Abstract: A process for preparing a functionalized polymer, the steps of the process involving contacting a metathesis catalyst under metathesis conditions with a composition comprising: (a) at least one ethylenically unsaturated polymer characterized in that the unsaturated polymer is substantially immune to metathesis degradation; (b) at least one functionalized ethylene containing cyclic or acyclic reagent compound, wherein the ethylenically unsaturated polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined degree of substitution of 4 or less than 4; and (c) optionally one or more solvents or diluents, and recovering the resulting functionalized polymeric reaction product.
METATHETIC PRODUCTION OF FUNCTIONALIZED POLYMERS

CROSS-REFERENCE TO RELATED APPLICATION: This application claims the benefit of US provisional application Serial No. 60/919223, filed March 21, 2007.

BACKGROUND OF THE INVENTION

The present invention relates to a process for preparing functionalized derivatives of polymers by metathesis of high molecular weight olefin copolymers containing pendant or non-backbone ethylenic unsaturation with a low molecular weight functionalized olefin. The resulting products are ideally suited for use in production of polyurethanes, polyesters, epoxies, and other condensation polymer compositions, as reactive diluents for high solid content coating formulations, as reagents for reactive injection molding applications, and as functionalized thermoplastics having improved paintability and/or compatibility with other functionalized polymers.

Numerous olefin metathesis processes are previously known in the art. In general, olefin metathesis involves catalytic cleavage of one or more olefins at a point of unsaturation and recombination of the resulting cleavage products to form different olefin containing reaction products. Often, low molecular weight olefins and cyclic olefins, such as ethylene, cyclopentene or cyclooctene are employed as reagents in the foregoing reaction mixtures in order to provide low viscosity reaction mixtures, well defined reaction products, reduced molecular weight products, and/or mixtures suitable for reaction injection molding (RIM) compositions and elastomers.


Metathetic degradation of polymeric olefins is well known in the art. In Macromol., 33, 1494-1496 (2000), solid polymers were depolymerized by surface contact with a metathesis catalyst. Reaction products of polymer metathetic degradation can include random or block copolymers, functionalized oligomers, and ring opened metathesis products. Examples of such processes are disclosed in US 6,867,274, US 6,410,110, US 5,603,985, US 5,559,190, US 5,446,102, US 4,049,616, and other references. Suitable unsaturated polymers for the foregoing processes include diene homopolymers and copolymers or partially hydrogenated derivatives thereof, ABS polymers and SB rubbers.

In US 3,692,872, US 3,891,816 and US 4,010,224 graft and block copolymers and interpolymer were prepared by metathesis of two polymers containing olefinic unsaturation, such as polybutadiene or polyisoprene. Processes involving the cross-metathesis of polybutadiene with
polycyclooctene or polycyclododecene as well as grafting of EPDM polymers via metathesis were disclosed in DE 2,131,355 and DE 2,242,794. A summary of this work also appeared in J. Mol. Catal., 15, 3-19 (1982).

In Macromol., 36, 9675-9677 (2003) the ethenolysis of polypropylene/ 1,3-butadiene copolymers to prepare polymers having slightly increased melting temperature for isotactic polymer segments due to improved packing of shorter chain segments was disclosed.

Telechelic polymers with crosslinkable end groups such as hydroxy, acrylate or epoxide groups are useful for the preparation of interpenetrating polymer networks, crosslinked polymeric materials, coatings, encapsulating compositions, and for the immobilization of biomaterials. In US 7,022,789, the depolymerization of copolymers prepared by ring opening metathesis polymerization (ROMP) of cyclooctadiene (COD) with either cis-4,7-dihydro-1,3-dioxepan or cis-4,7-dihydro-2-phenyl-1,3-dioxepan using ruthenium complexes, resulted in a polymer bearing both poly(butadiene) and acetal units along the backbone. Subsequent acid hydrolysis of these acetal units resulted in the formation of hydroxy telechelic poly(butadiene) (HTPBD) oligomers. Also disclosed was the direct preparation of telechelic polymers having crosslinkable end groups by reacting a functionalized chain transfer agent with a cycloalkene in the presence of certain ruthenium or osmium ROMP catalysts. Similar processes using difunctional olefins such as 2-butenedicarboxylic acid diesters under ROMP or metathesis degradation conditions were disclosed in German Democratic Republic patents DD 146,052 and DD 146,053, respectively. Suitable polymers for the latter process included, "1,4-cis-polybutadiene, and other copolymers as ABS rubber or SB rubber". According to US 7,022,789, the products were polydisperse rubbers indicating the presence of cross-linking and containing undesirable quantities of vinyl groups.

In Macromol. Chem. Rapid Commun., 14, 323-327 (1993) and Macromol., 36, 9675-9677 (2003) the ethenolysis of partially hydrogenated polybutadiene and of propylene/ 1,3-butadiene copolymers were disclosed. The former process yielded \( \alpha,\omega \)-divinyl polyethylene oligomers containing a high internal ethylenic unsaturation (approximately one internal C=C bond in every two polymer chains). Studies of the latter product showed increased melting points for the metathesized reaction product presumably due to closer packing of the crystalline polymer segments.

The previously discussed processes utilizing free radical or anionic techniques prepared polybutadiene or similar polymers which possess internal or backbone unsaturations. Metathesis of these polymers results in polymeric degradation and molecular weight reduction. If hydrogenation is employed to limit internal unsaturation, the process costs become excessive. Moreover, selectively removing internal unsaturation, but not pendant unsaturation, is extremely difficult, if not impossible.
It would be desirable if there were provided a process for the metathesis of unsaturated polymers that is specifically adapted for the formation of functionalized, commercially valuable polymers. In particular, it would further be desirable if the resulting products were thermoplastics, such as thermoplastic elastomers, suitable for use in molding operations or in the formation of compatibilized blends with other thermoplastics, as impact modifiers, and as adhesives.

SUMMARY OF THE INVENTION

According to the present invention there is now provided a process for preparing a functionalized polymer, the steps of the process comprising contacting a metathesis catalyst under metathesis conditions with a composition comprising:

a) at least one ethylenically unsaturated polymer characterized in that the unsaturated polymer is substantially immune to metathetic degradation;

b) at least one functionalized ethylene containing cyclic or acyclic reagent compound;

wherein the ethylenically unsaturated polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined degree of substitution of 4 or less than 4; and

c) optionally one or more solvents or diluents,

and recovering the resulting functionalized polymeric reaction product.

In a further embodiment there is provided a process for preparing a functionalized polymer, the steps of the process comprising contacting a metathesis catalyst under metathesis conditions with a composition comprising:

a) at least one ethylenically unsaturated polymer characterized in that the unsaturated polymer is substantially immune to metathetic degradation, wherein the unsaturation consists essentially of pendant ethylenically unsaturated moieties;

b) at least one functionalized ethylene containing cyclic or acyclic reagent compound,

wherein the ethylenically unsaturated polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined degree of substitution of 4 or less than 4; and

c) optionally one or more solvents or diluents, and

recovering the resulting functionalized polymeric reaction product.

In addition, there is provided a process for preparing a polymer product comprising pendant functional groups, the steps of the process comprising contacting a metathesis catalyst under metathesis conditions with a composition comprising:

a) at least one ethylenically unsaturated, non-functionalized, polymer that is substantially immune to metathetic degradation,
b) at least one functionalized ethylene containing cyclic or acyclic reagent compound, wherein the ethylenically unsaturated non-functionalized polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined degree of substitution of 4 or less than 4; and

c) optionally one or more solvents or diluents, and

recovering the resulting functionalized polymeric reaction product, characterized in that the unsaturation of the unsaturated polymer reagent consists essentially or entirely of pendant ethylenic groups.

For the purpose of this invention, the phrase "substantially immune to metathetic degradation" means that the molecular weight of the ethylenically unsaturated reactant polymer is not reduced by greater than 10 percent under the metathesis process conditions of the present invention. Accordingly, the polymeric products of the process of this invention possess a molecular weight essentially equal to or in close proximity to the molecular weight of the reactant polymer, specifically, a molecular weight not reduced by greater than 10 percent, as compared to the initial molecular weight of the reactant polymer. In fact, the molecular weight of the product polymer may be larger than the molecular weight of the reactant polymer.

For the purposes of this invention, the phrase "wherein the ethylenically unsaturated polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined degree of substitution of 4 or less than 4" means that the sum of chemical substituents (other than a hydrogen atom) on the olefinic carbon atoms in the functionalized ethylene containing cyclic or acyclic reagent compound and of chemical substituents (other than a hydrogen atom) on the olefinic carbon atoms in the ethylenically unsaturated reactant polymer totals 4 or less than 4.

Of course, in order to be "functionalized," the functionalized ethylene should have a degree of substitution of at least 1. The ethylenically unsaturated polymer reactant should also have a degree of substitution of at least 1 (e.g., pendant vinyl group). Accordingly, a degree of substitution of at least 2, but no greater than 4, is required for the process of this invention. The following example illustrates the calculation for the cross-metathesis of ethyl acrylate with an ethylenically-unsaturated ethylene/propylene/ethylene norbornene (EPDM) reactant polymer. In such a process, the degree of substitution of ethyl acrylate is 1; the degree of substitution of the EPDM reactant polymer is 3; and the total degree of substitution is 4. As a second example, the calculation is made for the cross-metathesis of dimethyl fumarate with an ethylenically-unsaturated propylene/butadiene reactant copolymer wherein the unsaturation is primarily in pendant vinyl groups. In such a case, the degree of substitution of dimethyl fumarate is 2; the degree of substitution of the unsaturated propylene/butadiene copolymer is 1; and the total degree of substitution is 3.
In another embodiment of the invention, there is provided a functionalized polymeric product prepared by or preparable according to one of the foregoing processes. Highly desired products have from 0.1 to 100, preferably from 0.5 to 50, and most preferably from 1 to 2.5 pendant functional groups per 1000 carbons, and number average molecular weights, Mn, from 1,000 to 1,000,000, preferably from 10,000 to 500,000. Such products can now be readily prepared according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Group or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups disclosed in, Nomenclature of Inorganic Chemistry: Recommendations 1990, G. J. Leigh, Editor, Blackwell Scientific Publications (1990). Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques, definitions (to the extent not inconsistent with any definitions provided herein) and general knowledge in the art.

The term "comprising" and derivatives thereof is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

As used herein with respect to a chemical compound, unless specifically indicated otherwise, the singular includes all isomeric forms and vice versa (for example, "hexane", includes all isomers of hexane individually or collectively). The terms "compound" and "complex" are used interchangeably herein to refer to organic-, inorganic- and organometal compounds. The term, "atom" refers to the smallest constituent of an element regardless of ionic state, that is, whether or not the same bears a charge or partial charge or is bonded to another atom. The term "heteroatom"
refers to an atom other than carbon or hydrogen. Preferred heteroatoms include: F, Cl, Br, N, O, P, B, S, Si, Sb, Al, Sn, As, Se and Ge.

The term, "hydrocarbyl" refers to univalent substituents containing only hydrogen and carbon atoms, including branched or unbranched, saturated or unsaturated, cyclic, polycyclic or noncyclic species. Examples include alkyl-, cycloalkyl-, alkenyl-, alkadienyl-, cycloalkadienyl-, aryl-, and alkynyl- groups. "Substituted hydrocarbyl" refers to a hydrocarbyl group that is substituted with one or more non-hydrocarbyl substituent groups. The term "heterocarbyl" refers to groups containing one or more carbon atoms and one or more heteroatoms and no hydrogen atoms. The bond between the carbon atom and any heteroatom as well as the bonds between any two heteroatoms, may be a single or multiple covalent bond or a coordinating or other donative bond. Examples include trichloromethyl-, perfluorophenyl-, cyano- and isocyanato-groups. The terms "heteroatom containing hydrocarbyl" or "heterohydrocarbyl" refer to univalent groups in which at least one atom other than hydrogen or carbon is present along with one or more carbon atom and one or more hydrogen atoms. Thus, an alkyl group substituted with a halo-, heterocycloalkyl-, aryl- substituted heterocycloalkyl-, heteroaryl-, alkyl- substituted heteroaryl-, alkoxy-, aryloxy-, dihydrocarbylboryl-, dihydrocarbylphosphino-, dihydrocarbylamo-, trihydrocarbylsilyl-, hydrocarbylthio-, or hydrocarbylseleno- group is within the scope of the term heterohydrocarbyl. Examples of suitable heteroalkyl groups include chloromethyl-, 2-cyanoethyl-, hydroxymethyl-, benzoylmethyl-, (2-pyridy) methyl-, chlorobenzyl-, and trifluoromethyl- groups.

As used herein the term "aromatic" refers to a polyatomic, cyclic, conjugated ring system containing \((4\delta+2)\) \(\pi\)-electrons, wherein \(\delta\) is an integer greater than or equal to 1. The term "fused" as used herein with respect to a ring system containing two or more polyatomic, cyclic rings means that with respect to at least two rings thereof, at least one pair of adjacent atoms is included in both rings. The term "aryl" refers to a monovalent aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. Examples of aromatic ring(s) include phenyl, naphthyl, anthracenyl, and biphenyl, among others.

"Substituted aryl" refers to an aryl group in which one or more hydrogen atoms bound to any carbon is replaced by one or more groups such as alkyl, alkenyl, substituted alkyl, substituted alkenyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halo, haloalkyl (for example, CF\(_3\)), hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and both saturated and unsaturated hydrocarbylene groups, including those which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be carbonyl as in benzophenone-, oxygen as in diphenylether- or nitrogen as in diphenylamine- groups.
"Ethylenic unsaturation" or "ethylenic group" refers to adjacent aliphatic carbon atoms bound together by double bonds (non-aromatic sp² electronic hybridization), preferably of the formula: \(-\text{CR}^*\text{=CR}^*,\) or \(-\text{CR}^*\text{=CR}^*\)₂, where \(\text{R}^*\) independently each occurrence is hydrogen, halo, nitrile, hydrocarbyl, or substituted hydrocarbyl containing up to 20 atoms not counting hydrogen. Percent ethylenic unsaturation as used herein is calculated based on total carbon-carbon bond content of the polymer and determined by \(^{13}\text{C}\) NMR or other suitable technique. The term "pendant" refers to groups or substituents attached to tertiary substituted carbons of the polymer. The term "terminal" refers to groups or substituents attached to a secondarily substituted carbon of the polymer.

