[0004] The composition distribution of an ethylene alpha-olefin copolymer refers to the distribution of comonomer, which form short chain branches, among the molecules that comprise the polyethylene polymer. When the amount of short chain branches varies among the polyethylene molecules, the resin is said to have a "broad" composition distribution. When the amount of comonomer per 1000 carbons is similar among the polyethylene molecules of different chain lengths, the composition distribution is said to be "narrow".

[0005] The composition distribution is known to influence the properties of copolymers, for example, stiffness, toughness, extractable content, environmental stress crack resistance, and heat sealing, among other properties. The composition distribution of a polyolefin may be readily measured by methods known in the art, for example, Temperature Raising Elution Fractionation (TREF) or Crystallization Analysis Fractionation (CRYSTAF).

[0006] It is generally known in the art that a polyolefin's composition distribution is largely dictated by the type of catalyst used and is typically invariable for a given catalyst system. Ziegler-Natta catalysts and chromium based catalysts produce resins with broad composition distributions (BCD), whereas metallocene catalysts normally produce resins with narrow composition distributions (NCD).

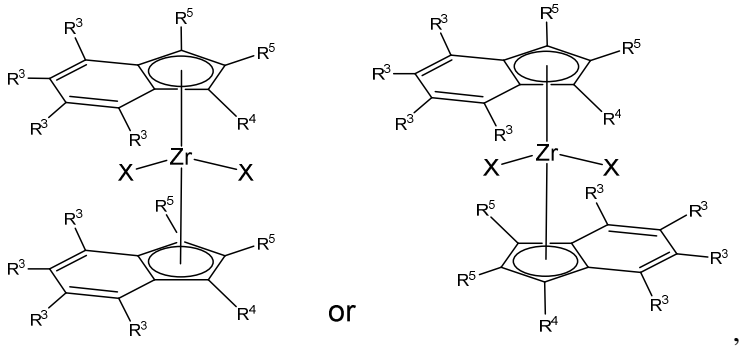
[0007] Resins having a broad orthogonal composition distribution (BOCD) in which the comonomer is incorporated predominantly in the high molecular weight chains can lead to improved physical properties, for example toughness properties and environmental stress crack resistance (ESCR). Because of the improved physical properties of resins with orthogonal composition distributions needed for commercially desirable products, there exists a need for controlled techniques for forming polyethylene copolymers having a broad orthogonal composition distribution.

SUMMARY

[0008] An example described herein provides a method of polymerizing olefins to produce a polyolefin polymer with a multimodal composition distribution, including contacting ethylene and a comonomer with a catalyst system. The catalyst system includes a first catalyst compound and a second catalyst compound that are co-supported to form a commonly supported catalyst system. The first catalyst compound includes a compound with the following formula:

$$(C_5H_aR^1{}_b)(C_5H_cR^2{}_d)HfX_2.$$

[0009] In this formula, each R^1 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; each R^2 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; a and c are ≥ 3; a+b = c+d = 5; at least one R^1 and at least one R^2 is a hydrocarbyl or substituted hydrocarbyl group; adjacent groups R^1 and R^2 groups may be coupled to form a ring; and each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group, or a divalent radical that links to an R^1 or R^2 group. The second catalyst compound includes at least one of the following formulas:



,

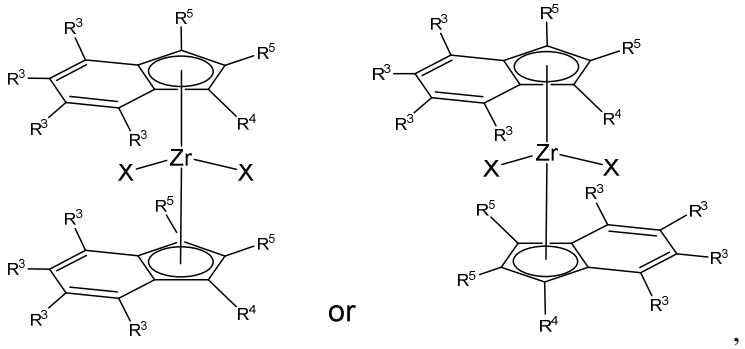
In these formulas, each R^3 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; R^4 is a hydrocarbyl group, a substituted hydrocarbyl group, or a heteoatom group; each R^5 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; wherein R^3, R^4, and R^5 may be the same or different; wherein R^3, R^4, or R^5 groups may be joined with R^3 , R^4, or R^5 groups on an opposing cyclopentadienyl structure to form one or more bridges if the number of atoms connecting the two cyclopentadienyl rings is ≥ 3; and each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group.

