the polymerization diluent temperature will typically be between -10-160 °C. The process can be carried out in a stirred tank reactor or tubular reactor, or more than one operated in series or parallel. See the general disclosure of U.S. patent 5,001,205 for general process conditions. All documents are incorporated by reference for description of polymerization processes, ionic activators and useful scavenging compounds.

Pre-polymerization of the supported catalyst of the invention may also be used for further control of polymer particle morphology in typical slurry or gas phase reaction processes in accordance with conventional teachings. For example such can be accomplished by pre-polymerizing a C_2-C_6 alpha-olefin for a limited time, for example, ethylene is contacted with the supported catalyst at a temperature of -15 to 30 °C. and ethylene pressure of up to about 250 psig (1724 kPa) for 75 min. to obtain a polymeric coating on the support of polyethylene of 30,000-150,000 molecular weight. The prepolymerized catalyst is then available for use in the polymerization processes referred to above. The use of polymeric resins as a support coating may additionally be utilized, typically by suspending a solid support in dissolved resin of such material as polystyrene with subsequent separation and drying. All documents are incorporated by reference for description of metallocene compounds, ionic activators and useful scavenging compounds.

Other olefinically unsaturated monomers besides those specifically described above may be polymerized using the catalysts according to the invention by coordination polymerization, for example, styrene, alkyl-substituted styrenes, ethylidene norbornene, vinyl norbornene, norbornadiene, dicyclopentadiene, and other olefinically-unsaturated monomers, including other cyclic olefins, such as cyclopentene, norbornene, and alkyl-substituted norbornenes. Additionally, alpha-olefinic macromonomers of up to 300 mer units, or more, may also be incorporated by copolymerization.

The following examples are presented to illustrate the foregoing discussion. All parts, proportions and percentages are by weight unless otherwise indicated. All examples were carried out in dry, oxygen-free environments and solvents. Although the examples may be directed to certain embodiments of the present invention, they are not to be viewed as limiting the invention in any specific respect. In these examples certain abbreviations are used to facilitate the description. These include standard chemical abbreviations for the elements and certain commonly accepted abbreviations, such as : Me = methyl, Et = ethyl, t-Bu = tertiary-butyl, Oct = octyl, Cp = cyclopentadienyl, Ind = indenyl, Flu = fluorenyl, THF (or thf) = tetrahydrofuran, Ph = phenyl, and pfp = pentafluorophenyl.

All molecular weights are weight average molecular weight unless otherwise noted. Molecular weights (weight average molecular weight (Mw) and number average molecular weight (Mn) were measured by Gel Permeation Chromatography, unless otherwise noted, using a Waters 150 Gel Permeation Chromatograph equipped with a differential refractive index (DRI) and low angle light scattering (LS) detectors and calibrated using polystyrene standards. Samples were run in 1,2,4-trichlorobenzene (135°C) using three Polymer Laboratories PC Gel mixed B columns in series. This general technique is discussed in

"Liquid Chromatography of Polymers and Related Materials III'" J. Cazes Ed., Marcel Decker, 1981, page 207, which is incorporated by reference for purposes of U.S. patent practice herein. No corrections for column spreading were employed; however, data on generally accepted standards, e.g. National Bureau of Standards Polyethylene 1475, demonstrated a precision with 0.2 units for Mw/Mn which was calculated from elution times.

EXAMPLES :

Synthesis of (p-Et_3Si-phenyl)$_2$C(2,7-$^tBu_2$Flu)(Cp)$HfMe_2$ (Catalyst A)

1. Synthesis of 1-Br,4-(Et_3Si)benzene

To a cold (–78 °C) slurry of 1,4-dibromobenzene (235 g, 0.99 mol) and anhydrous THF (1.5 L) was added a solution of nBuLi (1.0 mol), pentane (300 mL) and ether (100 mL). After stirring for 3 h, Et_3SiCl (150 g, 1.0 mol) was added. The mixture was allowed to slowly warm to room temperature, stirred for a total of ca. 60 h. then quenched with water (50 mL). The organic layer was separated, washed with additional water (2 x 50 mL), dried over $MgSO_4$, filtered, then reduced to an orange oil. Vacuum distillation (60 mtorr) gave product (bp 83 °C). Yield 124 g, 46 %.

2. Synthesis of 6, 6'-bis(p-Et_3Si-phenyl)fulvene

To a cold (–78 °C) slurry of 1-Br,4-(Et_3Si)benzene (124 g, 0.46 mol) and anhydrous THF (0.5 L) was added a solution of nBuLi (0.46 mol) and pentane (246 mL). After stirring for 75 min, ClC(O)NMe_2 (21 mL, 0.23 mol) was added. The mixture was slowly warmed to room temperature overnight then cooled in an ice bath. Cyclopentadiene (46 mL, 0.55 mol) was added then the color soon turned red. After stirring in an ice bath for 8 h, the mixture was warmed to room temperature overnight. The mixture was extracted with water (4 x 100 mL) in two stages (tot. 800 mL water), dried with $MgSO_4$ then reduced to an oil. The oil was taken up in ether (200 mL), dried with CaH_2, filtered, then reduced to a red oil. Yield of crude product 114.8 g.

3. Synthesis of (p-Et_3Si-phenyl)$_2$C(2,7-$^tBu_2$Flu)(Cp)$HfCl_2$.

2,7-^{t}Bu$_2$fluorenyl lithium (69.5 g, 0.25 mol) was added to a cooled (–30 °C) solution of the crude fulvene (114.8 g, 0.25 mol) and ether (500 mL). The mixture was warmed to room temperature overnight then reduced to an orange oil. Addition of pentane (0.5 L) caused a slurry to form. Filtration, pentane washing (2 x 100 mL) and drying yielded (*p*-Et$_3$Si-phenyl)$_2$C(2,7-^{t}Bu$_2$FluH)(CpLi) as a white solid (97 g, 53 %-assuming no ether present). 2M BuLi in pentane (64.5 mL, 0.129 mol) was added to a slurry of the monoanion (95 g, 0.129 mol) and ether (1 L). After stirring overnight, the orange mixture was cooled to –30 °C then treated with HfCl$_4$ (41.4 g, 1 equiv.). The mixture was warmed to room temperature, stirred for 24 h then reduced to a solid *in vacuo*. The solids were extracted with methylene chloride (500 mL total) then filtered through Celite. The filtrate was reduced to a solid, extracted with pentane (3 x 100 mL) then dried. The product was extracted from the solids with a mixture of toluene and hexane (1:1) at 60 °C then filtered through a 0.45 µm filter. Removing the solvent gave product. Yield 70 g, 55 %.

4. Synthesis of (*p*-Et$_3$Si-phenyl)$_2$C(2,7-^{t}Bu$_2$Flu)(Cp)HfMe$_2$ (Catalyst A)

A 1.4 M solution of MeLi in ether (21.8 mL, 30.5 mmol) was added to a solution of (*p*-Et$_3$Si-phenyl)$_2$C(2,7-^{t}Bu$_2$Flu)(Cp)HfCl$_2$ (15.0 g, 15.2 mmol) and toluene (125 mL). After stirring for 1 h, the mixture was filtered through a 4–8 µm frit then reduced to a solid invacuo. The product was extracted from the solids with hexane (250 mL) then filtered through a 0.45 µm filter. The crude product was crystallized from a minimum of hot hexane. Yield 8.9 g, 62 %.

Synthesis of (*p*-Et$_3$Si-phenyl)$_2$C(Flu)(Cp)HfMe$_2$ (Catalyst B)

5. *Synthesis of 6,6'-bis(p-Et$_3$Si-phenyl)fulvene*

This fulvene was prepared similarly as described above in 1 and 2 on a smaller scale.

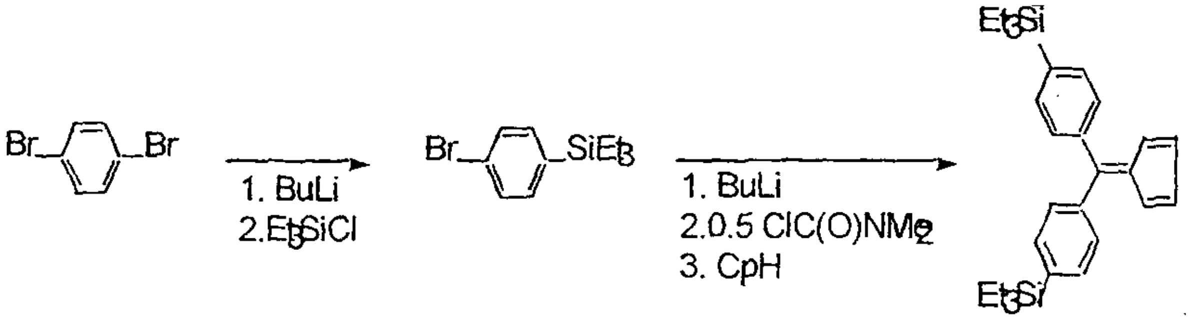
6. Synthesis of (*p*-Et$_3$Si-phenyl)$_2$C(Flu)(Cp)HfCl$_2$.

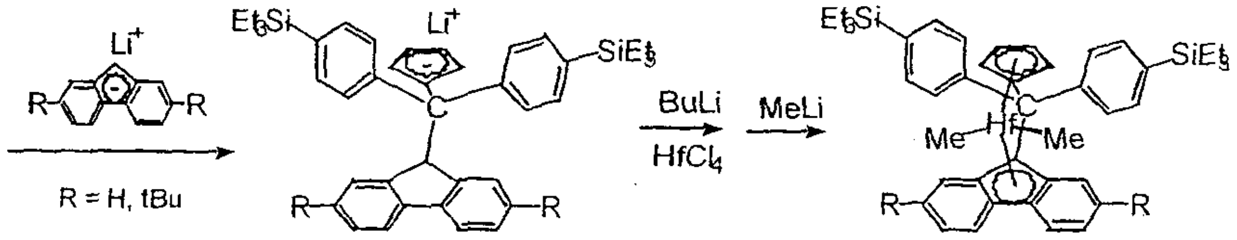
Fluorenyl lithium (3.90 g, 22.6 mmol) was added to a cold (–30 °C) solution of crude 6,6'-bis(*p*-Et$_3$Si-phenyl)fulvene (10.35 g, 22.6 mmol) and ether (100 mL). After stirring for 2 h, the solvent was removed and the remaining solid slurried with pentane (100 mL), filtered, washed with additional pentane (2 x 100 mL) then dried invacuo to give (p-Et_3Si-phenyl)$_2$C(FluH)(CpLi). Yield 6.41 g, 45 %-assuming no ether present. 2M BuLi in pentane (5.1 mL, 1 equiv.) was added to a slurry of the monoanion (6.4 g, 10.2 mmol) and ether (50 mL). The mixture was stirred overnight, cooled to –30 °C then treated with $HfCl_4$ (3.26 g, 1 equiv.). The mixture was warmed to room temperature, stirred for 8 h, filtered then washed with pentane (25 mL). The product was extracted from the orange solids with methylene chloride. Removing the solvent gave (p-Et_3Si-phenyl)$_2$C(Flu)(Cp)$HfCl_2$. Yield 6.15 g, 61 %.

7. Synthesis of (p-Et_3Si-phenyl)$_2$C(Flu)(Cp)$HfMe_2$ (Catalyst B)

A 1.4 M solution of MeLi in ether (1.65 mL, 2.31 mmol) was added to a solution of (p-Et_3Si-phenyl)$_2$C(Flu)(Cp)$HfCl_2$ (1.0 g, 1.15 mmol) and toluene (25 mL). After stirring overnight, toluene was removed. The product was extracted from the solids with hexane then filtered through a 0.45 µm filter. Removing the solvent gave product. Yield 0.565 g, 59 %.