The term "polymer" as used herein refers to a macromolecular compound comprising multiple repeating units and a molecular weight of at least 100, preferably at least 1000. Preferably, at least one repeating unit occurs, consecutively or non-consecutively, 6 or more times, more preferably 20 or more times, on average. Molecules containing less than 6 such repeating units on average are referred to herein as oligomers. The term includes homopolymers, copolymers, interpolymers, interpolymers, and so on. The term "interpolymer" is used herein interchangeably with the term copolymer to refer to polymers incorporating in polymerized form at least two differentiated repeating units, usually obtained from separate copolymerizable monomers. The least prevalent monomer in the resulting copolymer or interpolymer is generally referred to by the term "comonomer".

The term "block copolymer" refers to a polymer having two or more identifiable sections thereof (blocks) that are chemically distinguishable from one another. The term "unsaturated block copolymer" refers to a block copolymer that comprises ethylenic unsaturation either between blocks or within one or more blocks thereof. The term "amorphous" refers to a polymer, polymer block or polymer segment (collectively referred to here-in-after as polymeric entities) lacking a crystalline melting point. The term "crystalline" refers to a polymeric entity possessing a crystalline melting point. The term "semi-crystalline" refers to a polymeric entity possessing a crystalline melting point which is lower than that of a fully crystalline or more fully crystalline polymer entity of the same chemical composition. More specifically, semi-crystalline as used herein, refers to polymer entities possessing crystallinity that is less than 90 percent of the maximum attainable crystallinity for that polymer entity. For the avoidance of doubt, the term crystalline includes semi-crystalline polymer entities.

The term "backbone" refers to the longest continuous polymeric chain of a polymer. All other polymer chains are referred to as side chains, branches, or grafted polymer chains. Short chains or short chain branching refers to branches from the backbone resulting from polymerization of monomers containing three or more carbons. Polymerization of monomers containing two or
more ethylenic unsaturations, such as dienes, can result in the formation of branches containing unsaturation. Metathesis of polymers containing such unsaturated branches can result in formation of products having branches that are pendant from the central backbone chain and which contain functionality formed according to the present invention. The present invention is concerned with functionalizing polymers that contain all or substantially all pendant unsaturation, preferably pendant vinyl groups, as opposed to the metathesis of polymers containing substantial amounts of internal unsaturation in the polymer backbone.

The term "substantially immune to metathetic degradation" refers to polymers that are not reduced in Mn under the conditions of the present metathesis by greater than 10 percent, more preferably greater than 5 percent, and most preferably greater than 1 percent. More specifically, the term refers to the ethylenically unsaturated reactant polymer, because it is the unsaturated reactant polymer that provides the backbone for the functionalized product polymer. In practice, a comparison is made between the molecular weight, Mn, of the product polymer and the starting molecular weight of the ethylenically unsaturated reactant polymer. If the Mn of the product polymer is not reduced by greater than 10 percent, preferably, not greater than 5 percent, and more preferably, not greater than 1 percent, as compared to the Mn of the reactant polymer; then the reactant polymer meets the criteria of this invention of being immune to metathetic degradation. Generally, such polymer backbones are fully or substantially fully saturated or substituted with protecting groups capable of shielding internal ethylenic unsaturation from metathesis.

The phrase "wherein the ethylenically unsaturated polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined substitution of 4 or less than 4" means that the sum of substituents of the functionalized ethylenic reagent and of substituents of a representative olefin moiety in the ethylenically unsaturated reactant polymer is 4 or less than 4. With respect to this definition, it is emphasized that the substitution is tallied with respect to the substituents on the carbon atoms of the carbon-carbon double bonds.

"Functionalized ethylene containing cyclic or acyclic reagent compound," refers to ethylene being substituted with one or more polar groups or substituents. Preferred polar groups include halogens; alcohols; ethers; carboxylic acids; aliphatic or aromatic esters, ketones, sulfates, nitrates, phosphates, phosphites; metal salts of carboxylic acids, and siloxanes. Examples of such reagents correspond to the formula: \( CR^2 = CR^2', \) where \( R^2 \), independently each occurrence, is selected from the group consisting of hydrogen, \( C_{1-20} \) hydrocarbyl, halogen, -\( \text{OH} \), -\( \text{OR}^Y \), -\( \text{C(O)OR}^Y \), -\( \text{OC(O)R}^Y \), -\( \text{C(O)R}^Y \), -\( \text{C(O)OM} \), -\( \text{OSO}_3 \text{R}^Y \), -\( \text{NO}_3 \), -\( \text{OP(O)(OR}^Y)_2 \), \( \text{OP(OR}^Y)_2 \), -\( \text{CN} \), and -\( \text{OSiR}^Y_3 \), where \( R^Y \) independently each occurrence is hydrogen or \( C_{1-6} \) hydrocarbyl, and optionally two \( R^2 \) groups on the same carbon may be joined together to form a divalent derivative, with the proviso that in no more than three occurrences is \( R^2 \) hydrogen or \( C_{1-20} \) hydrocarbyl, and wherein \( M \) is a monovalent.
cation, for example H⁺ or an alkali metal ion, such as Na⁺. Examples of substituted ethylene containing cyclic or acyclic reagent compounds suitable for use herein include (Ci,-4 alkyl) acrylate, (Ci,-4 alkyl) methacrylate, di(Ci,-4 alkyl) fumarate, vinylchloride, vinylidene chloride, vinylacetate, vinylbutyrate, vinyl-n-butyl ether, N-vinylcarbazole, allyl ethyl ether, vinyl-Ci(-4 alkyl) alcohol, vinyl-Ci(-4 alkyl) methyl ketone, vinyl-Ci(-4 alkyl) acetate, allyl methyl sulfide, allyl(chloro)dimethylsilane, allyl isocyanate, allyldiphenylphosphine, allylurea, allylsilane, allyl Ci(-4 alkyl silane, allyl d(Ci,-4 alkyl) silane, allyl tri(Ci,-4 alkyl) silane, or maleic anhydride.

For the purposes of this invention, the term “functionalized polymer” refers to a product polymer containing a polar group or substituent that was not present in the reactant polymer. The polar substituent (or functionalization) in the product polymer arises from the metathesis of the reactant polymer with the functionalized ethylenically-unsaturated cyclic or acyclic compound.

The term "elastomeric" refers to polymeric entities having Tg less than 25 °C, preferably less than 0 °C and elastic recovery of at least 90 percent when tested according to ASTM D-1708 at 21 °C. Crystalline melting point (Tm) refers to the peak melting point determined by DSC according to ASTM D-3418 test method.

Suitable unsaturated polymer reagents employed in the present metathesis include copolymers prepared by addition polymerization of one or more olefins, preferably α-olefins having from 2 to 10 carbons, especially ethylene and or propylene, optionally one or more C4,8 α-olefin comonomers, and one or more conjugated or non-conjugated dienes, wherein the resulting polymer is substantially immune to metathetic degradation. Preferably, such unsaturated polymers are non-functionalized. That is, they lack polar functional groups. Examples of suitable polymers include copolymers of ethylene with a conjugated or non-conjugated diene, copolymers of propylene with a conjugated or non-conjugated diene, copolymers of ethylene and propylene with a conjugated or non-conjugated diene, as well as further interpolymers of the foregoing monomer pairs with one or more additional α-olefin monomers. Preferred polymers are those wherein the diene adds substantially completely or completely by means of a 1,2-addition, thereby generating ethylenically unsaturated pendant groups. The resulting copolymers comprising ethylenic unsaturation in the remnant formed from polymerization of the diene monomer do not substantially decrease polymer molecular weight upon metathesis. At least 75 percent, preferably at least 90 percent and most preferably at least 95 percent of the ethylenic unsaturation in the reagent polymer is pendant. When reacted with a functionalized ethylene containing cyclic or acyclic reagent under metathesis conditions, cross-metathesis takes place, without substantial polymer degradation as noted hereinbefore.
Desirably, the ethylenic content of the unsaturated polymer reagent is from 0.001 to less than 10 mole percent, more preferably from 0.01 to 5 mole percent. The quantity of ethylenic unsaturation in the polymer reagent may be controlled by the amount of diene comonomer. In addition, it may be adjusted by partial hydrogenation, in order to attain polymers having molecular weight ideally suited for subsequent conversion or use in particular end uses. It will be appreciated by the skilled artisan that by using unsaturated polymer reagents with higher unsaturation content, more highly functionalized polymer products will result. Most preferred unsaturated polymer reagents contain vinyl groups or exocyclic pendant unsaturation. That is, at least some of the ethylenically unsaturated pendant moieties thereof, and preferably substantially all or all such pendant moieties terminate with a \(-\text{CH}=\text{CH}_2\) group or contain, in polymerized form, the remnant of a cyclic diolefin, preferably ethylidene norbornene. In general, the number of such ethylenically unsaturated groups in the polymer reagent is equivalent to the number of ethylenically unsaturated groups in the resulting functionalized polymer if it is not subjected to hydrogenation, which is also equivalent to the number of functional groups in the resulting polymer product. Accordingly, functionality in the product may be indirectly measured by measurement of ethylenic unsaturation or sp\(^2\) carbons in the non-hydrogenated polymer product.

Examples of suitable unsaturated polymers for use as reagents or components of the reaction mixture herein include random copolymers, block copolymers, or pseudo-block copolymers of ethylene, optionally one or more \(\text{C}_3\) olefin monomers and one or more diolefins, and partially hydrogenated derivatives of the foregoing. Most preferred reagents are random copolymers of ethylene and/or propylene with a conjugated diene, especially 1,3-butadiene or ethylidene norbornene.

The unsaturated polymer reagents are desirably prepared by addition polymerization employing a Ziegler/Natta, metallocene, post-metallocene, or other coordination polymerization catalyst. By the term "Ziegler/Natta polymerization catalyst" is meant a catalyst composition suited for polymerization of olefins comprising an organometallic compound in which the metal is from groups 2, 12 or 13 of the Periodic Table of the Elements in combination with at least one other compound, especially a halide, oxide or oxyhalide, of a metal selected from groups 4, 5 or 6 of the Periodic Table of the Elements. The unsaturated polymer reagents containing pendant ethylenically unsaturated moieties derived from polycyclic dienes such as ethylidene norbornene may be prepared using similar addition polymerization techniques as well as conventional free radical polymerization techniques. The resulting polymers inherently possess pendant vinyl functionality resulting from addition polymerization of the cyclic olefin. The amount of ethylenic unsaturation in the reagent polymers and the resulting product can be determined by any suitable technique, such as iodine monochloride titration (ICl), NMR analysis or other technique. When appropriate, a
combination of these techniques can be used. ICl titration is a well known technique for determining the level of carbon-carbon unsaturation in a wide variety of polymers wherein iodine monochloride is used to react with any unsaturations present in the polymer. The method does not distinguish between internal (backbone) and terminal or pendant unsaturation.

NMR spectroscopic analysis has particular utility for use with homopolymers and copolymers of conjugated dienes, due to the fact that the amount of internal unsaturation in the polymers (resulting from 1,4-addition of the diene) as opposed to pendant unsaturation (resulting from 1,2-addition of the diene) may be determined using this technique. NMR techniques of polymer analysis include those disclosed in, NMR and Macromolecules; sequence, dynamic and domain structure, James C. Randall, ed.; ACS Symposium Series, 247; American Chemical Society, Washington, D.C. (1984).

The unsaturated reagent polymers prepared from aliphatic conjugated dienes are desirably prepared using standard addition polymerization techniques, such as by polymerizing an olefin mixture comprising one or more olefins in combination with at least one diene using a coordination catalyst, especially a transition metal compound, adapted for preferential 1,2-diene addition instead of 1,4-diene addition. Preferred polymers are ethylenically unsaturated copolymers formed by polymerization of ethylene or propylene with from 0.1 to 10 mol percent of a diene, preferably butadiene, and optionally one or more of 1-butene, 1-hexene or 1-octene in a total amount from 0 to 20 mole percent, especially 0-10 mole percent. More detailed description of the various methods of preparing the unsaturated polymer reagents follows.

Addition polymerization processes, such as transition metal catalyzed polymerizations more fully disclosed here-in-after, are compatible with a large number of monomers, normally excluding unprotected polar group containing monomers. Polymers made by polymerizing one or more addition polymerizable monomers along with a diene, preferably a conjugated alkadiene, especially 1,3-butadiene or ethylidene norbornene, form branched or linear polymers with primarily pendant unsaturation(s) are employed to prepare polymer reagents for use in the present invention. Additionally, chain end unsaturation may result due to beta-hydride elimination and/or a small quantity of backbone unsaturation(s) may result from a random dehydrogenation during the polymerization process. Highly desirably, the unsaturated polymer reagents are at least 95-, 96-, 97- or even 98 percent- backbone hydrogenated as measured by residual, non-terminal, sp² unsaturation content of the backbone, and non-functionalized.

A partial list of monomers suitably polymerized by addition polymerization techniques includes aliphatic and aromatic α-olefins and substituted olefins, conjugated and non-conjugated dienes, and cyclic olefins and polyolefins. Examples include: ethylene, propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-1-pentene, acrylonitrile, methylethacrylate, butylacrylate, styrene,
vinylcyclohexane, α-methylstyrene, p-vinyltoluene, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2,4-hexadiene, 2-methyl-3-ethyl-1,3-butadiene, 3-methyl-1,3-pentadiene, 2-methyl-3-ethyl-1,3-pentadiene, 2-ethyl-1,3-pentadiene, 3-methyl-1,3-heptadiene, 3-octadiene, 3-butyl-1,3-octadiene, 3,4-dimethyl-1,3-hexadiene, 3-n-propyl-1,3-pentadiene, 4,5-diethyl-1,3-octadiene, 2-phenyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2,3-di-n-propyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, chloroprene, fluoroprene, 2-methoxy-1,3-butadiene, 2-ethoxy-3-ethyl-1,3-butadiene, 2-ethoxy-3-methyl-1,3-hexadiene, decadiene, divinylbenzene, cyclohexene, vinylcyclohexene, benzocyclobutene, norbornene, norbornadiene, dicyclopentadiene, and ethylidene norbornene.

Preferred monomers are ethylene or propylene copolymerized with preferred comonomers selected from butadiene, isoprene, or ethylidene norbornene.