[0010] Another example provides a catalyst composition including a first catalyst compound and a second catalyst compound that are co-supported forming a commonly supported catalyst system. The first catalyst compound includes a compound with the following formula:

$$(C_5H_aR^1{}_b)(C_5H_cR^2{}_d)HfX_2.$$

In this formula, each R^1 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; each R^2 is independently a H, hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; a and c are ≥ 3; a+b = c+d = 5; at least one R^1 and at least one R^2 is a hydrocarbyl or substituted hydrocarbyl group; adjacent groups R^1 and R^2 groups

may be coupled to form a ring; and each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group, or a divalent radical that links to an R^1 or R^2 group. The second catalyst compound includes at least one of the following formulas:



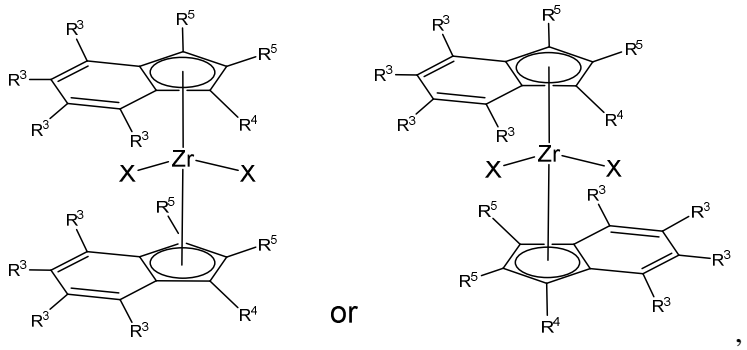
,

[0011] In these formulas, each R^3 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; R^4 is a hydrocarbyl group, a substituted hydrocarbyl group, or a heteoatom group; each R^5 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; wherein R^3, R^4, and R^5 may be the same or different; wherein R^3, R^4, or R^5 groups may be joined with R^3, R^4, or R^5 groups on an opposing cyclopentadienyl structure to form one or more bridges if the number of atoms connecting the two cyclopentadienyl rings is ≥ 3; and each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group. X may be a divalent radical that links to a R^3, R^4, or R^5 substituent.

[0011a] In one aspect, the present disclosure refers to a catalyst composition comprising a first catalyst compound and a second catalyst compound that are co-supported forming a commonly supported catalyst system, wherein the first catalyst compound comprises the following formula:

$$(C_5H_aR^1{}_b)(C_5H_cR^2{}_d)HfX_2$$

wherein each R^1 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; each R^2 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; a and c are ≥ 3; a+b = c+d = 5; at least one R^1 and at least one R^2 is a hydrocarbyl or substituted hydrocarbyl group; adjacent groups R^1 and R^2 groups may be coupled to form a ring; and each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group, or a divalent radical that links to an R^1 or R^2 group; and the second catalyst compound comprises at least one of the following formulas:



,

wherein each R^3 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; R^4 is a hydrocarbyl group, a substituted hydrocarbyl group, or a heteoatom group; each R^5 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; wherein R^3, R^4, and R^5 may be the same or different; wherein R^3, R^4, or R^5 groups may be joined with R^3 , R^4, or R^5 groups on an opposing cyclopentadienyl structure to form one or more bridges if the number of atoms connecting the two cyclopentadienyl rings is ≥ 3; and each X is independently a leaving group selected from a labile hydrocarbyl, a substituted hydrocarbyl, a heteroatom group, or a divalent radical that links to a R^3, R^4, or R^5 substituent.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 is a schematic of a gas-phase reactor system, showing the addition of at least two catalysts, at least one of which is added as a trim catalyst.

[0013] Fig. 2 is a plot of a series of polymers that were prepared to test the relative abilities of a series of metallocene catalysts to prepare a resin having about a 1 melt index (MI) and a density (D) of about 0.92.