As shown above preparation of the exemplary metallocenes required initial synthesis of 6,6'-bis(p-Et_3Si-phenyl)fulvene. This fulvene was prepared from the reaction of p-(Et_3Si)phenyllithium with ClC(O)NMe_2 then cyclopentadiene in an extension of a general procedure reported by H. Kurata and coworkers (*Tetrahedron Letters*, **1993**, *34*, 3445–3448). Further reaction of 6,6'-bis(p-Et_3Si-phenyl)fulvene with 2,7-$^tBu_2$fluorenyl lithium yielded (p-Et_3Si-phenyl)$_2$C(2,7-$^tBu_2$FluH)(CpLi). This monoanion displayed low solubility in pentane and was easily purified from contaminants. Subsequent treatment with BuLi then $HfCl_4$ gave the dichloride (p-Et_3Si-phenyl)$_2$C(Flu)(Cp)$HfCl_2$, which was readily methylated. This methodology can easily be extended to prepare a wide variety of silyl substituted metallocenes.





8. Solubility Studies

To a measured amount (typically 10^{-4} mol) of metallocene and a stirbar in a 20 mL scintillation vial was added dry hexane (ca. 2.65 mL). It was necessary to use a larger amount of <u>A</u> (3×10^{-4} mol) to determine its solubility. The mixture was stirred for ca. 1h then an aliquot removed and filtered through a 0.45 µm filter (aliquot mass 2.2–2.5 g). The mass of the sample was recorded then the hexane removed with a slow nitrogen stream. Weight % solubility of the metallocene was determined as 100(mass solid remaining) / (mass filtered aliquot). See Tables below.

催化剂符号 Catalyst Symbol	预催化剂化合物 Precatalyst Compound
A	$(p\text{-Et}_3\text{Si-Ph})_2\text{C}(2,7\text{-}({}^t\text{Bu})_2\text{Flu})(\text{Cp})\text{HfMe}_2$
B	$(p\text{-Et}_3\text{Si-Ph})_2\text{C}(\text{Flu})(\text{Cp})\text{HfMe}_2$
C (Comp)	$\text{Ph}_2\text{C}(2,7\text{-}({}^t\text{Bu})_2\text{Flu})(\text{Cp})\text{HfMe}_2$
D (Comp)	$\text{Ph}_2\text{C}(\text{Flu})(\text{Cp})\text{HfMe}_2$

SOLUBILITY TABLE

溶解度表

起始混合物(计算的)　　　过滤的等分部分

	Initial Mixture (Calculated)			Filtered Aliquot		
预催化剂	预催化剂	溶液质量	最大wt%	溶液质量	预催化剂	
Precatalyst	Precat	soln. mass	max. wt %	soln. mass	Precat	wt %
A	0.0905	2.6603	3.40 %	2.3715	0.0793	3.3 % [1]
A	0.2828	2.7653	10.23 %	2.521	0.2434	9.65 % [3]
A	0.2844	2.8224	10.08 %	2.5557	0.2338	9.15 % [3]
C (Comp)	0.0705	2.6191	2.69 %	2.236	0.0476	2.1 %
C (Comp)	0.1049	2.6805	3.91 %	2.383	0.0445	1.9 %
B	0.0848	2.6483	3.20 %	2.3898	0.0511	2.1 %
D (Comp)	0.0594	5.1069	1.16 %	3.7209	0.0045	0.1 % [2]
D (Comp)	0.0612	12.1902	0.50 %	11.5233	0.0079	<0.07 % [2]

[1] Control run using a fully dissolved catalyst A as determined by visual observation indicated ca. 3% error between the calculated "max wt%" and the actual measured wt% after filtering. [2] An upper limit of D solubility is 0.07% since an increase in hexane did not proportionally increase the amount of solids remaining. [3] Average A solubility is 9.4 %.

Example 9a. Polymerization Example.

Under a nitrogen atmosphere, a 1 L autoclave was charged with hexane (460 mL) and trioctylaluminum (0.04 mL of a 25 wt% solution in hexane diluted with hexane (10 mL)). The autoclave was stirred at ca. 1000 rpm, heated to 113.6 ± 0.4 °C (P = 47.2 ± 0.5 psig) then pressurized with propylene to 103.3 ± 0.3 psig then ethylene to 251 psig. Ethylene flow into the reactor was allowed during the copolymerization. A 3.94×10^{-5} M of hexane soluble activator $[((3,5\text{-}(Et_3Si)_2\text{-}Ph)_3C]^+ [B(C_6F_5)_4]^-$ solution in hexane (20 mL, 0.79 μmol) (hexane soluble activator) was pumped into the reactor. Then a 3.97×10^{-5} M $(p\text{-}Et_3Si\text{-}Ph)_2C(2,7\text{-}{}^tBu_2Flu)(Cp)HfMe_2$ solution in hexane was added at a variable rate sufficient to maintain ethylene flow into the reactor at < 1 L/min and the reaction exotherm < 0.5 °C. The mean temperature during the polymerizations was 113.7 ± 0.5 °C. Ethylene uptake was monitored with a calibrated mass-flow transducer. The polymerization was halted after ca. 12 g of polymer was produced. The reactor was vented and cooled. The polymer solution was poured from the reactor into a large beaker. The reactor was rinsed with additional hot hexane (ca. 500 mL). The polymer solutions were combined then treated with a stream of nitrogen to remove hexane; the polymer was further dried under vacuum at 80 °C. Polymerization data is given in table 1.

Example 9b.

The procedure of 9a. was repeated.

Example 9c.

The procedure of 9a. was repeated.

Example 10a.

The general procedure of 9a. was followed with an activator substitution: The reactor was charged with solvent, $AlOct_3$ then a slurry of the activator compound $PhNMe_2H^+ B(C_6F_5)_4^-$ (5 mg, 6.2 μmol) in hexane (20 mL) then heated to 113.5 °C and charged with propylene and ethylene. Then the precatalyst was added to this mixture.

Example 10b.

The procedure of 10a. was repeated using a slurry of the activator compound $[PhNMe_2H]^+ [B(C_6F_5)_4]^-$ (1.2 mg, 1.5 μmol) in hexane (20 mL).

Example 11a. Comparative Example

The general procedure of 9a. was followed with an activator substitution: A 1.5 x 10^{-4} M $B(C_6F_5)_3$ solution in hexane (25 mL, 3.78 μmol) was pumped into the reactor in place of the R1 solution used in example 9a. Due to low activity, the polymerization was halted after 2.92 g of polymer was prepared.

Example 11b. Comparative Example.

The procedure of 11a. was repeated. Due to low activity, the polymerization was halted after 0.7 g of polymer was prepared.

Example 12a. Polymerization Example.

The procedure of example 9a was followed with a precatalyst substitution: A mixture of (p-Et_3Si-$Ph)_2C(Flu)(Cp)HfMe_2$ (50 mg, 60.1 μmol) and hexane (2.5 g) was stirred for 30 min then allowed to sit for 10 min. An aliquot (150 μL) of the mixture was removed and diluted with hexane 80 mL. This precatalyst solution was added to a reactor as described in example 9a.

Example 12b. Polymerization Example.

The procedure of example 12a was repeated using the same precursor.

Example 12c. Comparative Example.

The procedure of example 9a was followed with a precatalyst substitution: A mixture of catalyst D above ($(Ph)_2C(Flu)(Cp)HfMe_2$) (50 mg, 82.9 μmol) and hexane (2.5 g) was stirred for 30 min then allowed to sit for 10 min. An aliquot (150 μL) of the mixture was removed and diluted with hexane 80 mL. This precatalyst solution was added to a reactor as described in example 9a.

Example 12d. Comparative Example.

The procedure of example 12c was repeated using the same mixture.

表1

TABLE 1

POLYMERIZATION RESULTS 聚合结果

Ex #	μmol Cat μmol 催化剂	μmol Act 活化剂	聚合物质量 Polymer mass	Wt % C_3 (IR)	M_w (LS)	M_w/M_n (DRI)
9a	0.13	0.79	12.41	32	629427	1.85
9b	0.11	0.79	11.79	31	647659	1.7
9c	0.12	0.79	10.33	32	575956	1.9
10a	0.056	6.2	11.42	32	557884	1.95
10b	0.094	1.5	11.28	32.5	589690	1.9
11a(Comp)	0.70	3.8	2.92	32	573913	1.9
11b(Comp)	0.893	3.8	0.7	a	a	a
12a	0.183[b]	0.79	12.60	31	510697	2.0
12b	0.183[b]	0.79	6.77	33.5	492952	2.0
12c(Comp)	c	0.79	0.4	a	a	a
12d(Comp)	c	0.79	0	a	a	a

(a) not measured (b, c) (p-Et_3Si-$Ph)_2C(Flu)(Cp)HfMe_2$ was completely soluble; $Ph_2C(Flu)(Cp)HfMe_2$ had little solubility under these conditions (c) μmol unknown.

The comparison presented in example 12 above illustrates that the productivity of a polymerization is proportional to the concentration of the catalyst precursor compound feed solution. Catalyst B is more soluble that catalyst D in hexane. Thus, the mixtures of B in hexane result in and increase in polymerization productivity, 6.8 to 12.6 g polymer, as compared to that of catalyst D, at 0 - 0.4 g polymer.

Example 13. Ethylene/Octene Copolymerizations

Under a nitrogen atmosphere, a 500 mL autoclave was charged with hexane (250 mL), triisobutylaluminum (0.2 mL of a 25.2 wt% solution in heptane diluted with toluene (5 mL)) and 1-octene (18 mL, 115 mmol). The autoclave was stirred at ca. 1500 rpm, heated to 140.1 °C (P = 75.7 psig) then pressurized with ethylene to 265.6 ± 1 psig. Ethylene flow into the reactor was allowed during the copolymerization. A solution of precatalyst (40–50 μmol), $PhNMe_2H^+ B(C_6F_5)_4^-$ (1 equiv.) and toluene (100 mL) was added to the stirred mixture over 30 min. at a variable rate sufficient to obtain 12–15 g isolated copolymer with an exotherm of less than 1.5 °C, typically less than 1 °C. The polymer was precipitated with 2-propanol (1.5 L), isolated, then dried under vacuum at 80 °C. See Table below.

预催化剂 Precatalyst	所用预催化剂 Precat. used (μMol)	共聚物产量(g) Copolymer Yield (g)	Mol% octene 辛烯	M_w (DRI)	M_w/M_n (DRI)	M_w (LS)
A	2.1	12.18	6.4	195692	3.12	225188
A	1.5	12.79	6.1	190771	2.30	210680
A	2.2	13.82	6.4	207125	2.30	248319
A	2.4	14.98	6.1	219112	2.43	254290
B	5.0	12.40	7.3	150225	2.22	177924
B	4.4	12.98	7.6	163758	2.22	194604
D	5.8	12.49	9.5	140664	2.25	173690
D	4.2	12.25	7.5	154822	2.20	189865

Molecular weights determined from GPC using a differential refractive index (DRI) or light scattering (LS) detector.

The solubility data above exhibits significant and unexpected increase in solubility for catalyst of the invention as compared with those of the prior art. The polymerization data illustrates equivalent activities such that the benefits of increased solubility in aliphatic solvents can be achieved without sacrifice of the levels of productivity previously achieved with the prior art catalysts.

Example 14. Continuous High Temperature Solution Process

The following polymerization reactions were performed in a stirred, liquid filled 2 L jacketed steel reactor equipped to perform continuous insertion polymerization in presence of an inert C_6 hydrocarbon (naphta) solvent at pressures up to 120 bar and temperatures up to 240 °C. The reactor was typically stirred at 1000 rpm during the polymerization. The reaction system was supplied with a thermocouple and a pressure transducer to monitor changes in temperature and pressure continuously, and with means to supply continuously purified ethylene, 1-octene, and solvent. In this system, ethylene dissolved in the hydrocarbon solvent, 1-octene, tri-n-octyl aluminum (TOA) used as a scavenger, and optionally H_2, are pumped separately, mixed, and fed to the reactor as a single stream, refrigerated to below 0 °C. The transition metal component (TMC) was dissolved in a solvent/toluene mixture (9/1 vol/vol) whereas the non-coordinating anion (NCA) activator was dissolved in toluene/solvent mixture (1/1 vol/vol). Both components were pumped separately, mixed at ambient temperature, and cooled to below about 0 °C prior to entering the reactor. The reactor temperature was set by adjusting the temperature of an oil bath used as a reservoir for the oil flowing through the reactor wall jacket. Next, the polymer molecular weight (MW) or MI was controlled independently by adjusting the ethylene conversion (% C_2) in the reactor via the catalyst flow rate. Finally, the polymer density was controlled by adjusting the ethylene/1-octene weight ratio in the feed. See Tables below.