A preferred process for preparing unsaturated reagent polymers for use herein is the addition polymerization employing a coordination catalyst capable of producing primarily 1,2-addition polymers. Suitable catalysts for such copolymerization include the well known transition metal based coordination catalysts previously disclosed for use in polymerizations of olefin monomers. Especially preferred catalysts comprise a Group 4 metal, especially zirconium or hafnium, and a heteroatom containing donor ligand. Desirable catalysts produce interpolymer products containing from 1 to 2 mole percent incorporated diene, principally or solely inserted in 1,2-configuration. The presence of unsaturation in the backbone of the polymer may be reduced by hydrogenation of the resulting interpolymer prior to contact with the metathesis catalyst, however this is typically not preferred due to the fact that pendant unsaturation is more susceptible to hydrogenation. Moreover, hydrogen may be employed during the addition polymerization process to selectively hydrogenate internal unsaturations under certain polymerization conditions. For example, it has been discovered that in the presence of a transition metal complex, especially an ansa-bis(cyclopentadienyl) Group 4 metallocenes, internal unsaturation formed via 1,4-addition of aliphatic conjugated dienes is hydrogenated in situ, whereas pendant or terminal unsaturation is relatively unaffected. Accordingly, by the use of such addition polymerization conditions, it is possible to produce addition polymers consisting essentially of pendant ethylenically unsaturated groups. Desirably, the incidence of ethylenic unsaturation in the unsaturated polymer is adjusted to between 0.01 and 10 mole percent, less than 1 percent of which is in the polymer backbone. In determining such values, the ethylene units and any substituents on either carbon thereof are included in the theoretical weights of the ethylenic unit.

Examples of suitable Group 4 metal complexes useful as coordination catalyst components include complexes of transition metals selected from Groups 3 to 15 of the Periodic Table of the Elements containing one or more delocalized, π-bonded ligands or polyvalent Lewis base ligands.
Examples include metallocene, half-metallocene, constrained geometry, and polyvalent pyridylamine-, polyether-, or other polychelating base complexes. The complexes are generically depicted by the formula: $\text{MK}_x\text{X}_z$ or a dimer thereof, wherein

$M$ is a metal selected from Groups 3-15, preferably 3-10, more preferably 4-8, and most preferably Group 4 of the Periodic Table of the Elements;

$K$ independently each occurrence is a group containing delocalized $\pi$-electrons or one or more electron pairs through which $K$ is bound to $M$, said $K$ group containing up to 50 atoms not counting hydrogen atoms, optionally two or more $K$ groups may be joined together forming a bridged structure, and further optionally one or more $K$ groups may be bound to $Z$, to $X$ or to both $Z$ and $X$;

$X$ independently each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more $X$ groups may be bonded together thereby forming a divalent or polyvalent anionic group, and, further optionally, one or more $X$ groups and one or more $Z$ groups may be bonded together thereby forming a moiety that is both covalently bound to $M$ and coordinated thereto;

$Z$ independently each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which $Z$ is coordinated to $M$;

$k$ is an integer from 0 to 3;

$x$ is an integer from 1 to 4;

$z$ is a number from 0 to 3; and

the sum, $k+x$, is equal to the formal oxidation state of $M$.

Suitable metal complexes include those containing from 1 to 3 $\pi$-bonded anionic or neutral ligand groups, which may be cyclic or non-cyclic delocalized $\pi$-bonded anionic ligand groups. Exemplary of such $\pi$-bonded groups are conjugated or non-conjugated, cyclic or non-cyclic diene and dienyl groups, allyl groups, boratabenzene groups, phosphole, and arene groups. By the term "$\pi$-bonded" is meant that the ligand group is bonded to the transition metal by a sharing of electrons from a partially delocalized $\pi$-bond.

Each atom in the delocalized $\pi$-bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl-substituted heteroatoms wherein the heteroatom is selected from Group 14-16 of the Periodic Table of the Elements, and such hydrocarbyl- substituted heteroatom radicals further substituted with a Group 15 or 16 hetero atom containing moiety. In addition two or more such radicals may together form a fused ring system, including partially or fully hydrogenated fused ring systems, or they may form a metallocycle with the metal. Included within the term "hydrocarbyl"
are C$_i$-straight, branched and cyclic alkyl radicals, C$_i$-aromatic radicals, C$_i$-alkyl-substituted aromatic radicals, and C$_i$-aryl-substituted alkyl radicals. Suitable hydrocarbyl-substituted heteroatom radicals include mono-, di- and tri-substituted radicals of boron, silicon, germanium, nitrogen, phosphorus or oxygen wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. Examples include N,N-dimethylamino, pyrrolidinyl, trimethylsilyl, trimethylsilyl, t-butyldimethylsilyl, methylid(t-butyl)silyl, triphenylgermyl, and trimethylgermyl groups. Examples of Group 15 or 16 hetero atom containing moieties include amino, phosphino, alkoxy, or alkylthio moieties or divalent derivatives thereof, for example, amide, phosphide, alkyleneoxy or alkylenefio groups bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group, π-bonded group, or hydrocarbyl- substituted heteroatom.

Examples of suitable anionic, delocalized π-bonded groups include cyclopentadienyl, indenyl, fluorenly, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups, phosphole, and boratabenzyl groups, as well as inertly substituted derivatives thereof, especially C$_i$-hydrocarbyl- substituted or tris(C$_i$-hydrocarbyl)silyl- substituted derivatives thereof. Preferred anionic delocalized π-bonded groups are cyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetramethylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenly, 2-methylindenyl, 2-methyl-4-phenylindenyl, tetrahydrofluorenyl, octahydrofluorenyl, 1-indacenyl, 3-pyrrolidinoinden-l-yl, 3,4-(cyclopenta/)phenanthren-l-yl, and tetrahydroindenyl.

The boratabenzyl ligands are anionic ligands which are boron containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in Organometallics, 14.1, 471-480 (1995). Preferred boratabenzyl ligands correspond to the formula:

![Boron ligand formula](attachment:formula.png)

wherein R$^1$ is an inert substituent, preferably selected from the group consisting of hydrogen, hydrocarbyl, silyl, halo or germly, said R$^1$ having up to 20 atoms not counting hydrogen, and optionally two adjacent R$^1$ groups may be joined together. In complexes involving divalent derivatives of such delocalized π-bonded groups one atom thereof is bonded by means of a covalent bond or a covalently bonded divalent group to another atom of the complex thereby forming a bridged system.
Phospholes are anionic ligands that are phosphorus containing analogues to a cyclopentadienyl group. They are previously known in the art having been described by WO 98/50392, and elsewhere. Preferred phosphole ligands correspond to the formula:

\[
\begin{array}{c}
\text{\textbf{Figure}} \\
\text{Phosphole structure}
\end{array}
\]

wherein \(R^1\) is as previously defined.

Preferred transition metal complexes for use herein correspond to the formula: \(MK_xX_2Z_2\), or a dimer thereof, wherein:

- \(M\) is a Group 4 metal;
- \(K\) is a group containing delocalized \(\pi\)-electrons through which \(K\) is bound to \(M\), said \(K\) group containing up to 50 atoms not counting hydrogen atoms, optionally two \(K\) groups may be joined together forming a bridged structure, and further optionally one \(K\) may be bound to \(X\) or \(Z\);
- \(X\) each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more \(X\) and one or more \(K\) groups are bonded together to form a metallocycle, and further optionally one or more \(X\) and one or more \(Z\) groups are bonded together thereby forming a moiety that is both covalently bound to \(M\) and coordinated thereto;
- \(Z\) independently each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which \(Z\) is coordinated to \(M\);
- \(k\) is an integer from 0 to 3;
- \(x\) is an integer from 1 to 4;
- \(z\) is a number from 0 to 3; and
- the sum, \(k+x\), is equal to the formal oxidation state of \(M\).

Preferred complexes include those containing either one or two \(K\) groups. The latter complexes include those containing a bridging group linking the two \(K\) groups. Preferred bridging groups are those corresponding to the formula \((ER'_2)_e\) wherein \(E\) is silicon, germanium, tin, or carbon, \(R'\) independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said \(R'\) having up to 30 carbon or silicon atoms, and \(e\) is 1 to 8. Preferably, \(R'\) independently each occurrence is methyl, ethyl, propyl, benzyl, tert-butyl, phenyl, methoxy, ethoxy or phenoxy.

Examples of the complexes containing two \(K\) groups are compounds corresponding to the formula:
wherein:

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

R³ in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R³ having up to 20 non-hydrogen atoms, or adjacent R³ groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system, and

X" independently each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two X" groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized π-electrons to M, whereupon M is in the +2 formal oxidation state, and

R', E and e are as previously defined.

Exemplary bridged ligands containing two π-bonded groups are:

- dimethylbis(cyclopentadienyl)silane, dimethylbis(tetramethylcyclopentadienyl)silane,
- dimethylbis(2-ethylcyclopentadien-1-yl)silane, dimethylbis(2-t-butylcyclopentadien-1-yl)silane,
- 2,2-bis(tetramethylcyclopentadienyl)propane, dimethylbis(inden-1-yl)silane,
- dimethylbis(tetrahydroinden-1-yl)silane, dimethylbis(fluoren-1-yl)silane,
- dimethylbis(tetrahydrofluoren-1-yl)silane, dimethylbis(2-methyl-4-phenylinden-1-yl)-silane,
- dimethylbis(2-methylinden-1-yl)silane, dimethyl(cyclopentadienyl)(fluoren-1-yl)silane,
- dimethyl(cyclopentadienyl)(octahydrofluoren-1-yl)silane,
- dimethyl(cyclopentadienyl)(tetracyclofluoren-1-yl)silane, (1, 1, 2, 2-tetramethy)-l, 2-bis(cyclopentadienyl)disilane, (1, 2-bis(cyclopentadienyl)ethane, and dimethyl(cyclopentadienyl)-l-(fluoren-1-yl)methane.

Preferred X" groups are selected from hydride, hydrocarbyl, silyl, germyl, halohydrocarbyl, halosilyl, silylhydrocarbyl and amino hydrocarbyl groups, or two X" groups together form a divalent derivative of a conjugated diene or else together they form a neutral, π-bonded, conjugated diene. Most preferred X" groups are Cl₂hydrocarbyl groups.
Examples of metal complexes of the foregoing formula include:

- bis(cyclopentadienyl)zirconiumdimethyl,
- bis(cyclopentadienyl)zirconiumdibenzyl,
- bis(cyclopentadienyl)zirconium methyl benzyl,
- bis(cyclopentadienyl)zirconium methyl phenyl,
- bis(cyclopentadienyl)zirconiumdiphenyl,
- bis(cyclopentadienyl)titanium-allyl,
- bis(cyclopentadienyl)zirconiummethyldimethoxide,
- bis(cyclopentadienyl)zirconiummethyldichloride,
- bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
- bis(pentamethylcyclopentadienyl)titaniumdimethyl,
- bis(indenyl)zirconiumdimethyl,
- indenylfluorenylzirconiumdimethyl,
- bis(indenyl)zirconiummethyl(2-(dimethylamino)benzyl),
- bis(indenyl)zirconiummethyltrimethylsilyl,
- bis(tetrahydroindenyl)zirconiummethyltrimethylsilyl,
- bis(pentamethylcyclopentadienyl)zirconiummethyldimethylbenzyl,
- bis(pentamethylcyclopentadienyl)zirconiummethyldienzbenzyl,
- bis(pentamethylcyclopentadienyl)zirconiummethyldimethoxide,
- bis(pentamethylcyclopentadienyl)zirconiummethyldichloride,
- bis(methylcyclopentadienyl)zirconiumdimethyl,
- bis(butycyclopentadienyl)zirconiumdibenzyl,
- bis(t-butycyclopentadienyl)zirconiumdimethyl,
- bis(ethyltetramethylcyclopentadienyl)zirconiumdimethyl,
- bis(methylpropylcyclopentadienyl)zirconiumdibenzyl,
- bis(trimethylsilylcyclopentadienyl)zirconiumdibenzyl,
- dimethylsilylbis(cyclopentadienyl)zirconiumdichloride,
- dimethylsilylbis(cyclopentadienyl)zirconiumdimethyl,
- dimethylsilylbis(tetramethylcyclopentadienyl)titanium (III) allyl
- dimethylsilylbis(2-butylcyclopentadienyl)zirconiumdichloride,
- dimethylsilylbis(n-butylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,
dimethylsilylbis(2-methylindenyl)zirconiumdimethyl,
dimethylsilylbis(2-methyl-4-phenylindenyl)zirconiumdimethyl,
dimethylsilylbis(2-methylindenyl)zirconium-1,4-diphenyl-1,3-butadiene,
dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium(II) 1,4-diphenyl-1,3-butadiene,
dimethylsilylbis(4,5,6,7-tetrahydroinden-1-yl)zirconiumdichloride,
dimethylsilylbis(4,5,6,7-tetrahydroinden-1-yl)zirconiumdimethyl,
dimethylsilylbis(tetrahydroindenyl)zirconium(II) 1,4-diphenyl-1,3-butadiene,
dimethylsilylbis(tetramethylcyclopentadienyl)zirconium dimethyl
dimethylsilylbis(fluorenyl)zirconiumdimethyl,
dimethylsilylbis(tetrahydrofluorenyl)zirconium bis(trimethylsilyl),
edthylenebis(indenyl)zirconiumdichloride,
edthylenebis(indenyl)zirconiumdimethyl,
edthylenebis(4,5,6,7-tetrahydroindenyl)zirconiumdichloride,
edthylenebis(4,5,6,7-tetrahydroindenyl)zirconiumdimethyl,
(isopropylidene)(cyclopentadienyl)(fluorenyl)zirconium dibenzyl,
and dimethylsilylbis(tetramethylcyclopentadienyl)(fluorenyl)zirconium dimethyl.

A further class of metal complexes utilized in addition polymerizations are compounds according to the preceding formula: MKZ, or a dimer thereof, wherein M, K, X, x and z are as previously defined, and Z is a substituent of up to 50 non-hydrogen atoms that together with K forms a metallocycle with M.

Preferred Z substituents include groups containing up to 30 non-hydrogen atoms comprising at least one atom that is oxygen, sulfur, boron or a member of Group 14 of the Periodic Table of the Elements directly attached to K, and a different atom, selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur that is covalently bonded to M.