[0014] Fig. 3 is a plot of the series of polymers of Fig. 2, showing the melt index ratio (MIR) of the series of polymers made by different metallocene (MCN) catalysts.

[0015] Fig. 4 is a flow chart of a method for making a co-supported polymerization catalyst.

DETAILED DESCRIPTION

[0016] It has been discovered that when a support is impregnated with multiple catalysts, new polymeric materials with an improved balance of stiffness, toughness and processibility can

CLAIMS

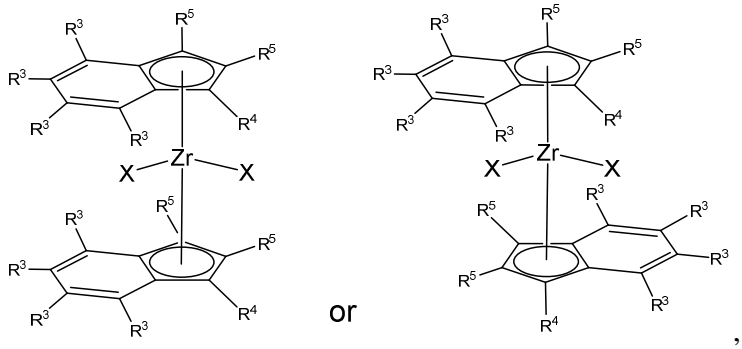
What is claimed is:

1. A catalyst composition comprising a first catalyst compound and a second catalyst compound that are co-supported forming a commonly supported catalyst system, wherein the first catalyst compound comprises the following formula:

$$(C_5H_aR^1{}_b)(C_5H_cR^2{}_d)HfX_2$$

wherein each R^1 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; each R^2 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; a and c are ≥ 3; a+b = c+d = 5; at least one R^1 and at least one R^2 is a hydrocarbyl or substituted hydrocarbyl group; adjacent groups R^1 and R^2 groups may be

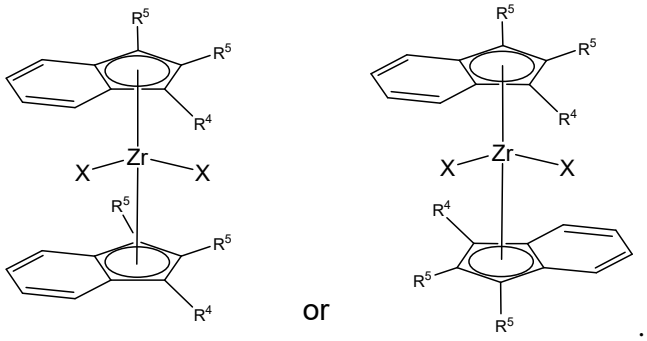
coupled to form a ring; and each X is independently a leaving group selected from a labile hydrocarbyl, substituted hydrocarbyl, or heteroatom group, or a divalent radical that links to an R^1 or R^2 group; and the second catalyst compound comprises at least one of the following formulas:



,

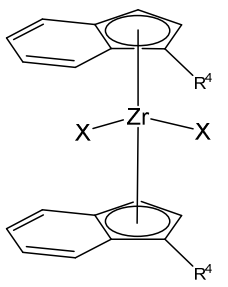
wherein each R^3 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; R^4 is a hydrocarbyl group, a substituted hydrocarbyl group, or a heteoatom group; each R^5 is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; wherein R^3, R^4, and R^5 may be the same or different; wherein R^3, R^4, or R^5 groups may be joined with R^3 , R^4, or R^5 groups on an opposing cyclopentadienyl structure to form one or more bridges if the number of atoms connecting the two cyclopentadienyl rings is ≥ 3; and each X is independently a leaving group selected from a labile hydrocarbyl, a substituted hydrocarbyl, a heteroatom group, or a divalent radical that links to a R^3, R^4, or R^5 substituent.

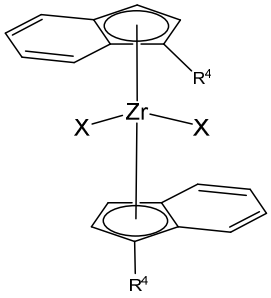
2. The catalyst composition of claim 1, wherein the second catalyst compound comprises at least one compound with the following formula:



.