Polymerization Conditions

聚合条件

催化剂 活化剂 催化剂进料 活化剂进料 烷基铝 [illegible] 温度 压力 溶剂 C_2 进料 C_8 进料

Exp 14 #	Cat	Act	Cat. Feed (mg/hr)	Act. Feed (mg/hr)	Alkyl-Al (mmol/l)	Rt (min)	Temp. (° C)	Press. (bar)	Solvent (kg/hr)	C_2 Feed (kg/hr)	C_8 Feed (kg/hr)
a)	A	$(F_5C_6)_4B^-$ (1)	3.3	2.7	0.015	7.2	190	85.8	5.5	1.16	0.53
b)	A	$(F_7C_{10})_4B^-$ (2)	5.2	5.8	0.015	7.0	196	85.8	5.7	1.17	0.54

(1) [N,N-dimethylanilinium][tetrakis(perfluorophenyl)boron] [N,N-二甲基苯胺阳离子][四(五氟苯基)硼]

(2) [N,N-dimethylanilinium][tetrakis(heptafluoronaphthyl)-boron] ["][四(七氟萘基)硼]

Product Analysis

产物分析

C_2 转化率 C_8 转化率 生产速率 催化剂效率 密度 C_8 结合量

Exp14 #	C_2 Conv (%)	C_8 Conv (%)	Prod Rate (kg/hr)	Cat. Prod. (kgPE/mg Cat)	MI (dg/min)	MIR (I21/12)	Density (kg/m^3)	C_8 Incorp. (wt %)	M_w (kg/mol)	PDI (M_w/M_n)
a)	84	48	1.46	440	0.84	39	903	17	95	2.3
b)	85	45	1.47	280	0.96	42	909	16	89	2.2

Claims:

1. A Group 4 organometallic compound comprising two ancillary monanionic ligands, each of which independently may be substituted or unsubstituted, wherein the ligands are bonded by a covalent bridge containing a substituted single Group 14 atom, the substitution on said Group 14 atom comprising aryl groups at least one of which contains at least one hydrocarbylsilyl substituent group.

2. The compound of claim 1 wherein said hydrocarbylsilyl substituent has the formula $R_n''SiR'_{3-n}$, where each R' is independently a C_1-C_{20} hydrocarbyl, hydrocarbylsilyl, hydrofluorocarbyl substitutent, R" is a C_1-C_{10} linking group between Si and the aryl group, and n = 0 or 1.

3. The organometallic compound of claim 2 wherein each R' is a linear C_1-C_6 linear or branched alkyl substituent.

4. The organometallic compound of claim 3 wherein said catalyst compound is a hafnium organometallic compound and said substituted Group 14 atom is a carbon atom.

5. The organometallic compound of claim 4 wherein said compound is a biscyclopentadienyl hafnium organometallic compound having

   i) at least one unsubstituted cyclopentadienyl or indenyl ligand,

   ii) one aromatic fused-ring substituted cyclopentadienyl ligand.

6. The organometallic compound of claim 4 wherein said aromatic fused-ring substituted cyclopentadienyl ligand is a substituted or unsubstituted fluorenyl ligand.

7. The organometallic compound of claim 6 wherein said unsubstituted cyclopentadienyl ligand or aromatic fused-ring substituted cyclopentadienyl ligand is an unsubstituted cyclopentadienyl ligand.

8. The organometallic compound of claim 7 wherein said hafnium compound is selected from the group consisting of di(p-trimethylsilyl-phenyl) methylene (cyclopentadienyl) (fluorenyl) hafnium dimethyl, di(p-trimethylsilyl-phenyl) methylene (cyclopentadienyl) (2,7-dimethyl-9-fluorenyl) hafnium dimethyl and di(p-trimethylsilyl-phenyl) methylene (cyclopentadienyl) (2,7-di-tert-butyl-9-fluorenyl) hafnium dimethyl, di(p-triethylsilyl-phenyl) methylene (cyclopentadienyl) (fluorenyl) hafnium dimethyl, di(p-triethylsilyl-phenyl) methylene (cyclopentadienyl) (2,7-dimethyl-9-fluorenyl) hafnium dimethyl, di(p-triethylsilyl-phenyl) methylene (cyclopentadienyl) (2,7-di-tert-butyl-9-fluorenyl) hafnium dimethyl, (p-triethylsilyl-phenyl) (p-tert-butylphenyl) methylene (cyclopentadienyl) (fluorenyl) hafnium dimethyl, (p-triethylsilyl-phenyl)) (p-n-butylphenyl) methylene (cyclopentadienyl) (2,7-dimethyl-9-fluorenyl) hafnium dimethyl, (p-triethylsilyl-phenyl) (p-n-butylphenyl) methylene (cyclopentadienyl) (2,7-di-tert-butyl-9-fluorenyl) hafnium dimethyl, and (p-triethylsilyl-phenyl) (p-n-butylphenyl) methylene (cyclopentadienyl) (2,7-dimethyl-9-fluorenyl) hafnium dimethyl.

9. A polymerization process for ethylene copolymers having a density of about 0.850 to about 0.940 comprising contacting, under solution polymerization conditions at a reaction temperature at or above 60 °C to 225 °C, ethylene and one or more comonomers capable of insertion polymerization with a catalyst compound derived from the Group 4 organometallic compound of claims 1-7.

10. The process of claim 9 wherein said catalyst compound is a hafnium organometallic compound and said substituted Group 14 atom is a carbon atom.

11. The process of claim 9 wherein said catalyst compound is derived by reacting with an activating cocatalyst compound.

12. The process of claim 11 wherein said cocatalyst compound comprises a halogenated tetraaryl-substituted Group 13 anion.

13. The process of claim 12 wherein the aryl substituent comprises at least one fused polycyclic aromatic ring.

14. The process of claim 13 wherein said halogenated tetraaryl Group-13 anion is [tetrakis(perfluoro-naphthyl)borate].

15. The process of any of claims 12-14 wherein said cocatalyst compound additionally comprises an essentially cationic complex selected from substituted or unsubstituted anilinium, ammonium, carbenium, silylium and metal cationic complexes.

16. The process of any of claims 9-15 wherein said solution polymerization conditions are adiabatically conducted in a continuous polymerization process.

17. The process of claim 16 wherein the reaction temperature is in a range of 160 °C to 250 °C.

18. The process of claim 17 wherein said homogeneous polymerization conditions are conducted in a continuous process at a pressure of at least 500 bar.

19. The process of any of claims 9-18 wherein said one or more comonomers capable of insertion polymerization are selected from the group consisting one or more of C_3-C_8 α-olefins, C_5-C_{15} diolefins, C_7-C_{20} cyclic olefins and diolefins, and C_7-C_{20} vinyl aromatic monomers.

20. The process of claim 19 wherein said one or more comonomers capable of insertion polymerization are selected from the group consisting of propylene, 1-butene, 1-hexene, 1-octene, 2-ethylidene-5-norbornene, and 2-vinyl-5-norbornene.

21. The process of claim 9 wherein said Group 4 organometallic compound comprises a monocyclopentadienyl, heteroatom-containing titanium compound.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/24944

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F210/02 C08F4/643

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 C08F C07F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SOGA, KAZUO ET AL: "Synthesis of a dinuclear ansa-zirconocene catalyst having a biphenyl bridge and application to ethene polymerization" J. MOL. CATAL. A: CHEM. (1998), 128(1-3), 273-278 , XP000879084	1,2,9, 11,12, 15,16, 19,20
Y	abstract page 276; scheme 1	11-13,15
A		10,13, 14,17, 18,21

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☒ 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
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Date of the actual completion of the international search 21 February 2000	Date of mailing of the international search report 16/03/2000
Name and mailing address of the ISA 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	Authorized officer Parry, J

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INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 99/24944

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	BAN H T ET AL: "POLYMERIZATION OF OLEFINS WITH A NOVEL DINUCLEAR ANSA-ZIRCONOCENE CATALYST HAVING A BIPHENYL BRIDGE" JOURNAL OF POLYMER SCIENCE, POLYMER CHEMISTRY EDITION,US,JOHN WILEY AND SONS. NEW YORK, vol. 36, no. 13, 30 September 1998 (1998-09-30), pages 2269-2274, XP000784246 ISSN: 0887-624X	1,2,9, 11,19,20
A	abstract; figure 1	10,12,13
Y	WO 96 28480 A (DOW CHEMICAL CO) 19 September 1996 (1996-09-19) page 11, line 5 -page 12, line 35 page 14, line 13 - line 17	11-13,15
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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代理人 刘金辉

权利要求书3页 说明书24页 附图页数0页

[54]**发明名称** 烯烃共聚合用的桥连茂金属

[57]**摘要**

本发明涉及在脂族溶剂中具有足够溶解性的桥连茂金属催化剂配合物，特别适用于溶液烯烃聚合法，使得可特别是在高聚合反应温度下以高分子量和催化剂活性制备烯烃共聚物。更具体地，本发明涉及一种制备密度为约0.850～0.940的乙烯共聚物的聚合方法，该方法包括在溶液聚合条件下，反应温度为60℃或大于60℃至250℃，使乙烯和一种或多种可插入聚合的共聚单体与桥连茂金属催化剂配合物接触，该茂金属催化剂配合物衍生自两个辅助配体，每一配体分别是取代的或未取代的，其中所述配体通过含取代的单一第14族原子的共价桥连部分键连，在所述第14族原子上的取代部分含有芳基，所述芳基的至少一个含有烃基甲硅烷基取代基；和B)一种活化助催化剂。

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知识产权出版社出版

权利要求书

1. 一种含两个辅助单阴离子配体的第4族有机金属化合物，所述每一配体可分别是取代的或未取代的，其中所述配体通过含取代的单一第14族原子的共价桥连部分键连，在所述第14族原子上的取代部分含有芳基，所述芳基的至少一个含有至少一个烃基甲硅烷基取代基。

2. 权利要求1的化合物，其中所述烃基甲硅烷基取代基的通式为$R''_nSiR'_{3-n}$，其中每一R'独立地表示C_1~C_{20}烃基、烃基甲硅烷基、氟代烃基取代基，R''为Si和芳基之间的C_1~C_{10}连接基团，n=0或1。

3. 权利要求2的有机金属化合物，其中每一R'为C_1~C_6线性或支化烷基取代基。

4. 权利要求3的有机金属化合物，其中所述催化剂化合物为铪有机金属化合物，所述取代的第14族原子为碳原子。

5. 权利要求4的有机金属化合物，其中所述化合物为二环戊二烯基铪有机金属化合物，该化合物具有

i) 至少一个未取代的环戊二烯基或茚基配体，

ii) 一个芳族稠环取代的环戊二烯基配体。

6. 权利要求4的有机金属化合物，其中所述芳族稠环取代的环戊二烯基配体为取代的或未取代的芴基配体。

7. 权利要求6的有机金属化合物，其中所述未取代的环戊二烯基配体或芳族稠环取代的环戊二烯基配体为未取代的环戊二烯基配体。

8. 权利要求7的有机金属化合物，其中所述铪化合物选自二(对-

三甲基甲硅烷基苯基)亚甲基(环戊二烯基)(芴基)二甲基铪，二(对-三甲基甲硅烷基苯基)亚甲基(环戊二烯基)(2,7-二甲基-9-芴基)二甲基铪，二(对-三甲基甲硅烷基苯基)亚甲基(环戊二烯基)(2,7-二叔丁基-9-芴基)二甲基铪，二(对-三乙基甲硅烷基苯基)亚甲基(环戊二烯基)(芴基)二甲基铪，二(对-三乙基甲硅烷基苯基)亚甲基(环戊二烯基)(2,7-二甲基-9-芴基)二甲基铪，二(对-三乙基甲硅烷基苯基)亚甲基(环戊二烯基)(2,7-二叔丁基-9-芴基)二甲基铪，(对-三乙基甲硅烷基苯基)(对-叔丁基苯基)亚甲基(环戊二烯基)(芴基)二甲基铪，(对-三乙基甲硅烷基苯基)(对-正丁基苯基)亚甲基(环戊二烯基)(2,7-二甲基-9-芴基)二甲基铪，(对-三乙基甲硅烷基苯基)(对-正丁基苯基)亚甲基(环戊二烯基)(2,7-二叔丁基-9-芴基)二甲基铪和(对-三乙基甲硅烷基苯基)(对-正丁基苯基)亚甲基(环戊二烯基)(2,7-二甲基-9-芴基)二甲基铪。