More specifically this class of Group 4 metal complexes includes "constrained geometry catalysts" corresponding to the formula:

\[
\begin{array}{c}
X-Y \\
/ \ \\
K^1 \longrightarrow M X_x
\end{array}
\]

wherein:

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

K\(^1\) is a delocalized, π-bonded ligand group optionally substituted with from 1 to 5 R\(^2\) groups,

R\(^2\) in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R\(^2\) having up to 20 non-
hydrogen atoms, or adjacent $R^2$ groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

each $X$ is a halo, hydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 non-hydrogen atoms, or two $X$ groups together form a neutral C5.30 conjugated diene or a divalent derivative thereof;

$x$ is 1 or 2;

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

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

$R'$ independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said $R'$ having up to 30 carbon or silicon atoms.

Specific examples of the foregoing constrained geometry metal complexes include compounds corresponding to the formula:

![](image)

wherein,

$Ar$ is an aryl group of from 6 to 30 atoms not counting hydrogen;

$R^4$ independently each occurrence is hydrogen, $Ar$, or a group other than $Ar$ selected from hydrocarbyl, trihydrocarbysilyl, trihydrocarbylgermyl, halide, hydrocarbyloxy, trihydrocarbysiloxy, bis(trihydrocarbysilyl)amino, di(hydrocarbyl)amino, hydrocarbadiylamino, hydrocarbylimino, di(hydrocarbyl)phosphino, hydrocarbadiylphosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy- substituted hydrocarbyl, trihydrocarbysilyl- substituted hydrocarbyl, trihydrocarbysiloxy- substituted hydrocarbyl, bis(trihydrocarbysilyl)amino- substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino- substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said $R$ group having up to 40 atoms not counting hydrogen atoms, and optionally two adjacent $R^4$ groups may be joined together forming a polycyclic fused ring group;

$M$ is titanium;

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

$Y$ is $-O-, -S-, -NR^5-, -PR^5-$; $-NR^5_2$, or $-PR^5_2$;
R5, independently each occurrence, is hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl, said R5 having up to 20 atoms other than hydrogen, and optionally two R5 groups or R5 together with Y or Z form a ring system;

R6, independently each occurrence, is hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, -NR52, and combinations thereof, said R6 having up to 20 non-hydrogen atoms, and optionally, two R6 groups or R6 together with Z forms a ring system;

Z is a neutral diene or a monodentate or polydentate Lewis base optionally bonded to R5, R6, or X;

X is hydrogen, a monovalent anionic ligand group having up to 60 atoms not counting hydrogen, or two X groups are joined together thereby forming a divalent ligand group;

x is 1 or 2; and
z is 0, 1 or 2.

Preferred examples of the foregoing metal complexes are substituted at both the 3- and 4- positions of a cyclopentadienyl or indenyl group with an Ar group.

Examples of the foregoing metal complexes include:

(3-phenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(3-phenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(3-phenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium (II) 1,3-diphenyl-1,3-butadiene;

(3-(pyrrol-1-yl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(3-(pyrrol-1-yl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(3-(pyrrol-1-yl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(3-(1-methylpyrrol-3-yl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(3-(1-methylpyrrol-3-yl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(3-(1-methylpyrrol-3-yl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(3,4-diphenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(3,4-diphenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(3,4-diphenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium (II) 1,3-pentadiene;

(3-(3-N,N-dimethylamino)phenyl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(3-(3-N,N-dimethylamino)phenyl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
dimethyl,
(3-(3-N,N-dimethylamino)phenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium
(II) 1,4-diphenyl-1,3-butyadiene;
(3-(4-methoxyphenyl)-4-methylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium
dichloride,
(3-(4-methoxyphenyl)-4-phenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium
(II) 1,4-diphenyl-1,3-butyadiene;
(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(3-phenyl-4-methoxycyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(3-phenyl-4-methoxycyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
diphenyl-1,3-butyadiene;
(3-phenyl-4-(N,N-dimethylamino)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium
dichloride,
(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(3-phenyl-4-methoxycyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
diphenyl-1,3-butadiene;
(2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(2,3-diphenyl-4-(n-butyl)cyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
diphenyl-1,3-butadiene;
(2,3,4,5-tetraphenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(2,3,4,5-tetraphenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium dimethyl, and
(2,3,4,5-tetraphenylcyclopentadien-l-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-
diphenyl-1,3-butadiene.

Additional examples of suitable metal complexes for addition polymerizations are polycyclic complexes corresponding to the formula:

\[
\begin{array}{c}
R^7 \\
R^8
\end{array}
\]

where M is titanium in the +2, +3 or +4 formal oxidation state;

R^7 independently each occurrence is hydride, hydrocarbyl, silyl, germyl, halide,
hydrocarbyloxy, hydrocarbysiloxy, hydrocarbysilylamino, di(hydrocarbyl)amino,
hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbyle-phosphino, hydrocarbylsulfido,
ahalo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl-substituted
hydrocarbyl, hydrocarbysiloxy-substituted hydrocarbyl, hydrocarbysilylamino-substituted
hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted
hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl, hydrocarbyle-phosphino-
substituted hydrocarbyl, or hydrocarbysulfido-substituted hydrocarbyl, said R^7 group having up to
40 atoms not counting hydrogen, and optionally two or more of the foregoing groups may together
form a divalent derivative;

R^8 is a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused
system with the remainder of the metal complex, said R^8 containing from 1 to 30 atoms not
counting hydrogen;
X is a divalent moiety, or a moiety comprising one \( \sigma \)-bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said \( X^a \) comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

\[ \text{X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of} \]

ligands that are cyclic, delocalized, \( \pi \)-bound ligand groups and optionally two X groups together form a divalent ligand group;

\[ Z \] independently each occurrence is a neutral ligating compound having up to 20 atoms;

\[ x \] is 0, 1 or 2; and

\[ z \] is zero or 1.

Preferred examples of such complexes are 3-phenyl-substituted s-indecenyl complexes corresponding to the formula:

![Diagram of s-indecenyl complex](image)

2,3-dimethyl-substituted s-indecenyl complexes corresponding to the formulas:

![Diagram of 2,3-dimethyl-substituted s-indecenyl complex](image)

or 2-methyl-substituted s-indecenyl complexes corresponding to the formula:

![Diagram of 2-methyl-substituted s-indecenyl complex](image)
Additional examples of metal complexes that are usefully employed as catalyst (A) according to the present invention include those of the formula:

Specific metal complexes include:

(8-methylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,

(8-methylene-1,8-dihydrodibenzo[e,z]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,

(8-methylene-1,8-dihydrodibenzo[e,z]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,

(8-methylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,

(8-methylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,

(8-methylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,
(8-difluoromethylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,
(8-difluoromethylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,
(8-difluoromethylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,
(8-difluoromethylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,
(8-difluoromethylene-1,8-dihydrodibenzo[e,h]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,
(8-methylene-1,8-dihydrodibenzo[e,h]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,
(8-methylene-1,8-dihydrodibenzo[e,z]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,
(8-methylene-1,8-dihydrodibenzo[e,z]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,
(8-methylene-1,8-dihydrodibenzo[e,z]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,
(8-methylene-1,8-dihydrodibenzo[e,z]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,
(8-methylene-1,8-dihydrodibenzo[e,z]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,
Further illustrative examples of metal complexes for use in addition polymerizations correspond to the formula:

\[
\begin{align*}
\text{R}^{10} \quad \text{R}^{10} \quad \text{R}^{10} \\
\text{R}^{10} \quad \text{R}^{10} \quad \text{R}^{10} \\
\text{T} \quad \text{M} \quad \text{X} \quad \text{Z} \\
\end{align*}
\]

where \( M \) is titanium in the +2, +3 or +4 formal oxidation state;

\( T \) is \(-\text{NR}^9\)- or \(-\text{O}-\);

\( \text{R}^9 \) is hydrocarbyl, silyl, germyl, dihydrocarbylboryl, or halohydrocarbyl or up to 10 atoms not counting hydrogen;

\( \text{R}^{10} \) independently each occurrence is hydrogen, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo- substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl- substituted hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino- substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylene phosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said \( \text{R}^{10} \) group having up to 40 atoms not counting hydrogen atoms, and optionally two or more of the foregoing adjacent \( \text{R}^{10} \) groups may together form a divalent derivative thereby forming a saturated or unsaturated fused ring;

\( X^a \) is a divalent moiety lacking in delocalized \( \pi \)-electrons, or such a moiety comprising one \( \sigma \)-bond and a neutral two electron pair able to form a coordinate-covalent bond to \( M \), said \( X' \) comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;
X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic ligand groups bound to M through delocalized π-electrons or two X groups together are a divalent anionic ligand group;

Z independently each occurrence is a neutral ligating compound having up to 20 atoms;

x is 0, 1, 2, or 3; and

z is 0 or 1.

Highly preferably T is =N(CH₃), X is halo or hydrocarbyl, x is 2, X’ is dimethylsilane, z is 0, and R⁰ each occurrence is hydrogen, a hydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, hydrocarbyleneamino, dihydrocarbylamino- substituted hydrocarbyl group, or hydrocarbyleneamino- substituted hydrocarbyl group of up to 20 atoms not counting hydrogen, and optionally two R⁰ groups may be joined together.

Illustrative metal complexes of the foregoing formula include the following compounds:

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2′,3′](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,
(cyclohexylamido)dimethyl-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) dimethyl,
(cyclohexylamido)dimethyl-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silane titanium (IV) dibenzyl,
(cyclohexylamido)dimethyl-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) bis(trimethylsilyl),
(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (II) 1,3-pentadiene,
(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) dichloride,
(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) dimethyl,
(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) dibenzyl,
(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) bis(trimethylsilyl),
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (II) 1,3-pentadiene,
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (III) 2-(N,N-dimethylamino)benzyl,
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) dichloride,
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) dimethyl,
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5,2',3'](1-methylisoindol)-(3H)-indene-2-y]silanetitanium (IV) dibenzyl; and
(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'][1-methylisoindol]-(3H)-indenyl]silanetitanium (IV) bis(trimethylsilyl).

Additional examples of Group 4 metal complexes include:

(tert-butylamido)(1,1-dimethyl-2,3,4,9,10-\(\eta^5\)-hexahydronaphthalenyl)dimethylsilanetitanium dimethyl,
(tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10-\(\eta^5\)-hexahydronaphthalenyl)dimethylsilanetitanium dimethyl,
(tert-butylamido)(tetramethyl-\(\eta^5\)-cyclopentadienyl) dimethylsilanetitanium dibenzyl,
(tert-butylamido)(tetramethyl-\(\eta^5\)-cyclopentadienyl)dimethylsilanetitanium dimethyl,
(tert-butylamido)(tetramethyl-\(\eta^5\)-cyclopentadienyl)1,2-ethanediyltitanium dimethyl,
(tert-butylamido)(tetramethyl-\(\eta^5\)-indenyl)dimethylsilanetitanium (III) 2-(dimethylamino)benzyl;
(tert-butylamido)(tetramethyl-\(\eta^5\)-cyclopentadienyl)dimethylsilanetitanium (III) allyl,
(tert-butylamido)(tetramethyl-\(\eta^5\)-cyclopentadienyl)dimethylsilanetitanium (III) 2,4-dimethylpentadienyl,
(tert-butylamido)(tetramethyl-\(\eta^5\)-cyclopentadienyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(tert-butylamido)(tetramethyl-\(\eta^5\)-cyclopentadienyl)dimethylsilanetitanium (II) 1,3-pentadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-butadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) isoprene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-butadiene,
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) isoprene
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dimethyl
ter (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dibenzyl
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-
1,3-butadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dimethyl,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dibenzyl,
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II)
1,4-diphenyl-1,3-butyadiene,
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,
(tert-butylamido)(tetramethyl-η^5^-cyclopentadienyl)dimethylsilanetitanium (IV)
1,3-butadiene,
(tert-butylamido)(tetramethyl-η^5^-cyclopentadienyl)dimethylsilanetitanium (IV)
2,3-dimethyl-1,3-butyadiene,
(tert-butylamido)(tetramethyl-η^5^-cyclopentadienyl)dimethylsilanetitanium (IV)
isoprene,
(tert-butylamido)(tetramethyl-η^5^-cyclopentadienyl)dimethylsilanetitanium (II)
1,4-dibenzyl-1,3-butadiene,
(tert-butylamido)(tetramethyl-η^5^-cyclopentadienyl)dimethylsilanetitanium (II)
2,4-hexadiene,
(tert-butylamido)(tetramethyl-η^5^-cyclopentadienyl)dimethylsilanetitanium (II)
3-methyl-1,3-pentadiene,
(tert-butylamido)(2,4-dimethylpentadien-3-yl)dimethylsilanetitanium dimethyl,
(tert-butylamido)(6,6-dimethylcyclohexadienyl)dimethylsilanetitanium dimethyl,
(tert-butylamido)(1,1-dimethyl-2,3,4,9,10- η-1,4,5,6,7,8-hexahydronaphthalen-4-
yl)dimethylsilanetitanium dimethyl,
(tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10- η-1,4,5,6,7,8-hexahydronaphthalen-4-
yl)dimethylsilanetitanium dimethyl
(tert-butylamido)(tetramethyl-η^5^-cyclopentadienyl methylphenylsilanetitanium (IV)
dimethyl,
(tert-butylamido)(tetramethyl-η^5^-cyclopentadienyl methylphenylsilanetitanium (II)
1,4-diphenyl-1,3-butadiene,
1-(tert-butylamido)-2-(tetramethyl- η^5^-cyclopentadienyl)ethanediyltitanium (IV)
dimethyl, and
l-(tert-butylamido)-2-(tetramethyl-η⁵-cyclopentadienyl)ethanediyl-titanium (II) 1,4-diphenyl-1,3-butadiene.

Other delocalized, π-bonded complexes, especially those containing other Group 4 metals, will, of course, be apparent to those skilled in the art, and are disclosed among other places in: WO 03/78480, WO 03/78483, WO 02/92610, WO 02/02577, US 2003/0004286 and US Patents 6,515,155, 6,555,634, 6,150,297, 6,034,022, 6,268,444, 6,015,868, 6,150,297, 6,034,022, 6,268,444, 6,015,868, 5,866,704, and 5,470,993.