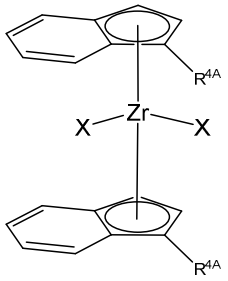
3. The catalyst composition of claim 1, wherein the second catalyst compound comprises at least one compound with the following formula:

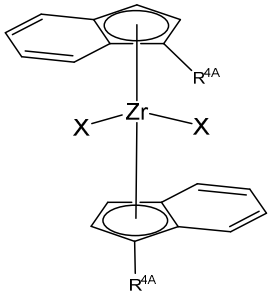


or


.

4. The catalyst composition of claim 1, wherein the second catalyst compound comprises at least one compound with the following formula:

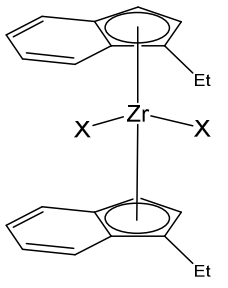


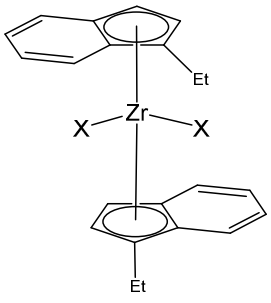
or


,

wherein each R^{4A} is independently a methyl, ethyl, propyl, pentyl, hexyl, octyl, nonyl, dodecyl, phenethyl, or other hydrocarbyl.

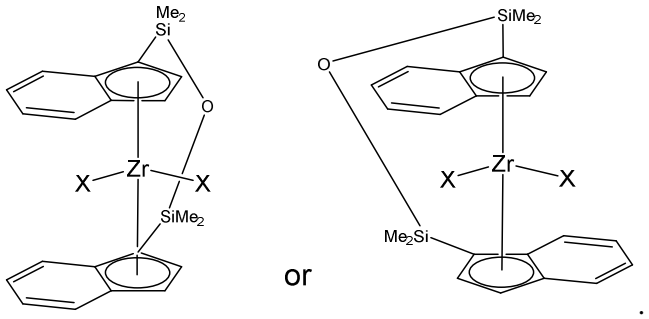
5. The catalyst composition of claim 1, wherein the second catalyst compound comprises at least one compound with the following formula:



or


.

6. The catalyst composition of claim 1, wherein the second catalyst compound comprises at least one compound with the following formula:



7. The catalyst composition of claim 1, wherein the ratio of the first catalyst compound to the second catalyst compound is between 10:1 to 1:10.

8. The catalyst composition of claim 1, wherein the ratio of the first catalyst compound to the second catalyst compound is between 3:1 to 1:3.

9. The catalyst composition of claim 1, comprising an activator comprising an acid derived from a weakly coordinating anion.

10. The catalyst composition of claim 9, wherein the activator comprises an aluminoxane compound, an organoboron, an organoaluminum compound or combinations thereof.

11. The catalyst composition of claim 9, wherein the activator comprises methyl aluminoxane or modified methylauminoxane.

12. The catalyst composition of claim 10, wherein the organoboron compound comprises BAr_aR_b, or $AlAr_aR_b$, wherein a+b = 3, a ≥2, and Ar is an aryl or heteroaryl group comprising a substituent containing fluorine and wherein R is independently H, a hydrocarbyl group, a substituted hydrocarbyl group or a heteroatom group.

13. The catalyst composition of claim 12, wherein Ar is C_6F_5, $C_{10}F_7$, or $C_6H_3(CF_3)_2$.

14. The catalyst composition of claim 9, wherein the weakly coordinating anion comprises BAr_cR_d-, or $AlAr_cR_d$-, or both, wherein c+d = 4, c ≥2, and Ar is an aryl or heteroaryl

group comprising a substituent containing fluorine, and R_d is a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group.

15. The catalyst composition of claim 14, wherein Ar is C_6F_5, $C_{10}F_7$, or $C_6H_3(CF_3)_2$.

16. The catalyst composition of claim 1, comprising a support comprising a mineral, a clay, a metal oxide, a metalloid oxide, a mixed metal oxide, a mixed metalloid oxide, a mixed metal-metalloid oxide, a polymer, or any combinations thereof.