9. 一种制备密度为约 0.850～0.940 的乙烯共聚物的聚合方法，该方法包括在溶液聚合条件下，反应温度为 60℃或大于 60℃至 225℃，使乙烯和一种或多种可插入聚合的共聚单体与衍生自权利要求 1～7 的第 4 族有机金属化合物的催化剂化合物相接触。

10. 权利要求 9 的方法，其中所述催化剂化合物为铪有机金属化合物，所述取代的第 14 族原子为碳原子。

11. 权利要求 9 的方法，其中所述催化剂化合物是通过与活化助催化剂化合物反应得来的。

12. 权利要求 11 的方法，其中所述助催化剂化合物含有卤代的四芳基取代的第 13 族阴离子。

13. 权利要求 12 的方法，其中芳基取代基含有至少一个稠合多环

芳环。

14. 权利要求13的方法，其中所述卤代的四芳基第13族阴离子为[四(全氟萘基)硼酸根]。

15. 权利要求12～14任一项的方法，其中所述助催化剂化合物还含有实质上为阳离子的配合物，该阳离子配合物选自取代的或未取代的苯胺阳离子、铵、碳阳离子、甲硅烷基阳离子和金属阳离子配合物。

16. 权利要求9～15任一项的方法，其中所述溶液聚合条件以连续聚合法绝热进行。

17. 权利要求16的方法，其中反应温度为160～250℃。

18. 权利要求17的方法，其中所述均相聚合条件是以连续法在至少500巴的压力下进行。

19. 权利要求9～18任一项的方法，其中所述一种或多种可插入聚合的共聚单体选自一种或多种C_3～C_8 α-烯烃、C_5～C_{15}二烯烃、C_7～C_{20}环状烯烃和二烯烃，以及C_7～C_{20}乙烯基芳族单体。

20. 权利要求19的方法，其中所述一种或多种可插入聚合的共聚单体选自丙烯、1-丁烯、1-己烯、1-辛烯、2-亚乙基-5-降冰片烯和2-乙烯基-5-降冰片烯。

21. 权利要求9的方法，其中所述第4族有机金属化合物包括单环戊二烯基、含杂原子的钛化合物。

说 明 书

烯烃共聚合用的桥连茂金属

技术领域

本发明涉及适用于烯烃聚合方法的含芳基取代的桥连部分的有机金属催化剂化合物。

背景技术

含有乙烯、至少一种或多种α-烯烃、以及任选一种或多种二烯烃的烯烃聚合物构成了聚烯烃聚合物的大部分，这里称其为“乙烯共聚物”。这些聚合物涉及结晶聚乙烯共聚物，如密度超过0.94的高密度聚乙烯，轻微结晶的聚乙烯，如密度为0.915~0.94的线性低密度聚乙烯，密度降至0.85且分子量相对较高的大部分为无定形的弹性体，以及一个新领域的半结晶“塑性体”，其密度为0.915~0.86，且分子量适中。特别地，与其独特性能如弹性性能和热-氧化稳定性能相关，乙烯共聚物塑性体现正成为一种广泛开发的具有多种用途的工业聚合物。塑性体的用途包括通用热塑性聚烯烃、膜、电线和电缆涂层、聚合物改性、注射成型、泡沫、鞋类、片材、官能化聚合物、以及粘合剂和密封配方用组分。

传统上，商品制备的乙烯共聚物是以大多基于钒或钛的催化剂体系，通过Ziegler-Natta聚合而制得。由于容易并入大量单体且聚合活性可潜在提高，较新的茂金属催化剂化合物得到了重视。USP 5324800公开了具有取代和未取代环戊二烯基配体的茂金属，它们适于生产高分子量烯烃聚合物，包括乙烯和少量α-烯烃的线性低密度共聚物。

在USP 5408017和5767208、以及EP 612768和612769中公开了在烯烃聚合中使用基于桥连茂金属的离子催化剂。每一文献均公开了

适于高温法烯烃共聚合用的桥连茂金属催化剂。在 USP 4892851、5155080 和 5132381 中公开了适用作烯烃聚合催化剂的茂金属的取代的单碳或亚甲基桥连基团。异亚丙基、单和二芳基亚甲基被确定为是特别适宜的。

烯烃溶液聚合法通常在脂族溶剂中进行，脂族溶剂既起到保持反应介质温度范围的作用，又起到对制得的聚合产物溶剂化的作用。然而，那些具有环戊二烯基衍生物和其它稠合的或侧基芳基取代基的含芳基的茂金属极不易溶于这类溶剂中，典型地是将它们引入到芳族溶剂如甲苯中。因此用甲苯会污染在脂族溶剂中的溶液聚合法，必须除去甲苯以保持方法的效率，并适应与工业生产和聚合物加工相关的健康要求。或者是，可通过淤浆法引入相对不溶的催化剂，但该法需要特殊的处理和泵送过程，这使工厂设计和操作复杂化并增加了大量的成本。若方法中在某一阶段包含低温操作，低溶解性也会带来不利，例如在环境温度较低的地区所运行的典型的绝热方法。此外，在特定催化剂溶剂的回收体系中，分离或阻止其聚集也成为问题。同时非常需要的是在烯烃聚合物中保持高分子量，而又在经济的优选高聚合反应温度和高聚合物生产速率下操作。因此需要提供一种特别是在高温下对乙烯聚合有活性的茂金属催化剂，而该催化剂在脂族溶剂中具有增加的溶解性。

发明概述

由此本发明具体涉及取代的桥连茂金属催化剂配合物，该配合物含有包含至少一个烃基甲硅烷基取代基的增溶共价桥连部分。它可被描述成一种含两个辅助单阴离子配体的第 4 族有机金属化合物，所述每一配体分别被取代或是未取代的，其中所述配体通过含取代的单一第 14 族原子的共价桥连部分键连，在所述第 14 族原子上的取代部分含有芳基，所述芳基的至少一个含有至少一个足以在脂族溶剂中提供增加的溶解性的烃基甲硅烷基取代基。此外，本发明涉及一种密度为

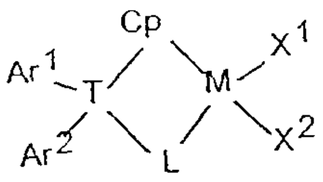
约 0.850～0.940 的乙烯共聚物的溶液聚合方法，该方法包括在 40～300℃的反应温度下，在超临界或溶液聚合条件下，使乙烯和一种或多种可进行插入聚合的共聚单体与茂金属催化剂配合物相接触，所述的茂金属催化剂配合物衍生自 A) 具有将环戊二烯基配体连接到另一辅助阴离子金属配体基团的共价桥连部分的茂金属化合物，所述桥连部分含有取代的单一第 14 族原子，在所述第 14 族原子上的取代部分含有芳基，所述芳基的至少一个含有至少一个通式为 $R^2{}_nSiR^1{}_{3-n}$ 的烃基甲硅烷基取代基，其中每一 R^1 独立地表示 C_1～C_{20} 烃基、烃基甲硅烷基、氟代烃基 (hydrofluorocarbyl) 取代基，R^2 为 Si 和芳基之间的 C_1～C_{10} 连接基团，n＝0、1 或 2。当 n＝0 时，Si 原子直接共价键连于芳基环碳原子上。

发明详述

本发明的桥连茂金属化合物是这样的一些化合物，它们具有桥连茂金属中心原子的两个辅助单阴离子配体的单一取代的碳原子或硅原子，两个配体例如为含取代的或未取代的环戊二烯基 (Cp) 的配体和/或取代的和未取代的第 13～16 族杂原子配体。桥连部分取代基为取代的芳基，取代基包括至少一个位于至少一个芳基桥连部分取代基上的增溶烃基甲硅烷基取代基。在环戊二烯基和/或杂原子配体上的取代基包括在那些配体上替换了一个或多个氢基团的 C_1～C_{30} 烃基、烃基甲硅烷基或氟代烃基，或者在环戊二烯基环上的稠合芳环上的那些。芳环可以是在环戊二烯基配体上的取代基，并包括环戊二烯基的茚基和芴基衍生物，及其氢化的相应物。典型地，这些可包括一个或多个选自线性、支化、环状、脂族、芳族或混合结构基团的芳环取代基，包括稠环或侧基构型。其实例包括甲基、异丙基、正丙基、正丁基、异丁基、叔丁基、新戊基、苯基、正己基、环己基、苄基和金刚烷基。本申请中，术语“烃”或“烃基”包括这样的化合物或基团，它们实质上具有烃的特征，但任选含有不超过约 10 摩尔％的非碳杂原子，如

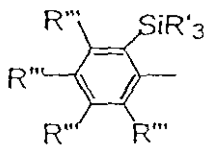
硼、硅、氧、氮、硫和磷。此外该术语还包括氟代烃基取代基。“烃基甲硅烷基”的非限定性例子有二烃基－和三烃基甲硅烷基，其中优选的烃基为桥连基团苯基的 C_1～C_{30} 取代烃基、烃基甲硅烷基或氟代烃基取代基。对于含杂原子的催化剂，参见 WO 92/00333。使用其中非碳的第 13、14、15 或 16 族原子置换了一个环碳原子的含杂原子的环或稠环，在本申请中也被认为是在术语“环戊二烯基”、“茚基”和“芴基”的范围之内。例如参见与 1997 年 12 月 29 日申请的 US 系列 No. 08/999214 有相同优先权的 WO 98/37106 的背景技术部分和说明书部分，以及与 1998 年 3 月 13 日申请的 US 系列 No. 09/042378 有相同优先权的 WO 98/41530，从美国专利实践的角度，这里将上述二者引为参考。

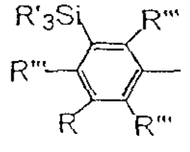
这些化合物可以下述通式表示：

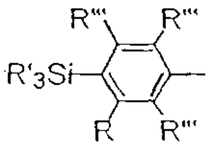


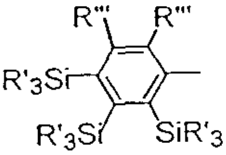
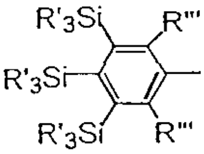
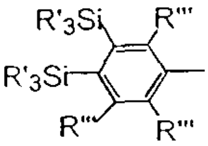
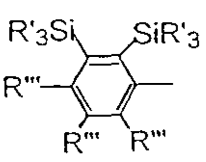
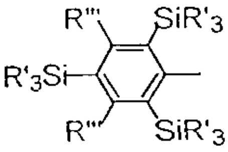
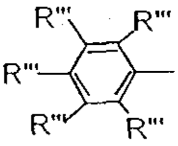
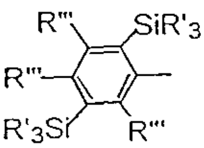
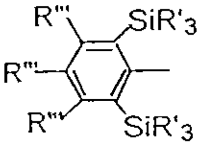
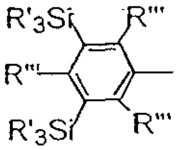
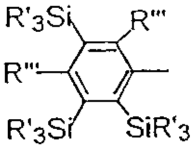
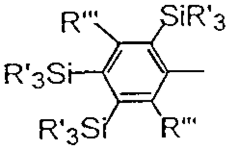
其中 Cp 为含取代的或未取代的环戊二烯基的辅助配体，L 独立地选自如上述所定义的 Cp 配体，或者是取代的或未取代的第 13～16 族杂原子配体，T 为含第 14 族元素的桥连基团，Ar^1 或 Ar^2 为可相同或不同的取代芳基，M 为第 3～6 族的金属，X^1 和 X^2 为相同或不同的不稳定配体，它们可被提取而活化并适于烯烃插入，或者可烷基化以成为可提取的并适于烯烃插入。这里所用的术语“辅助配体”是指稳定金属中心的庞大单阴离子配体，与金属中心键连而抵抗氧化反应（即通过化学反应的配体的键解离），术语“不稳定配体”是指从键连的金属中心上可很容易地被置换、提取或除去的配体。