Additional examples of metal complexes for addition polymerizations are metal complexes of polyvalent Lewis bases, such as compounds of the formulas:

\[
\begin{align*}
&\left[ (R^b)_g - X^b - Y^b - (R^b)_g \right], \text{ or } \left[ (R^b)_g - X^b - Y^b - (R^b)_g \right]_j \\
&(R^b)_g - X^b - Y^b - (R^b)_g, \text{ or } (R^b)_g - X^b - Y^b - (R^b)_g \\
&(R^b)_s - X^b - Y^b - (R^b)_g, \text{ or } (R^b)_s - X^b - Y^b - (R^b)_g \\
\end{align*}
\]

wherein \(T^b\) is a bridging group, preferably containing 2 or more atoms other than hydrogen, \(X^b\) and \(Y^b\) are each independently selected from the group consisting of nitrogen, sulfur, oxygen and phosphorus; more preferably both \(X^b\) and \(Y^b\) are nitrogen, \(R^b\) and \(R^b'\) independently each occurrence are hydrogen or C₁₋₅₅ hydrocarbyl groups optionally containing one or more heteroatoms or inertly substituted derivative thereof. Non-limiting examples of suitable \(R^b\) and \(R^b'\) groups include alkyl, alkenyl, aryl, aralkyl, (poly)alkylaryl and cycloalkyl groups, as well as nitrogen, phosphorus, oxygen and halogen substituted derivatives thereof. Specific examples of suitable Rb and Rb' groups include methyl, ethyl, isopropyl, octyl, phenyl, 2,6-dimethylphenyl, 2,6-di(isopropyl)phenyl, 2,4,6-trimethylphenyl, pentafluorophenyl, 3,5-trifluoromethylphenyl, and benzyl;
g is 0 or 1;

M<sup>b</sup> is a metallic element selected from Groups 3 to 15, or the Lanthanide series of the Periodic Table of the Elements. Preferably, M<sup>b</sup> is a Group 3-13 metal, more preferably M<sup>b</sup> is a Group 4-10 metal;

L<sup>b</sup> is a monovalent, divalent, or trivalent anionic ligand containing from 1 to 50 atoms, not counting hydrogen. Examples of suitable L<sup>b</sup> groups include halide; hydride; hydrocarbyl, hydrocarbyloxy; di(hydrocarbyl)amido, hydrocarbylamine, di(hydrocarbyl)phosphido; hydrocarbysulfido; hydrocarbyloxy, tri(hydrocarbylsilyl)alkyl; and carboxylates. More preferred L<sup>b</sup> groups are Ci<sub>2</sub>0 alkyl, C<sub>7</sub>2<sub>0</sub> aralkyl, and chloride;

h is an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3, and j is 1 or 2, with the value h x j selected to provide charge balance;

Z<sup>b</sup> is a neutral ligand group coordinated to M<sup>b</sup>, and containing up to 50 atoms not counting hydrogen. Preferred Z<sup>b</sup> groups include aliphatic and aromatic amines, phosphines, and ethers, alkenes, alkadienes, and inertly substituted derivatives thereof. Suitable inert substituents include halogen, alkoxy, aryloxy, alkoxy carbonyl, aryloxy carbonyl, di(hydrocarbyl)amine, tri(hydrocarbyl)silyl, and nitrile groups. Preferred Z<sup>b</sup> groups include triphenylphosphine, tetrahydrofuran, pyridine, and 1,4-diphenylbutadiene;

f is an integer from 1 to 3;

two or three of T<sup>b</sup>, R<sup>b</sup> and R<sup>b</sup>' may be joined together to form a single or multiple ring structure;

h is an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3;

indicates any form of electronic interaction, especially coordinate or covalent bonds, including multiple bonds, arrows signify coordinate bonds, and dotted lines indicate optional double bonds.

In one embodiment, it is preferred that R<sup>b</sup> have relatively low steric hindrance with respect to X<sup>b</sup>. In this embodiment, most preferred R<sup>b</sup> groups are straight chain alkyl groups, straight chain alkenyl groups, branched chain alkyl groups wherein the closest branching point is at least 3 atoms removed from X<sup>b</sup>, and halo, dihydrocarbylamino, alkoxy or trihydrocarbylsilyl substituted derivatives thereof. Highly preferred R<sup>b</sup> groups in this embodiment are Ci<sub>3</sub>8 straight chain alkyl groups.

At the same time, in this embodiment R<sup>b</sup>' preferably has relatively high steric hindrance with respect to Y<sup>b</sup>. Non-limiting examples of suitable R<sup>b</sup>' groups for this embodiment include alkyl or alkenyl groups containing one or more secondary or tertiary carbon centers, cycloalkyl, aryl, alkaryl, aliphatic or aromatic heterocyclic groups, organic or inorganic oligomeric, polymeric or cyclic groups, and halo, dihydrocarbylamino, alkoxy or trihydrocarbylsilyl substituted derivatives.
Preferred \( R'^{d} \) groups in this embodiment contain from 3 to 40, more preferably from 3 to 30, and most preferably from 4 to 20 atoms not counting hydrogen and are branched or cyclic.

Examples of preferred \( T^{b} \) groups are structures corresponding to the following formulas:

\[
R^{d} > \text{-C}^{'} \quad (R^{e})_{2} \quad R^{i} \quad \lambda \quad R^{e} \quad C - \text{-Si} \quad , \quad \text{-C-Ge} \quad , \quad (R^{e})_{2} \quad (R^{d})_{2} \quad C - C \quad (R^{e})_{2}
\]

\[
R^{d} \quad \text{-C-Sn} \quad (R^{e})_{2} \quad (R^{d})_{2} \quad (R^{e})_{2} \quad R^{d} \quad (R^{e})_{3} \quad R^{d} \quad R^{e} \quad \text{-C-C} \quad , \quad \text{-P-C} \quad , \quad \text{-C-P} \quad , \quad \text{-Ge} \quad , \quad \text{or} \quad \text{-C-C} \quad , \quad \text{wherein}
\]

Each \( R^{d} \) is \( C_{n} \) hydrocarbyl group, preferably methyl, ethyl, \( n \)-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. Each \( R^{e} \) is \( C_{n} \) hydrocarbyl, preferably methyl, ethyl, \( n \)-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. In addition, two or more \( R^{d} \) or \( R^{e} \) groups, or mixtures of \( R^{d} \) and \( R^{e} \) groups may together form a polyvalent derivative of a hydrocarbyl group, such as, 1,4-butylene, 1,5-pentylene, or a multicyclic, fused ring, polyvalent hydrocarbyl- or hetero-hydrocarbyl- group, such as naphthalene-1,8-diyl.

Preferred examples of the foregoing polyvalent Lewis base complexes include:
wherein each occurrence is independently selected from the group consisting of hydrogen and Cl_{50} hydrocarbyl groups optionally containing one or more heteroatoms, or inertly substituted derivative thereof, or further optionally, two adjacent R^d groups may together form a divalent bridging group;

d' is 4;

M^{b+} is a Group 4 metal, preferably titanium or hafnium, or a Group 10 metal, preferably Ni or Pd;

L^{b−} is a monovalent ligand of up to 50 atoms not counting hydrogen, preferably halide or hydrocarbyl, or two L^{b−} groups together are a divalent or neutral ligand group, preferably a C_{2a} hydrocarbylene, hydrocarbadiyl or diene group.

The polyvalent Lewis base complexes additionally include Group 4 metal derivatives, especially hafnium derivatives of hydrocarbylamine substituted heteroaryl compounds corresponding to the formula:

wherein:

R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen or a divalent derivative thereof;

T^{1} is a divalent bridging group of from 1 to 41 atoms other than hydrogen, preferably 1 to 20 atoms other than hydrogen, and most preferably a mono- or di- Cl_{2} hydrocarbyl substituted methylene or silane group; and
R$^{12}$ is a C$_{5\sim20}$ heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group or a divalent derivative thereof;

M$^{1}$ is a Group 4 metal, preferably zirconium or hafnium;

X$^{1}$ is an anionic, neutral or dianionic ligand group;

x’ is a number from 0 to 5 indicating the number of such X$^{1}$ groups; and

bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

Preferred complexes are those wherein ligand formation results from hydrogen elimination from the amine group and optionally from the loss of one or more additional groups, especially from R$^{12}$. In addition, electron donation from the Lewis base functionality, preferably an electron pair, provides additional stability to the metal center. Preferred metal complexes correspond to the formula:

\[
\begin{align*}
&\text{R}^{13}, \text{R}^{14}, \text{R}^{15} \text{ and } \text{R}^{16} \text{ are hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, or silyl group of up to 20 atoms not counting hydrogen, or adjacent R}^{13}, \text{R}^{14}, \text{R}^{15} \text{ or } \text{R}^{16} \text{ groups may be joined together thereby forming fused ring derivatives, and} \\
&\text{bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.}
\end{align*}
\]

More preferred examples of the foregoing metal complexes correspond to the formula:

\[
\begin{align*}
&\text{M}^{1}, \text{X}^{1}, \text{x}' \text{ are as previously defined,}
\end{align*}
\]
R, R^1, R^2, and R^3 are as previously defined, preferably R, R^1, and R^2 are hydrogen, or Ci-alkyl, and R^3 is C_6H_5aryl, most preferably naphthalenyl; 
R^4 independently each occurrence is Ci_4 alkyl, and a is 1-5, most preferably R^a in two ortho-positions to the nitrogen is isopropyl or t-butyl; 
R^17 and R^18 independently each occurrence are hydrogen, halogen, or a Ci_2alkyl or aryl group, most preferably one of R^17 and R^18 is hydrogen and the other is a C_6H_5aryl group, especially 2-isopropyl, phenyl or a fused polycyclic aryl group, most preferably an anthracenyl group, and bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

Highly preferred amine donor metal complexes correspond to the formula:

![Diagram](image)

wherein X^1 each occurrence is halide, N,N-dimethylamido, or Ci_4 alkyl, and preferably each occurrence X^1 is methyl; 
R^c, R^f and R^g independently each occurrence are halogen, Ci_20 alkyl, or C_6H_5aryl, or two adjacent R^c, R^f or R^g groups are joined together thereby forming a ring, c is an integer from 1 to 4, and f and g, independently is integers from 1-5; and 
R^h independently each occurrence is hydrogen or Ci_6 alkyl.

Most highly preferred examples of such amine donor metal complexes are compounds of the formulas:

![Diagram](image)
wherein $R^x$ is $C_i$ alkyl or cycloalkyl, preferably methyl, isopropyl, t-butyl or cyclohexyl; and

$X^1$ each occurrence is halide, $N,N$-dimethylamido, or $C_i$ alkyl, preferably methyl.

Examples include:

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(o-tolyl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(o-tolyl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(o-tolyl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(2-isopropylphenyl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(2-isopropylphenyl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(2-isopropylphenyl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(phenanthren-5-yl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(phenanthren-5-yl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(phenanthren-5-yl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;$$

$$[N-(2,6-di(l-methylethyl)phenyl)amido)(phenanthren-5-yl)(\alpha$-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(n-butyl);$$

$$[N-(2,6-bis(l-methylethyl)phenyl]$-\alpha[2-(1-methylethyl)phenyl]6(-(1,2-naphthalendiyl-$\kappa$-C$_2$)-2-pyridinemethanaminato(2^-KN$_1$, $\kappa$N$^2$)]hafnium dimethyl,}
[N-[2,4,6-tris(l-methylethyl)phenyl]-α-[2,6-di(l-methylethyl)phenyl]-5-(2-ethylbenzofuran-3-yl-κ-C^4)-2-(N'-methyl)imidazol-2-yl)methanaminato (2-)\(\kappa N\ K N^2\) hafnium di(methyl), and

[N-[2,4,6-tris(l-methylethyl)phenyl]-α-[2,6-bis(l-methylethyl)phenyl]-6-(1,2-naphthalenyl-κ-C^2)-2-pyridinemethanaminato (2-)\(\kappa N^1, \kappa N^2\)] hafnium di(n-butyl).

Additional suitable metal complexes of polyvalent Lewis bases include polyether compounds corresponding to the formula:

\[
\begin{align*}
\text{R}^{20} & \quad \text{O} \\
\quad & \quad \text{O} \\
\quad & \quad \text{O} \\
\quad & \quad \text{O} \\
\quad & \quad \text{M}^3 - \text{O} \\
\quad & \quad \text{Gg} \\
\end{align*}
\]

where:

\(\text{R}^{20}\) is an aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen, or a polyvalent derivative thereof;

\(\text{T}^3\) is a hydrocarbylene or silane group having from 1 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof;

\(\text{M}^3\) is a Group 4 metal, preferably zirconium or hafnium;

\(\text{G}\) is an anionic, neutral or dianionic ligand group; preferably a halide, hydrocarbyl or dihydrocarbylamide group having up to 20 atoms not counting hydrogen;

\(g\) is a number from 1 to 5 indicating the number of such \(\text{G}\) groups; and

bonds and electron donative interactions are represented by lines and arrows respectively.

Preferably, such complexes correspond to the formula:

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\quad & \quad \text{T}^3 \quad \text{O} \\
\quad & \quad \text{Ar}^2 \\
\quad & \quad \text{M}^3 \text{Gg} \\
\quad & \quad \text{Ar}^2 \\
\quad & \quad \text{O} \\
\quad & \quad \text{Gg} \\
\end{align*}
\]

wherein:

\(\text{T}^3\) is a divalent bridging group of from 2 to 20 atoms not counting hydrogen, preferably a substituted or unsubstituted, \(\text{C}_{36}\) alkylene group; and

\(\text{Ar}^2\) independently each occurrence is an arylene or an alkyl- or aryl-substituted arylene group of from 6 to 20 atoms not counting hydrogen;

\(\text{M}^3\) is a Group 4 metal, preferably hafnium or zirconium;

\(\text{G}\) independently each occurrence is an anionic, neutral or dianionic ligand group;

\(g\) is a number from 1 to 5 indicating the number of such \(X\) groups; and

electron donative interactions are represented by arrows.
Examples of metal complexes of foregoing formula include the following compounds:

where $M^3$ is Hf or Zr;

$Ar^4$ is C$_{6-20}$ aryl or inertly substituted derivatives thereof, especially 3,5-
5 di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl, and

$T^4$ independently each occurrence comprises a C$_{3-6}$ alkyne group, a C$_{3-6}$ cycloalkylene
5 independently each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, or
group, or an inertly substituted derivative thereof;

$R^{21}$ independently each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, or
5 trihydrocarbylsilylhydrocarbyl of up to 50 atoms not counting hydrogen; and

$G$, independently each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of
5 up to 20 atoms not counting hydrogen, or 2 $G$ groups together are a divalent derivative of the
5 foregoing hydrocarbyl or trihydrocarbylsilyl groups.