17. The catalyst composition of claim 16, wherein the support is a polyolefin or a polyolefin derivative.

18. The catalyst composition of claim 16, wherein the support has been thermally treated and/or chemically treated with an acid, an organosilane, an organoaluminum, or a fluoriding agent, or any combinations thereof.

19. The catalyst composition of claim 16, wherein the support has been thermally treated.

20. The catalyst composition of claim 16, wherein the support comprises silica, alumina, aluminosilicate, titanated silica, or titanated alumina, or any combinations thereof.

21. The catalyst composition of claim 1, comprising a silica support and a methyl aluminoxane activator.

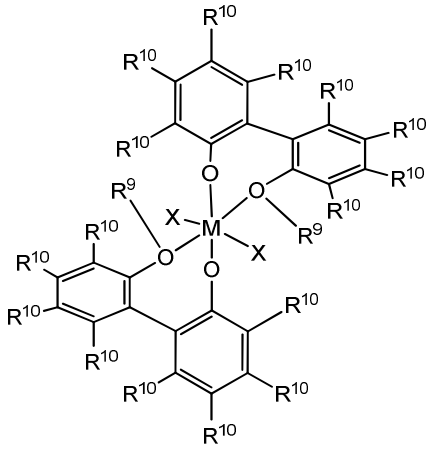
22. The catalyst composition of claim 1, comprising an organometallic agent comprising a compound of the following formula: $ER^6_nR^7_{V-n}$, wherein E is Al, B, Mg, Ca, Zn, Si, Ti, Zr, Hf; R^6 is H, or a hydrocarbyl; R^7 is a H, a C1 to C20 hydrocarbon group, or a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus; V is the valence of E, and n is 1-V.

23. The catalyst composition of claim 1, wherein $ER^6_nR^7_{V-n}$ is oligomeric or polymeric in structure.

24. The catalyst composition of claim 1, comprising a third catalyst compound comprising an inorganic or organometallic complexes of a lanthanide, an actinide, Ti, Zr, Hf, V, Cr, Fe, Ru, Co, Rh, Ni, or Pd.

25. The catalyst composition of claim 1, comprising a third catalyst compound comprising a formula of $Cp^A(A)Cp^BM'X'_n$, $Cp^A(A)QM'X'_n$ or $Cp^AM'Q_qX'^n$, wherein Cp^A and Cp^B may each be independently a cyclopentadienyl ligand, or a ligands isolobal to cyclopentadienyl, either or both Cp^A and Cp^B may contain heteroatoms, and either or both Cp^A and Cp^B may be substituted by one or more R^8 groups, wherein M' is selected from the group consisting of Groups 3 through 12 atoms and lanthanide Group atoms, wherein X' is an anionic leaving group, wherein n is 0 or an integer from 1 to 4, wherein A is selected from the group consisting of divalent alkyls, divalent lower alkyls, divalent substituted alkyls, divalent heteroalkyls, divalent alkenyls, divalent lower alkenyls, divalent substituted alkenyls, divalent heteroalkenyls, divalent alkynyls, divalent lower alkynyls, divalent substituted alkynyls, divalent heteroalkynyls, divalent alkoxys, divalent lower alkoxys, divalent aryloxys, divalent alkylthios, divalent lower alkyl thios, divalent arylthios, divalent aryls, divalent substituted aryls, divalent heteroaryls, divalent aralkyls, divalent aralkylenes, divalent alkaryls, divalent alkarylenes, divalent haloalkyls, divalent haloalkenyls, divalent haloalkynyls, divalent heteroalkyls, divalent heterocycles, divalent heteroaryls, divalent heteroatom-containing groups, divalent hydrocarbyls, divalent lower hydrocarbyls, divalent substituted hydrocarbyls, divalent heterohydrocarbyls, divalent silyls, divalent boryls, divalent phosphinos, divalent phosphines, divalent aminos, divalent amines, divalent ethers, divalent thioethers; wherein the R^8 groups are selected from the group consisting of alkyls, lower alkyls, substituted alkyls, heteroalkyls, alkenyls, lower alkenyls, substituted alkenyls, heteroalkenyls, alkynyls, lower alkynyls, substituted alkynyls, heteroalkynyls, alkoxys, lower alkoxys, aryloxys, alkylthios, lower alkyl thios, arylthios, aryls, substituted aryls, heteroaryls, aralkyls, aralkylenes, alkaryls, alkarylenes, haloalkyls, haloalkenyls, haloalkynyls, heteroalkyls, heterocycles, heteroaryls, heteroatom-containing groups, hydrocarbyls, lower hydrocarbyls, substituted hydrocarbyls, heterohydrocarbyls, silyls, boryls, phosphinos, phosphines, aminos, amines, ethers, thioethers wherein Q is selected from the group consisting of heteroatom-containing ligands, ROO-, RO–, R(O)–, –NR–, $-CR_2-$, –S–, $-NR_2$, $-CR_3$, –SR, $-SiR_3$, $-PR_2$, –H, and substituted and unsubstituted aryl groups; and wherein q is selected from 0 to 3.