为进一步说明，Ar^1 和 Ar^2 可独立地选自下述基团：





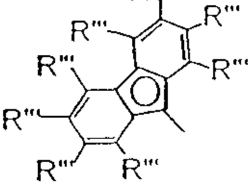
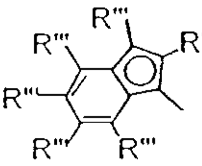
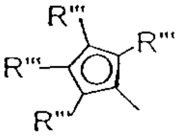













，

其中任何R'独立地为除H以外的任何下述基团，任何R'''独立地为任何下述基团：

H
CH_3
CH_2CH_3
$CH_2CH_2CH_3$
$CH_2(CH_2)_2CH_3$
$CH_2(CH_2)_{3\text{-}30}CH_3$
$CH_2C(CH_3)_3$
$CH{=}CH_2$
$CH(CH_3)_2$
$CH_2CH(CH_3)_2$
$CH_2CH_2CH(CH_3)_2$
$C(CH_3)_2CH(CH_3)_2$
$CH(C(CH_3)_3)CH(CH_3)_2$
$C(CH_3)_3$
$CH_2Si(CH_3)_3$
CH_2Ph
C_4H_7
C_5H_9
C_6H_{11}
C_7H_{13}
C_8H_{15}
C_9H_{17}
C_6H_5
CH_2SiR_3
$CH_2CH{=}CH_2$
$CH_2CH_2CH{=}CH_2$
$CH_2CH_2(CF_2)_7CF_3$
CF_3
$N(CH_3)_2$
$N(C_2H_5)_2$
$OC(CH_3)_3$

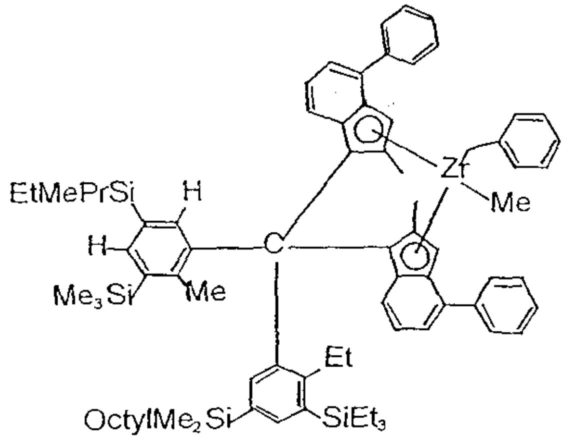
Cp和L可分别为任何下述的配体，其中R'''如上所示。

X^1和X^2可独立地为任何对R'''所列的基团，加上Cl、Br、I、-NH

R'''、-N(R''')$_2$或-OR'''中的任何一个。此外，X^1和X^2可连接在一起形成一个二齿配体，如环脂族烃基二齿配体或环烯基烃基配体。

一个代表性的说明例为：



其中Me为甲基，Et为乙基，Octyl为辛基。

桥连的铪催化剂的具体实例包括那些衍生自基于茚基的配合物，如下述的异构体或混合物：二(对-三乙基甲硅烷基苯基)亚甲基二(茚基)二甲基铪，二(对-三甲基甲硅烷基苯基)亚甲基二(茚基)二甲基铪，二(对-三正丙基甲硅烷基苯基)亚甲基二(茚基)二甲基铪，(对-三乙基甲硅烷基苯基)(对-叔丁基苯基)亚甲基(芴基)(茚基)二甲基铪，(对-三乙基甲硅烷基苯基)(对-甲基苯基)亚甲基(芴基)(茚基)二甲基铪，二(对-三乙基甲硅烷基苯基)亚甲基(2,7-二叔丁基芴基)(茚基)二甲基铪，(对-三甲基甲硅烷基苯基)(对-正丁基苯基)亚甲基(2,7-二叔丁基芴基)(茚基)二甲基铪，(对-三乙基甲硅烷基苯基)(对-正丁基苯基)亚甲基二(四氢茚基)二苄基铪，和二(对-三乙基甲硅烷基苯基)亚甲基二(四氢茚基)二甲基铪。

类似地，锆化合物的实例包括二(对-三乙基甲硅烷基苯基)亚甲基二(茚基)二甲基锆，二(对-三甲基甲硅烷基苯基)亚甲基二(茚基)二甲基锆，二(对-三正丙基甲硅烷基苯基)亚甲基二(茚基)二甲基锆，(对-三乙基甲硅烷基苯基)(对-叔丁基苯基)亚甲基(芴基)(茚基)二甲基锆，(对-三乙基甲硅烷基苯基)(对-甲基苯基)亚甲基(芴基)(茚基)二甲基锆，二(对-三乙基甲硅烷基苯基)亚甲基(2,7-二叔丁基芴基)(茚基)二甲基锆，(对-三甲基甲硅烷基苯基)(对-正丁基苯基)亚甲基

(2,7-二叔丁基芴基)(茚基)二甲基锆，(对-三乙基甲硅烷基苯基)(对-正丁基苯基)亚甲基二(四氢茚基)二苄基锆，和二(对-三乙基甲硅烷基苯基)亚甲基二(四氢茚基)二甲基锆。当按照本发明与增溶桥连基团一起制备时适用的其它优选锆茂金属描述于1999年2月17日申请的共同待审的US申请系列No. 09/251819和等同的WO 99/41294中，与它们一起公开的催化剂结构和溶液聚合方法特别适用于本发明，这里根据美国专利实践将其引为参考。

特别适用的基于环戊二烯基的配合物为下述化合物、异构体或混合物:(对-三甲基甲硅烷基苯基)(对-正丁基苯基)亚甲基(芴基)(环戊二烯基)二甲基铪，二(对-三甲基甲硅烷基苯基)亚甲基(2,7-二叔丁基芴基)(环戊二烯基)二甲基铪，二(对-三乙基甲硅烷基苯基)亚甲基(2,7-二叔丁基芴基)(环戊二烯基)二甲基铪，(对-三乙基甲硅烷基苯基)(对-叔丁基苯基)亚甲基(2,7-二叔丁基芴基)(环戊二烯基)二甲基或二苄基铪，和二(对-三乙基甲硅烷基苯基)亚甲基(2,7-二叔丁基芴基)(环戊二烯基)二甲基或二苄基铪。二茂锆的类似物为(对-三甲基甲硅烷基苯基)(对-正丁基苯基)亚甲基(芴基)(环戊二烯基)二甲基锆，二(对-三甲基甲硅烷基苯基)亚甲基(2,7-二叔丁基芴基)(环戊二烯基)二甲基锆，二(对-三乙基甲硅烷基苯基)亚甲基(2,7-二叔丁基芴基)(环戊二烯基)二甲基锆，(对-三乙基甲硅烷基苯基)(对-叔丁基苯基)亚甲基(2,7-二叔丁基芴基)(环戊二烯基)二甲基或二苄基锆，和二(对-三乙基甲硅烷基苯基)亚甲基(2,7-二叔丁基芴基)(环戊二烯基)二甲基或二苄基锆。现已发现，含取代的桥连部分的化合物，如上述的那些非对称化合物，特别适用于本发明中。

特别地，对于桥连的茂金属化合物，提高在芳族稠环取代的配体Cp上的取代程度对提高分子量有效，这些的例子例如为2,7-二甲基芴基、2,7-二叔丁基芴基和2,7-甲基-苯基芴基。优选地，在茂金属化合物中的芴基或茚基基团(ii)上的取代部分通常包含两个或多个C_1-C_{30}烃基或烃基甲硅烷基，它们对至少一个6元稠环的环氢原子来说是替代部分或取代部分，当为芴基时优选二者都有。

可以任何足以允许配位或阳离子聚合的方式来使本发明的桥连茂金属化合物活化而用以聚合催化。当一个配体可被提取，且另一个或者允许不饱和单体的插入，或者对于用一个配体置换来说是类似的可提取的时，可实现配位聚合，上述置换的配体可允许不饱和单体的插入(不稳定配体)，例如烷基、甲硅烷基或氢化物。配位聚合领域常用的活化剂在这里是适用的，典型地它们包括路易斯酸如铝氧烷化合物，以及离子化的阴离子前体化合物，这些前体化合物提取一个离子，使得桥连的茂金属金属中心离子化为阳离子，并提供抗衡非配位阴离子。

烷基铝氧烷和改性的烷基铝氧烷适用作催化剂活化剂，特别是对于本发明的含卤化物配体的金属化合物。典型地，适用作催化剂活化剂的铝氧烷组分为通式$(R''-Al-O)_n$表示的齐聚铝化合物，其为环状化合物，或者$R''(R''-Al-O)_nAlR''_2$，其为线性化合物。在铝氧烷通式中，R''独立地表示$C_1 \sim C_{10}$烷基，如甲基、乙基、丙基、丁基或戊基，“n”为约 1~50 的整数。最优选 R''为甲基，“n”至少为 4。可通过本领域公知的各种方法制备铝氧烷。例如，可将烷基铝用溶解在惰性有机溶剂中的水处理，或者将烷基铝与悬浮在惰性有机溶剂中的水合盐，如水合硫酸铜相接触，以制得铝氧烷。通常，无论如何制备，烷基铝与受限量的水的反应制得的是线性和环状铝氧烷的混合物。优选甲基铝氧烷和改性的甲基铝氧烷。进一步详细的内容参见 USP 4665208，4952540，5041584，5091352，5206199，5204419，4874734，4924018，4908463，4968827，5329032，5248801，5235081，5157137，5103031，以及 EP 561476A1，EP 279586B1，EP 516476A，EP 594218A1 和 WO 94/10180，这里根据美国专利实践将它们全部引为参考。

当活化剂为铝氧烷时，优选过渡金属化合物与活化剂的摩尔比为 1: 2000 至 10: 1，更优选约 1: 500 至 10: 1，进一步更优选约 1: 250 至 1: 1，最优选约 1: 100 至 1: 1。

术语“非配位的阴离子”是指或者不与金属阳离子配位，或者仅与其弱配位的阴离子，由此保持足够的被中性路易斯碱，如烯属或炔属不饱和单体置换的不稳定性。任何可以抗衡阳离子电荷而不损害或

妨碍烯烃聚合的配合物，包括不能与茂金属阳离子反应以使它们呈中性并保持足够的不稳定性以能够在聚合位置被烯烃单体置换的配合物，均适用于本发明。典型地，这些配合物基于第 8 ~ 14 族的准金属或金属元素，特别是硼或铝的离子盐或中性路易斯酸，其中硼或铝具有取代的芳基，这些芳基被取代以通过过渡金属中心与键连到第 13 族原子的芳基间的反应提供对配合物氧化的空间或电子阻碍。此外特别适宜的还有既含阳离子又含阴离子电荷的符合上述功能要求的第 13 族元素的两性配合物。

其它适宜的阴离子在本领域是公知的，并适用于本发明的茂金属催化剂。特别是可参见 USP 5278119 和 S. H. Strauss 的综述文章“有关较大和较弱配位阴离子的研究”，Chem. Rev., 93, 927-942(1993)，以及 C. A. Reed, “碳硼烷:一类新的用于强亲电试剂、氧化剂和超强酸的弱配位阴离子”, Acc. Chem. Res., 31, 133-139(1998)。