Especially preferred are compounds of the formula:
wherein \( A r^4 \) is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-lH-pyrrole-1-yl, or anthracen-5-yl, 
\( R^2 \) is hydrogen, halo, or \( C_{i4} \) alkyl, especially methyl 
\( T^4 \) is propan-1,3-diyl or butan-1,4-diyl, and 
\( G \) is chloro, methyl or benzyl.

A most highly preferred metal complex of the foregoing formula is:

![Image of a metal complex]

The foregoing polyvalent Lewis base complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of the transition metal and the neutral polyfunctional ligand source. In addition, the complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding Group 4 metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum. Other techniques may be used as well. These complexes are known from the disclosures of, among others, US patents 6,320,005, 6,103,657, WO 02/38628, WO 03/40195, and US 04/0220050.

Cocatalysts for Unsaturated Polymer Reagent Synthesis

Generally the foregoing metal complexes are rendered active for olefin polymerization by contact with an activating cocatalyst. Suitable cocatalysts include those compounds previously known in the art for use with Group 4 metal olefin polymerization complexes. Examples of suitable activating cocatalysts include neutral Lewis acids, such as \( C_{i3} \) hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluorophenyl)borane; nonpolymeric, compatible,

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

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

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

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

\[(L^\ast \cdot H)^{+} (A)^{-}\]

wherein:

- \(L^\ast\) is a neutral Lewis base;
- \((L^\ast \cdot H)^{+}\) is a conjugate Bronsted acid of \(L^\ast\);
- \(A^{-}\) is a noncoordinating, compatible anion having a charge of \(g^{-}\), and
- \(g\) is an integer from 1 to 3.

More preferably \(A^{-}\) corresponds to the formula: 

\([M^\prime Q_4]^{-}\),

wherein:

- \(M^\prime\) is boron or aluminum in the +3 formal oxidation state; and
- \(Q\) independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxide, halosubstituted-hydrocarbyl, halosubstituted-hydrocarbyloxy, and halo-substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said \(Q\) having up to 20 carbons with the proviso that in not more than one occurrence is \(Q\) halide. Examples of suitable hydrocarbyloxide \(Q\) groups are disclosed in US-A-5,296,433.

In a more preferred embodiment, \(g\) is one, that is, the counter ion has a single negative charge and is \(A^{-}\). Activating cocatalysts comprising boron which are particularly useful in addition polymerizations may be represented by the following general formula:

\[(L^\ast \cdot H)^{+} (BQ_4)^{-}\]

wherein:

- \(L^\ast\) is as previously defined;
- \(B\) is boron in a formal oxidation state of 3; and
- \(Q\) is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is \(Q\) hydrocarbyl.

Preferred Lewis base salts are ammonium salts, more preferably trialkylammonium salts containing one or more \(C_{12-40}\) alkyl groups. Most preferably, \(Q\) is each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in addition polymerizations are
tri-substituted ammonium salts such as:

- trimethylammonium tetrakis(pentafluorophenyl) borate,
- triethylammonium tetrakis(pentafluorophenyl) borate,
- tripropylammonium tetrakis(pentafluorophenyl) borate,
- tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
- tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate,
- N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
- N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate,
- N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate,
- N,N-dimethylanilinium tetrafluorophenoxytris(pentafluorophenyl) borate,
- N,N-diethylanilinium tetrakis(pentafluorophenyl) borate,
- N,N-diethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate,
- dimethyloctadecylammonium tetrakis(pentafluorophenyl) borate,
- methylldioctadecylammonium tetrakis(pentafluorophenyl) borate,
- dialkyl ammonium salts such as:
  - di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate,
  - methylldioctadecylammonium tetrakis(pentafluorophenyl) borate,
- methylldioctadecylammonium tetrakis(pentafluorophenyl) borate, and
dioctadecylammonium tetrakis(pentafluorophenyl) borate;
- tri-substituted phosphonium salts such as:
  - triphenylphosphonium tetrakis(pentafluorophenyl) borate,
  - methylldioctadecylphosphonium tetrakis(pentafluorophenyl) borate, and
tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate;
- di-substituted oxonium salts such as:
  - diphenyloxonium tetrakis(pentafluorophenyl) borate,
  - di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and
di(octadecyloxy)onium tetrakis(pentafluorophenyl) borate;
- di-substituted sulfonium salts such as:
  - di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and
  methylcotadecylsulfonium tetrakis(pentafluorophenyl) borate.

Preferred (L²-H)+ cations are methylldioctadecylammonium cations, dimethyldecylammonium cations, and ammonium cations derived from mixtures of trialkyl amines containing one or 2 C₁₈ alkyl groups. A particularly preferred example of the latter
compound is based on a commercially available long chain amine and is referred to as: bis-
(hydrogenated tallowalkyl)methylammonium tetrakis(pentafluorophenyl)borate.

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

\[(\text{Ox}^{b+})_g(\text{A}^{-})_h\]

wherein:

\[
\text{Ox}^{b+} \text{ is a cationic oxidizing agent having a charge of } h^+; \\
h \text{ is an integer from 1 to 3; and} \\
\text{A}^{-} \text{ and } g \text{ are as previously defined.}
\]

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

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

\[[\text{C}]^+\text{A}^-\]

wherein:

\[
\text{[C]}^+ \text{ is a } \text{C}_{20} \text{ carbenium ion; and} \\
\text{A}^- \text{ is a noncoordinating, compatible anion having a charge of -1. A preferred carbenium ion is the trityl cation, which is triphenylmethylum.}
\]

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

\[(\text{Q}^1_3\text{Si})^+\text{A}^-\]

wherein:

\[
\text{Q}^1 \text{ is } \text{CI-io hydrocarbyl, and A}^- \text{ is as previously defined.}
\]


Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present invention. Such cocatalysts are disclosed in US-A-5,296,433.
A class of cocatalysts comprising non-coordinating anions generically referred to as expanded anions, further disclosed in US Patent 6,395,671, may be suitably employed to activate metal complexes for olefin polymerization. Generally, these cocatalysts (illustrated by those having imidazolide, substituted imidazolide, imidazolinide, substituted imidazolinide, benzimidazolide, or substituted benzimidazolide anions) may be depicted as follows:

![Diagram]

wherein:

- $A^{+}$ is a cation, especially a proton containing cation, and preferably is a trihydrocarbyl ammonium cation containing one or two $Q_{0-40}$ alkyl groups, especially a methylid

- $Q^3$, independently each occurrence, is hydrogen or a halo, hydrocarbyl, halocarbyl, halohydrocarbyl, silylhydrocarbyl, or silyl, (including mono-, di- and tri(hydrocarbyl)silyl) group of up to 30 atoms not counting hydrogen, preferably $C_{10}$ alkyl, and

- $Q^2$ is tris(pentfluorophenyl)borane or tris(pentfluorophenyl)alumane).

Examples of these catalyst activators include trihydrocarbylammonium salts, especially, methylid(Ci$_{4-20}$alkyl)ammonium salts of:

- bis(tris(pentfluorophenyl)borane)imidazolide,
- bis(tris(pentfluorophenyl)borane)-2-undecylimidazolide,
- bis(tris(pentfluorophenyl)borane)-2-heptadecylimidazolide,

- bis(tris(pentfluorophenyl)borane)-4,5-bis(undecyl)imidazolide,
- bis(tris(pentfluorophenyl)borane)-4,5-bis(heptadecyl)imidazolide,
- bis(tris(pentfluorophenyl)borane)imidazolinide,
- bis(tris(pentfluorophenyl)borane)-2-undecylimidazolinide,
- bis(tris(pentfluorophenyl)borane)-2-heptadecylimidazolinide,

- bis(tris(pentfluorophenyl)borane)-4,5-bis(undecyl)imidazolinide,
- bis(tris(pentfluorophenyl)borane)-4,5-bis(heptadecyl)imidazolinide,
- bis(tris(pentfluorophenyl)borane)-5,6-dimethylbenzimidazolide,
- bis(tris(pentfluorophenyl)borane)-5,6-bis(undecyl)benzimidazolide,
- bis(tris(pentfluorophenyl)alumane)imidazolide,
bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolide,
bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolide,
bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolide.
bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide,
bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide,
bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide,
bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolide, and
bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolide.

Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2"-nonafluorobiphenyl) fluoroaluminate. Combinations of activators are also contemplated, for example, alumoxanes and ionizing activators in combinations, see for example, EP-A-O 573120, PCT publications WO 94/07928 and WO 95/14044 and US Patents 5,153,157 and 5,453,410. WO 98/09996 describes activating catalyst compounds with perchlorates, periodates and iodates, including their hydrates. WO 99/18135 describes the use of organoboroaluminum activators. WO 03/10171 discloses catalyst activators that are adducts of Bronsted acids with Lewis acids. Other activators or methods for activating a catalyst compound are described in US Patents 5,849,852, 5,859, 653, 5,869,723, EP-A-615981, and PCT publication WO 98/32775.

As previously mentioned, suitable activating cocatalysts include polymeric or oligomeric alumoxanes, especially methylalumoxane (MAO), trisobutyl aluminum modified methylalumoxane (MMAO), or isobutylalumoxane; Lewis acid modified alumoxanes, especially perhalogenated tri(hydrocarbyl)aluminum- or perhalogenated tri(hydrocarbyl)boron modified alumoxanes, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, and most especially tris(pentafluorophenyl)borane modified alumoxanes. Such cocatalysts are previously disclosed in USP's 6,214,760, 6,160,146, 6,140,521, and 6,696,379.

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used by itself as an activating cocatalyst, may be employed in lower quantity (<100:1) than the predominant catalyst literature, which is generally at least 100 times the quantity of metal complex on a molar basis, and more often around 1000 times this quantity. Tris(pentafluorophenyl)borane, where used as an activating cocatalyst is employed in a molar ratio to the metal complex of from 0.5:1 to 10:1, more preferably from 1:1 to 6:1 most preferably from 1:1 to 5:1. The remaining
activating cocatalysts are generally employed in approximately equimolar quantity with the metal complex.

Polymer Metathesis Conditions

The metathesis is desirably conducted by contacting the functionalized ethylene containing cyclic or acyclic reagent compound or a compound capable of forming such ethylenically unsaturated functional group containing compound (precursor) with the unsaturated polymer in the presence of a metathesis catalyst. The compound or precursor should be present in an amount to provide approximately one equivalent of ethylene functionality for each unsaturation in the unsaturated reagent polymer(s), thereby forming fully functionalized reaction products. A solvent or diluent, especially a saturated hydrocarbon or halogenated hydrocarbon may be employed to achieve intimate contact between the reaction components.

Suitable catalysts for the metathesis are known from the prior art, and include homogeneous and heterogeneous catalyst systems. In general, the catalysts suitable for the process are based on a transition metal from transition group 6, 7 or 8 of the Periodic Table, with preference being given to the use of catalysts based on Mo, W, Re and Ru. Examples of homogeneous catalyst systems generally include one or more transition metal compounds, optionally in combination with a cocatalyst which are capable of forming a catalytically active metal carbene complex, which is thought to be the active catalyst composition.

Such compositions are described, for example, in "Comprehensive Organometallic Chemistry", R. H. Grubbs, ed., Pergamon Press, Ltd., New York, Volume 8, page 499 ff. (1982). Specific catalyst/cocatalyst compositions based on W, Mo and Re may comprise, for example, at least one soluble transition metal compound and an alkylating agent. Examples include MoCl₅(NO)₂(P(C₆H₄)₃)₂ZnCl₂(CH₃)SCI₃, WCl₆/BuLi, WCl₂(C₂H₅)AlCl₂(Sn(CH₃)₄)/C₂H₅OH; WOCl₂/Sn(CH₃)₄; WOCl₂(O-[2,6-Br₂-C₆H₄])/Sn(CH₃)₄, and CH₃Re(VC₂H₅)AlCl₃.

Further suitable catalysts include transition metal-alkylidene complexes in, Ace. Ch. Res., Volume 23, page 158 ff. (1990). In general, these complexes are tetracoordinated Mo- and W-alkylidene complexes additionally containing two bulky alkoxy ligands and one imido ligand. Examples include: ((CH₃)₃CO)₂Mo(=N-[2,6-(i-C₃H₇)₂C₆H₃])=CHC(CH₃)₂C₆H₃ and [((CF₃)₂C(CH₃)O]₂Mo(=N-[2,5-(i-C₃H₇)₂C₆H₃])=(CHC(CH₃)₂C₆H₃).

Suitable heterogeneous catalyst systems generally comprise a transition metal compound on an inert support, said compound being capable without a cocatalyst of forming a catalytically active alkylidene complex by reaction with an olefin. Examples include Re₂O₇ and CH₃ReO₃. Suitable inorganic supports are metal oxides or metalloid oxides, especially silicon oxides and aluminum oxides, aluminosilicates, zeolites, carbides, nitrides, and mixtures thereof. Preferred supports are Al₂O₃, SiO₂ and mixtures thereof, in combination with B₂O₃ or Fe₂O₃ if desired.

Further suitable metathesis catalysts for use herein include homogeneous ruthenium catalysts including first-generation Grubbs catalysts, exemplified by bis(tricyclohexylphosphine)-benzylidene ruthenium dichloride, and second-generation Grubbs catalysts, exemplified by tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium dichloride. "First-generation and second-generation Grubbs catalysts," named for their principle inventor Robert H. Grubbs, are disclosed in WO 96/04289 and WO 02/083742 and references disclosed therein. First-generation and second-generation Grubbs catalysts tend to be relatively tolerant towards air, moisture, and are preferred for industrial usage.

Additional examples of suitable catalyst compositions include organic or inorganic derivatives of transition metals selected from Groups 5-10, preferably molybdenum, tantalum, tungsten, ruthenium, or rhenium, either in the form of solids, dispersions, suspensions, solutions, or neat. In the solid form, the catalyst or the individual components thereof may be supported on the surface of an inert carrier or support, such as a high surface area metal oxide, metalloid oxide, metal carbide, metal boride, metal nitride, zeolite or clay. Preferred compounds include ruthenium, molybdenum or tungsten compounds or complexes, especially halides, oxyhalides, tetraorganooammonium tungstates, tetraorganooammonium molybdenates, Lewis base derivatives thereof, and mixtures of the foregoing.