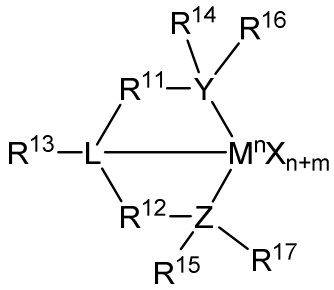
26. The catalyst composition of claim 1, further comprising a catalyst compound of the following formula:



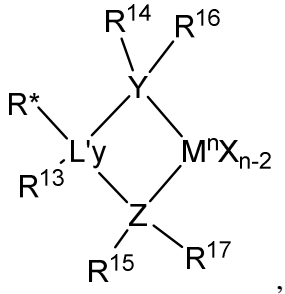
wherein M is Ti, Zr, or Hf;

wherein R^9 is H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; and wherein each R^9 may be joined together to form a ring; wherein each R^{10} is independently H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group.

27. The catalyst composition of claim 1, further comprising at least one Group 15 containing catalyst compound represented by the formula:



or



,

wherein:

M is a Group 4, 5, or 6 metal;

y is 0 or 1, wherein when y is 0, group L′ is absent;

n is the oxidation state of M;

m is the formal charge of the ligand represented by YZL and YZL′;

L, L′, Y and Z are each a Group 15 element;

each R^{11} and R^{12} is independently a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group;

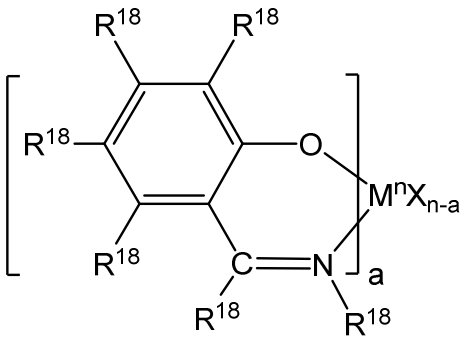
R^{13} is absent or is H, a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group;

each R^{14} and R^{15} is independently a hydrocarbyl group, an aryl group, substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, a cyclic arylalkyl group, a substituted cyclic arylalkyl group or multiple ring system;

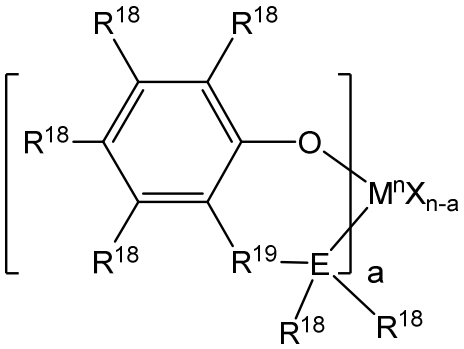
each R^{16} and R^{17} is independently a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; and

R^{*} is absent, or is hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group.

28. The catalyst composition of claim 1, further comprising at least one catalyst compound having the following formula:



or



,

wherein each R^{18} is independently a hydrocarbyl group, a substituted hydrocarbyl group, or a heteroatom group; and each R^{19} is independently a hydrocarbyl group, a substituted hydrocarbyl group, a heteroatom group, an aryl, a substituted aryl, a heteroaryl, an aralkyl, an aralkylene, an alkaryl, an alkarylene, a halide, a haloalkyl, a haloalkenyl, a haloalkynyl, a heteroalkyl, a heterocycle, a heteroaryl, a heteroatom-containing group, a silyl, a boryl, a phosphino, a phosphine, an amino, or an amine.