适用于配位聚合的含有过渡金属阳离子和非配位阴离子的那些离子催化剂的具体描述公开于 USP 5064802, 5132380, 5198401, 5278119, 5321106, 5347024, 5408017, 5599671 和国际申请 WO 92/00333, WO 93/14132 和 WO 97/35893 中。这些文献教导了优选的制备方法，其中茂金属被非配位的阴离子前体质子化，使得通过质子化，烷基、链烯基或氢化物从过渡金属中被提取出来，以使过渡金属既呈阳离子，又被非配位的阴离子电荷平衡。

使用不含活性质子但可以生成茂金属阳离子和非配位阴离子的离子化离子化合物也是适宜的。参见 EP-A-426637、EP-A-573403 和 US 5387568 的离子化合物部分。非布朗斯台德酸的离子化离子化合物的反应性阳离子包括二茂铁阳离子、银、䓬鎓离子、三苯基碳阳离子和三乙基甲硅烷基阳离子，或者碱金属或碱土金属阳离子，如钠、镁或锂阳离子。另一类适用于本发明的非配位阴离子前体是含有如上所述的碱金属或碱土金属阳离子和非配位阴离子的水合盐。水合盐可通过金属阳离子-非配位阴离子盐与水反应制备，例如通过商品可得或容易合成的 $LiB(pfp)_4$的水解，它可制得$[Li\bullet xH_2O][B(pfp)_4]$，其中(pfp)

为五氟苯基或全氟苯基。

任何可形成抗水(或其它布朗期台德酸或路易斯酸)降解的配位配合物的金属或准金属均可使用或包含在非配位阴离子中。适宜的金属包括但不限于铝、金、铂等。适宜的准金属包括但不限于硼、磷和硅等。上述段落中有关非配位阴离子及其前体的描述的文献，这里根据美国专利实践将其引为参考。

其它制备本发明的活性聚合催化剂的方法使用起始为中性路易斯酸，但在与本发明的化合物反应时形成茂金属阳离子和非配位阴离子的离子化阴离子前体，例如三(五氟苯基)硼，其作用是提取一个烃基、氢化物或甲硅烷基配体，以生成茂金属阳离子和稳定化非配位阴离子，详细说明参见 EP-A-427697 和 EP-A-520732。还可参见 EP-A-495375 的方法和化合物。类似地，这些文献中有关非配位阴离子及其前体的说明也根据美国专利实践引入本发明中作为参考。

当 X_1 和 X_2 不稳定配体不是氢化物、烃基或甲硅烷基烃基，如氯化物、氨基（amido）或烷氧基配体，且不能用离子化阴离子前体化合物进行离散离子化提取时，这些 X 配体可通过公知的烷基化反应，用有机金属化合物如锂或铝的氢化物或烷基化物、烷基铝氧烷、格式试剂等进行转化。参见 EP-A-500944、EP-A-570982 和 EP-A-612768 中的类似方法，它们描述了在加入活化非配位阴离子前体化合物时或之前，烷基铝化合物与二卤化物取代的茂金属化合物的反应。

本发明优选的活化助催化剂，即前体离子化化合物，含有第 13 族元素配合物(这些配合物具有至少两个卤代芳族配体，如公认的现有技术所例举的卤代四苯基硼和铝化合物)。优选的芳族配体由容易得到的苯基、多环芳族烃和芳环组合体组成，其中两个或多个环(或稠环体系)相互或一起直接连接。这些可相同或不同的配体直接与金属/准金属中心共价键连。在一个优选实施方案中，芳基为卤代的，优选氟代的四芳基第 13 族元素阴离子配合物，这些配合物含有至少一个稠合多环芳烃或侧基芳环。卤代配体还表示为那些具有氟代烷基的芳基配体。萘基、萘基、蒽基、庚搭烯基和联苯基配体为芳基配体的例子。参见 1999

年 3 月 3 日申请的共同待审的 US 申请系列 No. 09/261627 以及等同的 WO 99/45042，这里根据美国专利实践将它们引为参考。

特别优选的用于溶液聚合方法的助催化剂配合物是那些可溶于脂族溶剂中的，不管是在第 13 族元素配体上取代还是在前体阳离子上取代，例如参见 USP 5502017 和 WO 97/35893。当离子性非配位阴离子前体的阳离子部分为布朗斯台德酸如质子或质子化的路易斯碱(水除外)，或者可还原的路易斯酸如二茂铁或银阳离子，或碱金属或碱土金属阳离子如钠、镁或锂阳离子时，过渡金属与活化剂的摩尔比可以是任何比例，但优选约 10：1 至 1：10，更优选约 5：1 至 1：5，进一步更优选约 2：1 至 1：2，最优选约 1.2：1 至 1：1.2，摩尔比为约 1：1 是最优选的。

因此配位和碳阳离子聚合用的适宜的活性催化剂配合物可通过用本领域公知的常规茂金属活化剂活化来制备，典型地是用烷基铝氧烷和离子化卤代芳基硼或铝化合物。由此，活性催化剂为含有按照本发明的配合物及活化助催化剂化合物的催化活性组分，其中所述配合物衍生自本发明的含将辅助配体键连于一起的增溶桥连部分的茂金属化合物。

本发明的催化剂组分适用于通常已知在配位聚合条件或阳离子聚合条件下可聚合的不饱和单体的聚合。这些条件是公知的并包括溶液聚合、超临界相聚合、淤浆聚合以及低、中和高压气相聚合。本发明的催化剂可被负载，这样将特别适用于公知的使用固定床、移动床、流化床或淤浆法的操作方式，这些方法以单一、串联或并联反应器进行，其附加的优点是，提高的溶解性将适用于甲苯引入量降低或避免使用浆液泵送引入方式的催化剂合成方法中。

当使用本发明的催化剂时，整个催化剂体系通常还将含有一种或多种有机金属化合物。本申请及其权利要求中所用的这些化合物包括可从反应体系中有效除去极性杂质并提高催化剂活性的那些化合物。在引入任何聚合反应组分，特别是溶剂、单体和催化剂物料时，会不经意地引入杂质，杂质会对催化剂活性和稳定性产生不利影响。它可

降低或甚至于消除催化活性，特别是当离子化阴离子前体活化催化剂体系时。极性杂质或催化剂毒物包括水、氧、金属杂质等。优选在将这些引入反应器中之前采取步骤，例如在各组分的合成或制备之后或其过程中，通过化学处理或细心的分离技术，但通常在聚合方法本身中仍将使用一些少量的有机金属化合物。

典型地，这些化合物是有机金属化合物，例如 USP 5153157、5241025 和 WO -A-91/09882、WO -A-94/03506、WO -A-93/14132 和 WO 95/07941 中所提到的第 13 族有机金属化合物。其实例包括三乙基铝、三乙基硼烷、三异丁基铝、甲基铝氧烷和异丁基铝氧烷。优选具有共价键连到金属或准金属中心上的庞大或 C_6～C_{20} 线性烃基取代基的那些化合物，以使得对活性催化剂的不利相互影响最小化。其实例包括三乙基铝，但更优选体积大的化合物，如三异丁基铝、三异戊二烯基铝，和长链线性烷基取代的铝化合物，如三正己基铝、三正辛基铝或三正十二烷基铝。当使用铝氧烷作为活化剂时，任何超过活化存在的催化剂所需的量，均可作为毒物清除剂化合物，并且不需要加入额外的有机金属化合物。铝氧烷也可以与其它的活化方式一起以清除量使用，例如甲基铝氧烷和三异丁基铝氧烷与基于硼的活化剂一起使用。这些与本发明的催化剂化合物一起使用的化合物的量在聚合反应过程中应最小化至可提高活性的有效量(若以双重角色使用时，其量必须要能够活化催化剂化合物)，因为过量的可起催化剂毒物的作用。

在本发明方法的优选实施方案中，以液相(溶液、淤浆、悬浮液、本体相或其结合)、高压液相或超临界流体相的形式使用催化剂体系。这些方法的每一个均可用于单一、并联或串联反应器中。液体方法包括在一适宜的稀释剂或溶剂中使烯烃单体与上述催化剂体系相接触，并使得所述单体反应足够时间，以制得本发明的共聚物。对于溶液法来说，脂族溶剂和混合脂族溶剂是工业上适宜的，并且是特别优选的。

本发明的方法特别适用于基本上也是绝热的均相溶液聚合，也就是说聚合热被变通为聚合反应器内容物（这里主要是溶剂）的温度升高。典型地，这种绝热法没有内部冷却，而且适宜地也没有外部冷却。

反应器出口物流从反应器中带走了聚合热。可通过在引入反应器之前冷却入口溶剂和/或单体物流，以允许更大的聚合放热，来提高这种绝热法的产率。因此有利地，可将公开于本申请中的催化剂、助催化剂和清除剂以连续溶液法操作，操作温度为高于或等于140℃，高于150℃或高于160℃，至多约250℃。典型地，该方法可在20~200巴的压力下，在线性、环状或支化脂族或芳族惰性烃溶剂中进行。这些催化剂在较高温度下生产商业所需聚合物的能力带来的是更大的放热、由于粘度低聚合物在反应器中的含量高、在蒸发和回收溶剂中所消耗的能量较低、以及单体和共聚单体的转化更好。例如参见US 5767208和1999年3月3日申请的共同待审的US申请系列No. 09/261637，及其等同的WO 99/45041，这里根据美国专利实践将其全部引为参考。

按照本发明的催化剂可被负载，以用于气相、本体和淤浆聚合法中，或者按需要确定。许多负载方法在烯烃共聚合领域是公知的，在最广的范围内，任一种均适用于本发明方法。例如参见USP 5057475和5227440公开的铝氧烷活化的催化剂。负载离子催化剂的一个实例公开于WO 94/03056。对于离子催化剂，特别有效的方法公开于USP 5427991、5647847和WO 98/55518。可按照USP 5001205和5229478中对于乙丙橡胶所公开的，使用本体或淤浆法，这些方法中使用了由铝氧烷助催化剂活化的负载的所述发明的茂金属化合物，这些方法也将适用于本申请的催化剂体系。按照本领域的技术常识，既可使用无机氧化物也可使用聚合物载体。例如参见USP 5422325、5427991、5498582、5466649，均在1995年6月24日申请的共同待审的US专利申请系列08/265532和08/265533，以及国际申请WO 93/11172和WO 94/07928。上述各文献均根据美国专利实践引入作为参考。

典型地，本体和淤浆法是通过使催化剂与液体单体或稀释剂的浆液接触来进行的，其中催化剂体系是负载的。气相法典型地是使用载体催化剂，并以任何公知的适用于通过配位聚合制备乙烯均聚物或共聚物的方式进行。其说明性实例可在USP 4543399、4588790、5028670、5382638、5352749、5436304、5453471和5463999，以及WO 95/07942

中找到。将上述各文献根据美国专利实践引入作为参考。

通常，聚合反应的温度可以在约-50～300℃变化。优选的反应温度条件为-20～250℃，并且在高温绝热溶液法中，最优选的是约120～230℃，包括120℃和230℃。压力可以在约1mmHg～2500巴之间变化，优选0.1～1600巴，最优选1.0～500巴。

可使用本发明的催化剂在通常的溶液聚合法（如上）条件下，或者通过将乙烯气体引入浆液中，使用α-烯烃或环状烯烃或其与其它可聚合或不可聚合的单体的混合物，作为本发明催化剂悬浮于其中的聚合稀释剂，来制备高分子量和第结晶度的乙烯-α-烯烃(包括乙烯-环状烯烃和乙烯-α-烯烃-二烯烃)弹性体。典型地，乙烯压力为10～1000磅/平方英寸(69～6895kPa)，聚合稀释剂温度为-10～160℃。聚合可在搅拌罐反应器或管状反应器中进行，或者多个反应器以串联或并联操作。对于总的聚合方法条件，参见USP 5001205的公开内容。引入所有文献作为对聚合方法、离子活化剂和适用的清除剂化合物描述的参考。