Examples of suitable homogeneous catalyst compositions employed in the practice of this invention include those previously disclosed in USP 4,010,224, especially compositions comprising: (A) at least one organometallic compound wherein the metal is selected from Groups 1, 2, 12 or 13 of the Periodic Table of Elements, (B) at least one metal derivative wherein the metal is selected from the group consisting of metals of Groups 5, 6, or 7, especially molybdenum or tungsten and, optionally, (C) at least one chelating- or Lewis base- material. Examples of the latter compounds include ethers, carboxylic acid esters, ketones, aldehydes, carbonates, nitriles, alcohols, thiols, water, and mixtures thereof.

Representative examples of organometallic compounds from which component (A) may be selected include lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, aluminum, gallium, indium, and thallium compounds, with
lithium, sodium, magnesium, aluminum, zinc and cadmium compounds being preferred and with aluminum compounds being most preferred.

Representative examples of organometallic compounds useful as catalyst component (A) are organoaluminum compounds having at least one aluminum-to-carbon bond. Representative of such compounds are tri(Ci-io)hydrocarblyaluminum compounds such as trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisopropylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, tritolyaluminum, tribenzylaluminum, and triphenylaluminum; organoaluminum halides such as diethylaluminum chloride, di-n-propylaluminum chloride, diisobutylaluminum chloride, diethylaluminum bromide, diethylaluminum iodide and diethylaluminum fluoride, ethylaluminum dichloride, ethylaluminum sesquichloride, ethylaluminum dibromide, propylaluminum dichloride, isobutylaluminum dichloride, ethylaluminum diiodide, phenylaluminum dibromide, tolylaluminum dibromide, benzylaluminum dibromide, phenylaluminum diiodide, tolylaluminum diiodide, benzylaluminum diiodide, diphenylaluminum chloride, ditolylaluminum chloride, and dibenzylaluminum bromide; organoaluminum hydride compounds such as diphenylaluminum hydride and phenylaluminum dihydride; and mixtures of the foregoing.

Additional suitable organometallic compounds are alkali metal compounds such as ethyllithium, n-butyllithium, t-butyllithium, amylsodium, butylpotassium, phenylpotassium, phenylsodium, phenyllithium, lithium-aluminum tetrabutyl, lithium-aluminum tetraethyl, lithium-aluminum triethyl chloride, and sodium aluminum tetraethyl; alkaline earth metal compounds such as diphenylmagnesium, diethylmagnesium, ethylmagnesium chloride, phenylmagnesium chloride, butylmagnesium bromide, butyl calcium chloride, and diethylbarium; Group 12 organometal compounds such as diethylzinc, diphenylzinc, ethylzinc chloride, diethylcadmium, and dibutylcadmium; phenylmagnesium bromide, butylmagnesium chloride, butylmagnesium bromide, and ethylmagnesium chloride; and mixtures of the foregoing compounds. Preferred compounds for use as component (A) are trialkylalumiums, dialkylaluminum halides, alkylaluminum dihalides and aluminumsesquihalides, containing up to 4 carbons in each alkyl group.

Suitable derivatives of molybdenum and tungsten useful as component (B) of the metathesis catalyst include the corresponding halides-, acetylacetonates-, sulphates-, phosphates-, nitrates-, and alcoholates. Examples include: chlorides, bromides, iodides and fluorides, such as molybdenum pentachloride, tungsten hexachloride, molybdenum pentabromide, tungsten hexabromide, molybdenum pentaiodide, molybdenum pentafluoride, molybdenum hexafluoride and tungsten hexafluoride. Other examples include molybdenum phosphate, tungsten phosphate, molybdenum nitrate, tungsten nitrate, molybdenum acetylacetonate, tungsten acetylacetonate, molybdenum sulphate, and tungsten sulphate. Mixtures of these compounds may also be employed. The
tungsten- and molybdenum halides, representative of which are tungsten hexachloride and molybdenum pentachloride, are especially preferred.

Suitable compounds for use as component (C) of the catalyst composition are compounds of the general formula R-Y-H wherein Y is selected from the group of oxygen and sulfur and wherein R is hydrogen, or a hydrocarbyl or substituted hydrocarbyl group having up to 20 carbons total, and wherein the substituent(s) on the hydrocarbyl group are selected from the group consisting of hydroxy, thio, hydrocarbyloxy, hydrocarbylthio, oxy- and sulfo-. Examples include water, hydrogen sulfide, alkanols, aromatic alcohols, mercaptans, hydrocarbylperoxides, polyalcohols, polymercaptans, hydroxy mercaptans, alkanolethers, alkanolthioethers, mercaptoethers and mercaptothioethers. Representative examples of the materials for use as component (C) include alcohols such as methanol, ethanol, isopropanol, tertiarybutyl alcohol, amyl alcohol, benzyl alcohol, allyl alcohol, 1,1-dimethyl benzyl alcohol, phenol, tertiarybutyl catechol, cresol, alpha and beta naphthyl alcohol; mercaptans such as methyl-, ethyl-, propyl-, isopropyl-, butyl-, amyl- or allylmercaptan, thiophenol, 4-methylthiophenol, or 4-mercaptophenol; hydroperoxides, such as, cumyl hydroperoxide, tertiarybutyl hydroperoxide; hydrodisulfides such as cumyl hydrodisulfide, and $s$-butyl hydrodisulfide; polyalcohols, such as ethylene glycol, glycerol, polyethylene glycol, catechol, resorcinol, hydroquinone, pyrogallol; polymercaptans, such as 1,3-propane dithiol, 1,4-dithiobenzene; and hydroxymercaptans, such as, 1-hydroxy-2-thioethane or 1-hydroxy-4-thiobenzene.

The quantity of component (C) employed in the foregoing catalyst composition is adjusted to control the activity of the catalyst composition. Generally, the catalyst composition exhibits higher activity when the quantity of component (C) employed is relatively small, including none.

Generally the quantities of the respective catalyst components are adjusted to be within a molar ratio of (B)/(C) ranging from 0.3/1 to 20/1 and the molar ratio of (A)/(B) is within the range of 0.5/1 to 15/1. More preferred ratios of (B)/(C) are from 0.5/1 to 5/1 and (A)/(B) from 0.5/1 to 8/1. Still more preferred ratios of (B)/(C) are 1/1 to 2/1 and (A)/(B) are 0.75/1 to 5/1.

The foregoing catalyst compositions may be prepared by mixing the components by known techniques, either prior to combination with the olefin containing polymer or "in situ". By the "preformed" method the catalyst components are mixed together prior to exposure of any of the catalyst components to the olefin containing polymer to be used in the process of this invention. In the "in situ" method the catalyst components are added separately to the reaction mixture containing the unsaturated polymer to be subjected to metathesis. The catalyst components may be mixed either as pure compounds or as suspensions or solutions in liquids which do not adversely affect the catalyst activity of the olefin metathesis reaction. Representative of such liquids are saturated hydrocarbons such as hexane, pentane, benzene, toluene or mixtures thereof.
The order of addition of the three catalyst components to each other may be varied. All of the following practices may suitably be employed:

1. simultaneous addition of components (A), (B) and (C);
2. sequential addition of components (A), (B) and (C) in any order;
3. contacting of any two components, optionally with recovery or purification of the reaction product, followed by addition of the binary product to the remaining component; or
4. contacting of mixtures of any two components with subsequent contact of the resulting binary mixtures or reaction products, whether purified or unpurified.

The amount of catalyst employed in the reactions of this invention may be varied over wide concentrations and has not been found to be critical. The optimum amount of catalyst composition employed depends upon a number of factors such as temperature, purity of reactants, molecular weight of the resulting product, and the desired reaction time. Desirably, the amount of catalyst employed (based on quantity of component (B)) is from 0.01 to 1 percent based on the weight of unsaturated polymer reagent employed.

In one preferred embodiment, the catalyst composition comprises at least one organoaluminum halide and at least one tungsten derivative. Preferred organoaluminum halides are dialkylaluminum chloride, di-n-propylaluminum chloride, diisobutylaluminum chloride, diethylaluminum bromide, diethylaluminum iodide, diethylaluminum fluoride, ethylaluminum sesquichloride, ethylaluminum sesquibromide, ethylaluminum dichloride, ethylaluminum dibromide, propylaluminum dichloride, isobutylaluminum dichloride, ethylaluminum diiodide, phenylaluminum dibromide, tolylaluminum dibromide, benzylaluminum dibromide, phenylaluminum diiodide, tolylaluminum diiodide, benzylaluminum diiodide, diphenylaluminum chloride, ditolyllaluminum chloride, dibenzylaluminum bromide, and mixtures of the foregoing.

Preferred tungsten derivatives include halides-, sulfates-, phosphates-, nitrates- and carboxylates- of tungsten in the +4 or +6 oxidation state, preferably tungsten hexachloride, tungsten hexabromide, tungsten hexafluoride, tungsten hexaphosphate, tungsten hexanitrate, tungsten triacetylacetonate, tungsten oxychloride, and tungsten trisulphate. A most preferred tungsten derivative is tungsten hexachloride.

The molar relationship between the two catalyst components in this embodiment are generally from 0.5/1 to 15/1, more preferably from 0.7/1 to 8/1, and a still more preferably from 0.8/1 to 5/1. The catalyst components may be reacted together as pure compounds or in solutions or suspensions in inert, aliphatic or aromatic liquids. Representative of such liquids are pentane, hexane, benzene, and toluene. The catalyst is desirably employed in an amount (based on weight of component (B)) from 0.01 to 1 percent based on weight of unsaturated polymer.
A further catalyst composition that is effective in promoting the present metathesis process comprises an aluminum trihalide and an organic or inorganic derivative of a Group 5, 6 or 7 compound, preferably a tungsten compound, especially those wherein the tungsten is in an oxidation state from 4 to 6. The preferred aluminum trihalides are aluminum trichloride or aluminum tribromide. Preferred tungsten compounds are terra-, penta- and hexa- chlorides, bromides, and iodides, tungsten hexafluoride and the tungsten oxychlorides. Optionally an organometallic compound may be present in the catalyst composition as an aid in the suppression of gel formation and in order to increase polymerization rates at lower catalyst levels. Examples of suitable optional organometallic compounds include alkyl-, aryl-, and alkaryl derivatives of lithium, sodium, magnesium, calcium, strontium and barium; alkylhalide-, arylhalide-, and alkarylhalide derivatives of magnesium, calcium, strontium or barium and alkyl-, aryl- or alkaryl- derivatives of Group 12 metals such as dialkyl- and diarylzinc, said alkyl, aryl or alkaryl group having up to 10 carbons.

Other classes of catalysts which are effective in promoting the polymerizations of this invention are those disclosed in USP 4,994,535, and generally include an organometal derivative of a Group 13-14 metal, especially organo- or organohalo- derivatives of aluminum or tin, preferably tetraalkyl tin, trialkyl aluminum and dialkylaluminum halides, containing up to 10 carbons in each alkyl group; at least one derivative of a Group 5, 6, or 7 metal, especially molybdenum or tungsten; and optionally, a chelating agent, such as a Lewis base.

Additional suitable metathesis catalysts for use in the present invention are ruthenium or osmium complexes such as those disclosed in USP’s 6,838,489, 6,818,586, 6,806,325, 6,624,265, 6,313,332, 5,977,393, 5,917,071, 5,710,298, 5,750,815, 5,728,917, 5,312,940, and 5,342,909. Examples of the foregoing metathesis catalysts include ruthenium and osmium carbene complexes possessing metal centers that are formally in the +2 oxidation state, have an electron count of 16, and are penta-coordinated. These complexes are of the general formula:

\[
\begin{align*}
\text{M}^A & \quad \text{C} \quad \text{R}^A \\
\text{L}^A & \quad \text{X}^B \\
\text{L}^B & \quad \text{X}^A \\
\end{align*}
\]

wherein:

- \text{M}^A \text{ is ruthenium or osmium;}
- \text{X}^A \text{ and } \text{X}^B \text{ are the same or different anionic ligands, preferably chloride;}
- \text{L}^A \text{ is a neutral electron donor ligand;}
- \text{L}^B \text{ is a neutral electron donor ligand or a nitrogen containing heterocyclic carbene; and}

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RA and RB are independently each occurrence hydrogen, or an alkyl, alkenyl, alkynyl, aryl, carboxylate, alkoxy, alkenyloxy, alkynyloxy, aryloxy, alkoxycarbonyl, alkylthio, alkylsulfonyl, alkylsulfanyl, or silyl group of up to 20 atoms not counting hydrogen, an alkyl, alkoxy, aryl, aralkyl, haloalkyl, haloalkoxy, haloaryl or haloalkaryl substituted derivative thereof; or a functionalized derivative of any of the foregoing wherein the functional group is hydroxyl, thiol, alcohol, sulfonic acid, phosphine, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, imide, imido, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carboimidate, carboalkoxy, carbamate, acetal, ketal, boronate, cyano, cyanohydrin, hydrazine, oxime, hydrazide, enamine, sulfone, sulfide, sulfonyl, or halogen.

In a preferred embodiment, the metal complexes are ruthenium derivatives wherein LB is a tertiary phosphine, especially triphenylphosphine, and LA is either a tertiary phosphine or a nitrogen containing heterocyclic ligand, especially an imidazolidinyl- or triazolyl- ligand of the formula:

\[
\begin{align*}
\text{Ar} & \text{N} \quad \text{N} \quad \text{Ar} \\
\text{or}
\end{align*}
\]

wherein Ar independently each occurrence is an aryl group, especially phenyl or 2,4,6-trimethylphenyl, and Rc independently each occurrence is hydrogen or an anionic ligand group or multiple Rc groups collectively may form one or more rings that are fused to the imidazolidine ring.

The inclusion of an imidazolidinyl or triazolyl ligand to the previously described ruthenium or osmium catalysts improves the properties of the complexes in olefin metathesis processes. In particular, the catalysts maintain the general functional group tolerance towards olefins of ruthenium-phosphine complexes while possessing enhanced metathesis activity comparable to tungsten- and molybdenum- salt ternary compositions. Such catalysts (referred to as Grubbs II catalysts) are particularly desired for metathesis of polar group containing polymers.

The operating conditions which are employed in the processes of this invention may vary. The reactions can be conveniently carried out in a liquid form, including in a melt or in solution. Solvents which can be used when solution conditions are employed include any inert liquid that dissolves or swells the polymers employed. Convenient solvents are aliphatic, aromatic or cycloaliphatic hydrocarbons or halohydrocarbons which do not themselves inhibit or interfere with the metathesis reaction, such as pentane, hexane, benzene, toluene, chloromethane, dichloromethane, and cyclohexane. When one or more of the olefin reactants is a liquid, the reaction can be conducted in bulk, that is, in the absence of a separately added solvent.
Generally, the quantity of functionalized ethylene containing cyclic or acyclic reagent compound employed is from 0.5 to 100 moles, preferably from 0.5 to 50 moles, per mole of polymer. Preferred functionalized ethylenically unsaturated reagents include ethyl acrylate, methyl methacrylate, ethyl fumarate, vinyl chloride, vinylidene chloride, and vinyl acetate.

Once the metathesis has proceeded to the extent desired, preferably to equilibrium, the catalyst may be inactivated, and if desired, the resulting polyolefinic product recovered. Suitable methods of inactivating the metathesis catalyst include reaction with water; an alcohol; a carboxylic acid, or a metal salt or ester derivative thereof; or carbon monoxide. The resulting catalyst residue may be removed from the polymer by filtration, solvent extraction, or other suitable technique, or may be left in the polymer. As previously disclosed, the functionalized polymer product may also be hydrogenated to adjust residual unsaturation, especially vinyl content, if desired. Suitable hydrogenation catalysts include those previously known in the art, especially noble metal catalysts such as platinum or palladium containing compounds or complexes.

Suitable metathesis conditions for use herein especially include sequential or simultaneous contacting of the reaction components. The metathesis may take place in the liquid phase, such as by use of solvents or diluents, such as carbon dioxide (see, USP 5,840,820), in melts of one or more polymers, in an excess of the functionalized ethylenically unsaturated reagent, or in a solid state process, and does not require that polymers be completely miscible or soluble at all times during the process. The unsaturated polymer reagent can be synthesized in parallel or series with the present metathesis in one or more bulk, solution, slurry, suspension, gas phase, or other polymerization reactors, either as one unit operation of the present process or separately. In one embodiment, the polymer reagent for the present metathesis is coproduced concurrently with the metathesis, and subjected to metathesis without recovery or isolation, thereby avoiding the need for remelting, dissolution and/or blending of the unsaturated polymer reagent. Highly desirably, the temperature and reaction medium are chosen so that the unsaturated polymer is molten or sufficiently solubilized to provide a fluid reaction medium.

In general temperatures from 20 to 120° C, in particular from 40 to 80° C are employed for the metathesis. The reaction is preferably conducted at an increased pressure from 0.2 to 2.0 MPa, preferably from 0.3 to 1.5 MPa, in particular from 0.4 to 1.2 MPa.

Suitable reaction apparatuses are known to the skilled worker and are described, for example, in Ullmanns Enzyklopädie der technischen Chemie, Volume 1, page 743 ff. (1951). They include, for example, stirred vessels for use in batch processes and tubular reactors for use in continuous processes.
Metathesis Products

The polydispersity (Mw/Mn) of the resulting functionalized polymer products is dependent on the polydispersity and functionality of the parent unsaturated polymer. Suitable ranges of Mw/Mn for the resulting polymer products are from 1.5 to 100, and preferably from 1.8 to 10.

The fraction of saturated compounds in the product mixture may be characterized by any suitable analytical technique, such as IR or NMR analysis. In general, the quantity of such components is relatively low, ranging from 0 to 1 percent, preferably from 0 to 0.5 percent.

The resulting polymer product comprises pendant polar group functionality as well as residual unsaturation, in as much as the metathesis results in an exchange of ethylenic groups rather than destruction of any unsaturation. Accordingly, functionality in the resulting polymer may be measured directly or indirectly, by measuring the ethylenic unsaturation content thereof. Thus, the unsaturation level of the product polymer is substantially the same as that of the ethylenically unsaturated unfunctionalized polymer reagent.

The skilled artisan will readily appreciate that additional functionality may be introduced into the polymers resulting from the metathesis by use of a functionalized olefin chain terminating agent according to known teachings in the art. Examples of such terminating agents include 2-butene-1,4-diol and derivatives thereof, especially the diacetate or dibenzyl ether derivatives.

The recovered products may be purified by filtration, extraction, distillation or other suitable technique to remove reaction by-products (primarily low molecular weight degradation or ring-forming products) as well as spent catalyst residues, or used as molding resins or blending components without further purification. Use of the resulting product mixture to produce further derivatives such as polyurethanes, polyesters, epoxies, surfactants, paints, varnishes and other coatings is conducted according to well known processes, optionally employing a catalyst. For example, suitable techniques for polyurethane production are disclosed in J. Chem. Soc. C, 1967, 2663; J. Chem. Soc. C. 1968, 1479; J. Chem. Soc. Perkin Trans. 2, 1029 (1985); Synthesis, 1989, 131, and elsewhere.

EXAMPLES

It is understood that the present invention is operable in the absence of any component which has not been specifically disclosed and may be combined with any other suitable reaction or process in a multistep system design. The following examples are provided in order to further illustrate the invention and are not to be construed as limiting. Unless stated to the contrary, all parts and percentages are expressed on a weight basis.
Example 1

To a stirring solution containing ethylene/propylene/ethylidene norbornene EPDM interpolymer (0.5 g of NORDEL™ IP 5565 containing 7.5 weight percent polymerized ethylidene norbornene) in 2 mL of chlorobenzene and 10 mL of dichloromethane warmed to 35 °C, ethyl acrylate (0.31 g; 10 mol equiv) is added, followed by 0.005 g of [(L,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium catalyst (0.02 mol equiv with respect to the ethylidene norbornene content of the EPDM polymer) in 1 mL of chlorobenzene. It is noted that the degree of substitution of ethyl acrylate is 1; the degree of substitution of the EPDM interpolymer is 3; and the total degree of substitution is 4. The resulting solution is heated and stirred at 35°C for 20 hours. A solid forms, which is precipitated from the cooled solution by the addition of 20 mL of methanol and then collected by filtration. The collected solids are dried under pressure to remove volatile components yielding a polymer product. An IR spectrum of the product shows a carbonyl stretching band located at 1730 cm⁻¹, demonstrating functionalization of the unsaturated polymer. A comparison of molecular weight and polydispersivities (measured versus polystyrene standards) of the starting NORDEL™ polymer (Mₜₐₚ = 39,504 g/mol, PDI = 2.14) and the functionalized polymer product (Mₜₐₚ = 43,732 g/mol, PDI = 2.16) indicates functionalization of the unsaturated polymer has taken place without substantial polymer degradation.

Example 2

An ethylenically unsaturated propylene/butadiene copolymer in which substantially all of the unsaturation is in the form of pendant vinyl functional groups is metathesized in the presence of dimethyl fumarate reagent and [(L,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene)(tricyclohexylphosphine) ruthenium catalyst (0.02 mol equivalent with respect to butadiene content of the copolymer). It is noted that the degree of substitution of the propylene/butadiene copolymer is 1; the degree of substitution of the dimethyl fumarate is 2; and the total degree of substitution is 3. The ethylenically unsaturated polymer is prepared by batch solution polymerization of propylene and butadiene. A 1.8 L stirred, temperature controlled autoclave reactor is charged with 550 grams of mixed alkanes diluent and 30 grams of butadiene are added. The reactor is pressurized with 180 grams propylene and 0.186 liters hydrogen and heated to 70 °C. 1.8 micromoles of dimethylsilyldiyl bis(2-methyl-4-phenylindenyl)zirconium (II) 1,4-diphenylbutadiene are mixed with bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolidole.

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cocatalyst, (1.8 µmol) and injected into the reactor. An exotherm is detected and the reaction is allowed to proceed for 20 minutes before discharging the contents of the reactor into a container. A total mass of 19.8 grams of polymer is obtained after evaporation of the volatile components. GPC analysis reveals Mw = 92,400 and Mn = 48,125 g/moles. NMR analysis reveals 1.9 mole percent polymerized butadiene content with >99 percent side-chain vinyl (ethenyl) content. Metathesis results in substantially complete conversion of the side chains to methyl-2-propenoate (-CH₂=CH₂-C(O)OCH₃) groups.
CLAIMS:

1. A process for preparing a functionalized polymer, the steps of the process comprising contacting a metathesis catalyst under metathesis conditions with a composition comprising:

   a) at least one ethylenically unsaturated polymer characterized as substantially immune to metathetic degradation;

   b) at least one functionalized ethylene containing cyclic or acyclic reagent compound, wherein the ethylenically unsaturated polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined degree of substitution of 4 or less than 4; and

   c) optionally one or more solvents or diluents, and

   recovering the resulting functionalized polymeric reaction product.

2. A process for preparing a functionalized polymer, the steps of the process comprising contacting a metathesis catalyst under metathesis conditions with a composition comprising:

   a) at least one ethylenically unsaturated polymer characterized as substantially immune to metathetic degradation, wherein the unsaturation consists essentially of pendant ethylenically unsaturated moieties;

   b) at least one functionalized ethylene containing cyclic or acyclic reagent compound, wherein the ethylenically unsaturated polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined degree of substitution of 4 or less than 4; and

   c) optionally one or more solvents or diluents, and

   recovering the resulting functionalized polymeric reaction product.

3. A process for preparing a polymer product comprising pendant functional groups, the steps of the process comprising contacting a metathesis catalyst under metathesis conditions with a composition comprising:

   a) at least one ethylenically unsaturated, non-functionalized, polymer that is substantially immune to metathetic degradation,

   b) at least one functionalized ethylene containing cyclic or acyclic reagent compound, wherein the ethylenically unsaturated polymer and the functionalized ethylene containing cyclic or acyclic reagent compound have a combined degree of substitution of 4 or less than 4; and

   c) optionally one or more solvents or diluents, and

   recovering the resulting functionalized polymeric reaction product, characterized in that the unsaturation of the unsaturated, non-functionalized, polymer reagent consists essentially or entirely of pendant ethylenic groups.
4. The process of any one of Claims 1 to 3 wherein the ethylenically unsaturated reactant polymer has a molecular weight that is not reduced under metathesis conditions by greater than 5 percent.

5. A process according to any one of Claims 1 to 4 wherein the unsaturated polymer reagent subjected to metathesis comprises from 0.001 to 10 mole percent ethylenic unsaturation.

6. A process according to Claim 5 wherein the unsaturated polymer is a copolymer of ethylene and butadiene, and optionally one or more C3-H olefins, or a partially hydrogenated derivative thereof.

7. A process according to any one of Claims 1 to 6 wherein the unsaturated polymer is a copolymer of ethylene, propylene and ethyldiene norbornene.

8. A process according to any one of Claims 1 to 7 wherein the metathesis catalyst comprises (A) at least one organometallic compound wherein the metal is selected from Groups 1, 2, 12 or 13 of the Periodic Table of Elements, (B) at least one metal derivative wherein the metal is selected from the group consisting of metals of Groups 5, 6, or 7, preferably molybdenum or tungsten, and, optionally, (C) at least one chelating- or Lewis base-material.

9. A process according to any one of claims 1-4 wherein the metathesis catalyst is a compound of the general formula:

```
    X^A M^A C - R^A
      \     /                / \\
       X^B   \               \  \  \\
             L^B \             \   \\
                             L^A
```

wherein:

M^A is ruthenium or osmium;
X^A and X^B are the same or different anionic ligand;
L^A is a neutral electron donor ligand;
L^B is a neutral electron donor ligand or a nitrogen containing heterocyclic carbene; and
R^A and R^B are independently each occurrence hydrogen, or an alkyl, alkenyl, alkynyl, aryl, carboxylate, alkoxy, alkenyloxy, alkynylxoy, aryloxy, alkoxycarbonyl, alkylthio, alkylsulfonyl, alkylsulfinyl, or silyl group of up to 20 atoms not counting hydrogen, an alkyl, alkoxy, aryl, aralkyl, haloalkyl, haloalkoxy, haloaryl or haloalkaryl substituted derivative thereof; or a functionalized derivative of any of the foregoing wherein the functional group is hydroxyl, thiol, alcohol, sulfonic acid, phosphine, thioether, ketone, aldehyde, ester, ether, amine, imine, amide, imide, imido, nitro, carboxylic acid, disulfide, carbonate, isocyanate, carbodiimide, carboalkoxy, carbamate, acetal,
ketal, boronate, cyano, cyanohydrin, hydrazine, oxime, hydrazide, enamine, sulfone, sulfide, sulfenyl, or halogen.

10. A process according to Claim 9 wherein the catalyst comprises a ruthenium derivative wherein LB is a tertiary phosphine, and LA is either a tertiary phosphine or a nitrogen containing heterocyclic ligand.

11. A process according to Claim 10 wherein LA is an imidazolidinyl- or triazolyl-ligand of the formula:

\[
\begin{align*}
R^c & \quad \text{wherein } Ar \text{ independently each occurrence is an aryl group of up to 50 atoms, and}\\
R^c & \quad \text{independently each occurrence is hydrogen or an anionic ligand group or multiple } R^c \\
\end{align*}
\]

12. A process according to Claim 11 wherein Ar independently each occurrence is phenyl or 2,4,6-trimethylphenyl.

13. A process according to any one of Claims 1 to 12 wherein the functionalized ethylene containing cyclic or acyclic reagent compound is a (C\textsubscript{i-4} alky) acrylate, (C\textsubscript{i-4} alky) methacrylate, (U(C\textsubscript{i-4} alky) fumarate, vinylchloride, vinylidene chloride, vinylacetate, vinylbutyrate, vinyl-n-butyl ether, N-vinylcarbazole, allyl ethyl ether, vinyl-C(i\textsubscript{-4} alky) alcohol, vinyl-C(i\textsubscript{-4} alky) methyl ketone, vinyl-C(i\textsubscript{-4} alky) acetate, allyl methyl sulfide, allyl(chloro)dimethylsilane, allyl isocyanate, allyldiphenylphosphine, allylurea, allylsilane, allyl C\textsubscript{i-4} alky silane, allyl di(C\textsubscript{i-4} alky) silane, allyl tri(C\textsubscript{i-4} alky) silane, or maleic anhydride.

14. A functionalized polymeric product prepared by or preparable according to any one of Claims 1 to 13 and having from 0.1 to 100 pendant functional groups per 1,000 carbons and a number average molecular weight, Mn, from 1,000 to 1,000,000.

15. The product of Claim 14 having from 0.5 to 50 pendant functional groups per 1,000 carbon atoms.

16. The product of Claim 15 having from 1 to 2.5 pendant functional groups per 1,000 carbon atoms.

17. The product of any one of Claims 14 to 16 having a number average molecular weight, Mn, from 10,000 to 500,000.

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