按照通常的教导，典型地在淤浆或气相反应法中，也可以使用本发明载体催化剂的预聚合，以进一步控制聚合物粒子的形态。例如通过C_2～C_6α-烯烃预聚合一段有限的时间来完成这一步，例如将乙烯与载体催化剂在-15～30℃下接触75分钟，乙烯压力至多为约250磅/平方英寸(1724kPa)，以在载体上得到分子量为30000～150000的聚乙烯聚合物涂层。然后预聚合的催化剂可用于上述的聚合方法。此外还可以使用聚合物树脂作为载体涂层，典型地是通过将固体载体悬浮在溶解的例如聚苯乙烯树脂中，随后分离并干燥。引入所有文献作为对茂金属化合物、离子活化剂和适用的清除剂化合物描述的参考。

除以上具体描述的之外的其它烯属不饱和单体可使用本发明的催化剂通过配位聚合来实现聚合，例如苯乙烯、烷基取代的苯乙烯、亚乙基降冰片烯、乙烯基降冰片烯、降冰片二烯、二聚环戊二烯和其它的烯属不饱和单体，包括其它的环状烯烃，如环戊烯、降冰片烯和烷基取代的降冰片烯。此外，还可以通过共聚合而结合入上至300或更

多的mer单元的α-烯烃大单体。

给出下述实施例以进一步说明上面的描述。除非另加说明，所有的份数、比例和百分数均以重量计。所有的实施例均在干燥无氧的环境和溶剂中进行。尽管实施例可能涉及本发明的某些实施方案，但不应把它们理解成为是以任何方式限制本发明。在这些实施例中，使用某些缩写以简化叙述。这些包括标准的化学元素缩写和某些通用的缩写，例如：Me＝甲基，Et＝乙基，t-Bu＝叔丁基，Oct＝辛基，Cp＝环戊二烯基，Ind＝茚基，Flu＝芴基，THF(或thf)＝四氢呋喃，Ph＝苯基，pfp＝五氟苯基。

除非另加说明，所有的分子量均为重均分子量。由凝胶渗透色谱法测定分子量(重均分子量(Mw))和数均分子量(Mn)，除非另加说明，使用配有差示折光指数(DRI)和小角光散射(LS)检测器的Waters 150凝胶渗透色谱仪，并用聚苯乙烯标准物进行校正。用串联的三个Polymer Laboratories PC Gel混合B柱，使样品在1,2,4-三氯苯(135℃)中通过。这一通用的技术公开于"聚合物和相关材料的液相色谱III"J. Cazes Ed., Marcel Decker, 1981, 第207页，这里根据美国专利实践将其引入作为参考。没有使用对柱扩散的校正；但是以通常可接受的标准，例如National Bureau of Standards Polyethylene 1475给出的数据说明对于由洗脱时间计算的Mw/Mn，精度为0.2个单位。

实施例：

(对-Et_3Si-苯基)$_2$C(2,7-二叔丁基芴基)(环戊二烯基)$HfMe_2$(催化剂A)的合成

1. 1-溴,4-(Et_3Si)苯的合成

向冷的(-78℃)1,4-二溴苯(235g, 0.99mol)和无水THF(1.5L)的浆液中加入正丁基锂(1.0mol)、戊烷(300mL)和乙醚(100mL)的溶液。搅拌3小时后，加入Et_3SiCl(150g, 1.0mol)。将混合物缓慢地加热至室温，总计搅拌约60小时，然后用水(50mL)淬灭。分离出有机层，用

额外的水(2 ×50mL)洗涤，用硫酸镁干燥，过滤，然后提炼（reduce）为桔色油状物。通过真空(60 毫毛)蒸馏得到产物(沸点 83℃)。产量 124g，46％。

2. 合成 6,6'-二(对- Et_3Si-苯基)富烯

向冷的(-78 ℃)1-溴,4-(Et_3Si)苯(124g，0.46mol)和无水 THF(0.5L)的浆液中加入正丁基锂(0.46mol)和戊烷(246mL)的溶液。搅拌 75 分钟后，加入 $ClC(O)NMe_2$(21mL，0.23mol)。将混合物缓慢地加热至室温过夜，然后在冰浴中冷却。加入环戊二烯(46mL，0.55mol)，颜色迅速变成红色。在冰浴中搅拌 8 小时后，将混合物加热至室温过夜。在两步中(总计 800mL 水)用水(4 ×100mL)萃取混合物，用硫酸镁进行干燥，然后提炼为油状物。在乙醚(200mL)中吸收油状物，用氢化钙干燥，过滤，然后提炼为红色油状物。粗产物产量为 114.8g。

3. (对-Et_3Si-苯基)$_2$C(2,7-二叔丁基芴基)(环戊二烯基)$HfCl_2$的合成

在冷的(-30℃)粗富烯(114.8g，0.25mol)和乙醚(500mL)的溶液中加入 2,7-二叔丁基芴基锂(69.5g，0.25mol)。将混合物加热至室温过夜，然后提炼为桔色油状物。加入戊烷(0.5L)，形成浆液。过滤，戊烷洗涤(2 ×100mL)并干燥，得到白色固体状(对-Et_3Si-苯基)$_2$C(2,7-二叔丁基 FluH)(CpLi)(97g，53%，假定没有乙醚存在)。向该单阴离子(95g，0.129mol)和乙醚(1L)的浆液中加入 2M 丁基锂的戊烷(64.5mL，0.129mol)溶液。搅拌过夜后，将桔色的混合物冷却至-30℃，然后用 $HfCl_4$(41.4g，1 当量)处理。将混合物加热至室温，搅拌 24 小时，然后在真空下提炼为固体。用二氯甲烷(总计 500mL)萃取该固体，然后用硅藻土过滤。将滤液提炼为固体，用戊烷(3 ×100mL)萃取然后干燥。60℃下，用甲苯和己烷(1:1)的混合物从该固体中萃取出产物，然后经 0.45μm 的过滤器过滤。除去溶剂得到产物。产量 70g，55％。

4. (对-Et_3Si-苯基)$_2$C(2,7-二叔丁基芴基)(环戊二烯基)$HfMe_2$(催化剂 A)的合成

向(对-Et_3Si-苯基)$_2$C(2,7-二叔丁基芴基)(环戊二烯

基)HfCl$_2$(15.0g, 15.2mmol)和甲苯(125mL)的溶液中加入 1.4M MeLi 的乙醚溶液(21.8mL, 30.5mmol)。搅拌1小时后，经4~8μm的玻璃料过滤器对混合物进行过滤，然后在真空下提炼为固体。用己烷(250mL)从该固体中萃取产物，然后经0.45μm的过滤器过滤。用少量热的己烷对粗产物进行结晶。产量8.9g，62%。

(对-Et$_3$Si-苯基)$_2$C(Flu)(Cp)HfMe$_2$（催化剂B）的合成

5. 6,6'-二(对-Et$_3$Si-苯基)富烯的合成

比较小规模如上述1和2所述类似地制备这一富烯。

6. (对-Et$_3$Si-苯基)$_2$C(Flu)(Cp)HfCl$_2$的合成

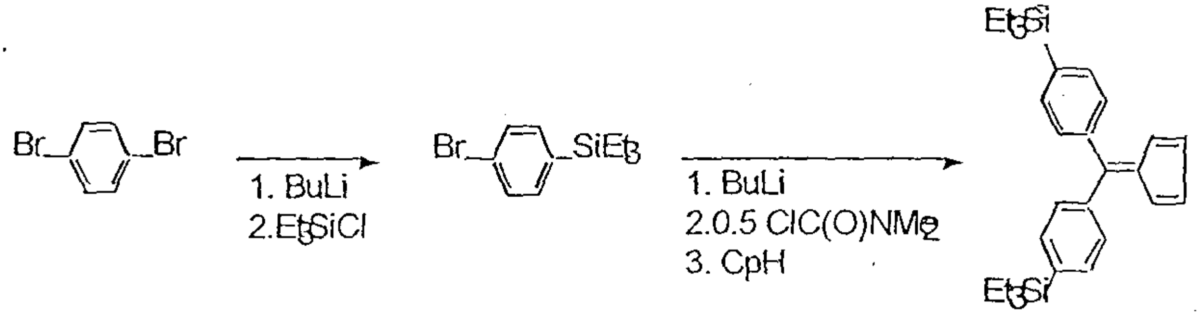
在冷的(-30℃)粗6,6'-二(对-Et$_3$Si-苯基)富烯(10.35g, 22.6mmol)和乙醚(100mL)的溶液中加入芴基锂(3.90g, 22.6mmol)。搅拌2小时后除去溶剂，并用戊烷(100mL)将剩余的固体浆液化，过滤，用额外的戊烷(2×100mL)洗涤，然后在真空下干燥，得到(对-Et$_3$Si-苯基)$_2$C(FluH)(CpLi)。产量6.41g，45%，假定无乙醚存在。向该单阴离子(6.4g, 10.2mmol)和乙醚(50mL)的浆液中加入2M丁基锂的戊烷(5.1mL, 1当量)溶液。搅拌过夜后冷却至-30℃，然后用HfCl$_4$(3.26g, 1当量)处理。将混合物加热至室温，搅拌8小时，过滤，然后用戊烷(25mL)洗涤。用二氯甲烷从橙色固体中萃取产物。除去溶剂，得到(对-Et$_3$Si-苯基)$_2$C(Flu)(Cp)HfCl$_2$。产量6.15g，61%。

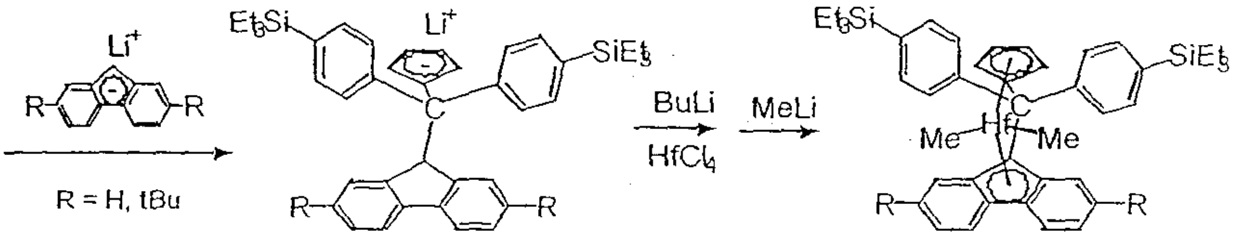
7. (对-Et$_3$Si-苯基)$_2$C(Flu)(Cp)HfMe$_2$(催化剂B)的合成

向(对-Et$_3$Si-苯基)$_2$C(Flu)(Cp)HfCl$_2$(1.0g, 1.15mmol)和甲苯(25mL)的溶液中加入1.4M MeLi的乙醚溶液(1.65mL, 2.31mmol)。搅拌过夜后除去甲苯。用己烷从固体中萃取产物，然后经0.45μm的过滤器过滤。除去溶剂得到产物。产量0.565g，59%。

如上所示，例举的茂金属的制备需要首先合成6,6'-二(对-Et$_3$Si-苯基)富烯。由H. Kurata及其合作者(Tetrahedron Letters, 1993, 34, 3445-3448)所报导的一般方法扩展一下，从对-(Et$_3$Si)苯基锂与ClC(O)NMe$_2$，然后再与环戊二烯反应，制备这一富烯。6,6'-二(对-Et$_3$Si-

苯基)富烯与 2,7-二叔丁基芴基锂进一步反应，得到(对-Et_3Si-苯基)$_2$C(2,7-二叔丁基 FluH)(CpLi)。该单阴离子在戊烷中的溶解性较低，并且它易于从污染物中提纯。随后用丁基锂然后再用 $HfCl_4$ 处理，得到二氯化物(对-Et_3Si-苯基)$_2$C(Flu)(Cp)$HfCl_2$，该二氯化物易于甲基化。可很容易地对这一方法进行扩展，以制备多种甲硅烷基取代的茂金属。





8. 溶解性研究

在 20mL 的闪烁瓶中放入测试量的(典型地 10^{-4}mol)茂金属和一搅拌棒，向其中加入干燥的己烷(约 2.65mL)。必需使用更大量的 A(3×10^{-4}mol)，以测定其溶解性。将该混合物搅拌约 1 小时，然后取出一等份试样，并经 0.45μm 的过滤器过滤(等份试样量 2.2～2.5g)。记录下样品的质量，然后用缓慢的氮气流除去己烷。以 100(剩余的固体质量)/(过滤的等份试样质量)确定茂金属的重量%溶解度。参见下表。

催化剂符号	预催化剂化合物
A	(p-Et_3Si-Ph)$_2$C(2,7-(^{t}Bu)$_2$Flu)(Cp)$HfMe_2$
B	(p-Et_3Si-Ph)$_2$C(Flu)(Cp)$HfMe_2$
C (Comp)	Ph_2C(2,7-(^{t}Bu)$_2$Flu)(Cp)$HfMe_2$
D (Comp)	Ph_2C(Flu)(Cp)$HfMe_2$

溶解度表

	起始混合物（计算的）			过滤的等份试样		
预催化剂	预催化剂	溶液质量	最大 wt%	溶液质量	预催化剂	wt%
A	0.0905	2.6603	3.40%	2.3715	0.0793	3.3%[1]
A	0.2828	2.7653	10.23%	2.521	0.2434	9.65%[3]
A	0.2844	2.8224	10.08%	2.5557	0.2338	9.15%[3]
C(Comp)	0.0705	2.6191	2.69%	2.236	0.0476	2.1%
C(Comp)	0.1049	2.6805	3.91%	2.383	0.0445	1.9%
B	0.0848	2.6483	3.20%	2.3898	0.0511	2.1%
D(Comp)	0.0594	5.1069	1.16%	3.7209	0.0045	0.1%[2]
D(Comp)	0.0612	12.1902	0.50%	11.5233	0.0079	<0.07%[2]

[1] 用由肉眼观察确定完全溶解的催化剂 A 进行对照试验，该试验显示，过滤后在计算的“最大 wt%”和实测的 wt%之间有大约 3% 的差别。

[2] 由于在己烷中的增加并不成比例地增加剩余固体的量，因此 D 的上限溶解度为 0.07%。

[3] A 的平均溶解度为 9.4%。

实施例 9a　　聚合实施例

在氮气下，向 1L 高压釜中加入己烷(460mL)和三辛基铝(0.04mL 25wt% 的己烷溶液，用己烷(10mL)稀释)。高压釜在大约 1000rpm 下搅拌，加热至 113.6±0.4℃ (P=47.2±0.5 磅/平方英寸)，然后用丙烯加压至 103.3±0.3 磅/平方英寸，再用乙烯加压至 251 磅/平方英寸。在共聚合过程中使乙烯物流加入到反应器中。向反应器中泵入 3.94×10^{-5}M 己烷可溶解的活化剂 $[((3,5\text{-}(Et_3Si)_2Ph)_3)C]^+[B(C_6F_5)_4]^-$ 的己烷溶液(20mL, 0.79μmol)（己烷可溶活化剂）。然后以可变的速率加入 3.97×10^{-5}M（对-Et_3Si-苯基)$_2$C(2,7-二叔丁基芴基)（环戊二烯基)$HfMe_2$ 的己烷溶液，使得足以保持乙烯物流以小于 1L/分钟的速率加入反应器，并且反应器的放热小于 0.5℃。聚合过程中的平均温度为 113.7±0.5℃。用校正的质量流量传感器检测乙烯的摄入量。在制得约 12g 聚合物后停止聚合。排空反应器并冷却。将聚合物溶液从反

应器倒入大的烧杯中。用额外的热己烷(约 500mL)清洗反应器。混合聚合物溶液，然后用氮气流处理以除去己烷；真空 80℃下进一步干燥聚合物。聚合数据见表 1。

实施例 9b

重复 9a 的过程。

实施例 9c

重复 9a 的过程。

实施例 10a

将活化剂进行替换，然后再进行 9a 的一般过程：向反应器中加入溶剂、三辛基铝，然后加入活化剂化合物 $PhNMe_2H^+ B(C_6F_5)_4^-$(5mg，6.2μmol)在己烷(20mL)中的浆液，然后加热至 113.5℃，并加入丙烯和乙烯。然后向该混合物中加入预催化剂。

实施例 10b

用活化剂化合物 $[PhNMe_2H]^+ [B(C_6F_5)_4]^-$(1.2mg，1.5μmol)在己烷(20mL)中的浆液，重复 10a 的过程。

实施例 11a　　对比例

将活化剂进行替换，然后再进行 9a 的一般过程：向反应器中泵入 1.5×10^{-4}M $B(C_6F_5)_3$ 的己烷溶液(25mL，3.78μmol)，代替实施例 9a 中使用的 R1 溶液。由于活性低，在制得 2.92g 聚合物后，聚合停止。

实施例 11b　　对比例

重复 11a 的过程。由于活性低，在制得 0.7g 聚合物后，聚合停止。

实施例 12a　　聚合实施例

将预催化剂进行替换，然后再进行实施例 9a 的过程：将(对-Et_3Si-苯基)$_2$C(Flu)(Cp)$HfMe_2$(50mg，60.1μmol)和己烷(2.5g)的混合物搅拌 30 分钟，然后使其静置 10 分钟。取出该混合物的一等份试样(150μL)，并用 80mL 己烷稀释。如实施例 9a 所述将该预催化剂溶液加入到反应器中。

实施例 12b　聚合实施例

使用相同的前体重复实施例 12a 的过程。

实施例 12c　对比例

将预催化剂进行替换，然后再进行实施例 9a 的过程：将上述催化剂 D((Ph)$_2$C(Flu)(Cp)$HfMe_2$)(50mg，82.9μmol)和己烷(2.5g)的混合物搅拌 30 分钟，然后使其静置 10 分钟。取出混合物的一等份试样(150μL)，并用 80mL 己烷稀释。如实施例 9a 所述将该预催化剂溶液加入到反应器中。

实施例 12d　对比例

用相同的混合物重复实施例 12c 的过程。

表 1 聚合结果

Ex #	μmol 催化剂	μmol 活化剂	聚合物质量	Wt % C_3 (IR)	M_w (LS)	M_w/M_n (DRI)
9a	0.13	0.79	12.41	32	629427	1.85
9b	0.11	0.79	11.79	31	647659	1.7
9c	0.12	0.79	10.33	32	575956	1.9
10a	0.056	6.2	11.42	32	557884	1.95
10b	0.094	1.5	11.28	32.5	589690	1.9
11a(Comp)	0.70	3.8	2.92	32	573913	1.9
11b(Comp)	0.893	3.8	0.7	a	a	a
12a	0.183[b]	0.79	12.60	31	510697	2.0
12b	0.183[b]	0.79	6.77	33.5	492952	2.0
12c(Comp)	c	0.79	0.4	a	a	a
12d(Comp)	c	0.79	0	a	a	a

(a) 未测定 (b, c) (对-Et_3Si-苯基)$_2$C(Flu)(Cp)$HfMe_2$ 是完全可溶的；在这些条件下(Ph)$_2$C(Flu)(Cp)$HfMe_2$ 几乎无溶解性 (c) μmol 未知

上述实施例 12 中所提供的对比显示，聚合产率与催化剂前体化合物进料溶液的浓度成正比例。在己烷中催化剂 B 比催化剂 D 的溶解度更大。因此，与催化剂 D 的情形 0～0.4g 聚合物相比，催化剂 B 在己烷中的混合物导致聚合产率提高，为 6.8～12.6g。

实施例 13 乙烯/辛烯共聚合

氮气气氛下，向 500mL 的高压釜中加入己烷(250mL)、三异丁基铝(0.2mL 25.2wt%的庚烷溶液，用甲苯(5mL)稀释)和 1-辛烯(18mL, 115mmol)。高压釜在约 1500rpm 下搅拌，加热至 140.1℃ (P=75.7 磅/平方英寸)，然后用乙烯加压至 265.6±1 磅/平方英寸。在共聚合过程中使得乙烯物流加料到反应器中。在可变的速率下，在 30 分钟内向搅拌的混合物中加入预催化剂 $PhNMe_2H^+ \ B(C_6F_5)_4^-$溶液(40～50 μmol)(1 当量)和甲苯(100mL)，使得足以能够得到 12～15g 分离出的共聚物，且放热小于 1.5℃，典型地小于 1℃。用 2-丙醇(1.5L)沉淀出聚合物，分离，然后在真空 80℃下干燥。见下表。

预催化剂	所用预催化剂 (μmol)	共聚物产量 (g)	Mol% 辛烯	M_w (DRI)	M_w/M_n (DRI)	M_w (LS)
A	2.1	12.18	6.4	195692	3.12	225188
A	1.5	12.79	6.1	190771	2.30	210680
A	2.2	13.82	6.4	207125	2.30	248319
A	2.4	14.98	6.1	219112	2.43	254290
B	5.0	12.40	7.3	150225	2.22	177924
B	4.4	12.98	7.6	163758	2.22	194604
D	5.8	12.49	9.5	140664	2.25	173690
D	4.2	12.25	7.5	154822	2.20	189865

用差示折光指数(DRI)或光散射(LS)检测器由 GPC 测定分子量。

与现有技术的催化剂相比，本发明催化剂的上述溶解度数据显示出明显和不可预期的溶解度提高。聚合数据说明了等同的活性，使得可以在不牺牲现有技术催化剂所获得的产率下，获得在脂族溶剂中溶解度提高所带来的有利之处。

实施例 14　　连续高温溶液法

下述聚合反应在搅拌的充满液体的 2L 夹套钢反应器中进行，在惰性 C_6 烃(naphta)溶剂存在下，压力高达 120 巴，温度高达 240℃下进行连续插入聚合。典型地，在聚合过程中以 1000rpm 搅拌反应器。反应体系配有热电偶和压力传感器，以检测温度和压力的连续变化，并配有连续加入纯的乙烯、1-辛烯和溶剂的装置。在该体系中，溶解在烃溶剂中的乙烯，1-辛烯、用作清除剂的三正辛基铝(TOA)以及任选的 H_2 可分开泵送，混合，并以单一物料流（冷冻至 0℃以下）加入到反应器中。过滤金属组分(TMC)溶解于溶剂/甲苯混合物(9/1　v/v)中，而非配位阴离子(NCA)活化剂溶解于甲苯/溶剂混合物(1/1　v/v)中。两种组分在进入反应器之前均分别泵送，在室温下混合，并冷却至低于约 0℃。通过调节油浴的温度设定反应器的温度，油浴用作流经反应器器壁夹套的油的储存器。接下来通过由催化剂流率调节乙烯在反应器中的转化率(%C_2)，独立地控制聚合物分子量(MW)或 MI。最后，通过调节乙烯/1-辛烯的进料重量比控制聚合物的密度。见下表。

聚合条件

实施例 14 #	催化剂	活化剂	催化剂进料 (mg/hr)	活化剂进料 (mg/hr)	烷基铝 (mmol/l)	Rt (min)	温度 (℃)	压力 (巴)	溶剂 (kg/hr)	C_2进料 (kg/hr)	C_8进料 (kg/hr)
a)	A	$(F_5C_6)_4B^{-}$(1)	3.3	2.7	0.015	7.2	190	85.8	5.5	1.16	0.53
b)	A	$(F_7C_{10})_4B^{-}$(2)	5.2	5.8	0.015	7.0	196	85.8	5.7	1.17	0.54

(1) [N,N－二甲基苯胺阳离子][四（五氟苯基）硼]

(2) [N,N－二甲基苯胺阳离子][四（七氟萘基）硼]

产物分析

实施例 14 #	C_2转化率 (%)	C_8转化率 (%)	生产速率 (kg/hr)	催化剂效率 (kgPE/mg Cat)	MI (dg/min)	MIR (I21/12)	密度 (kg/m^3)	C_8结合量 (wt%)	M_w (kg/mol)	PDI (M_w/M_n)
a)	84	48	1.46	440	0.84	39	903	17	95	2.3
b)	85	45	1.47	280	0.96	42	909	16	89	2.2