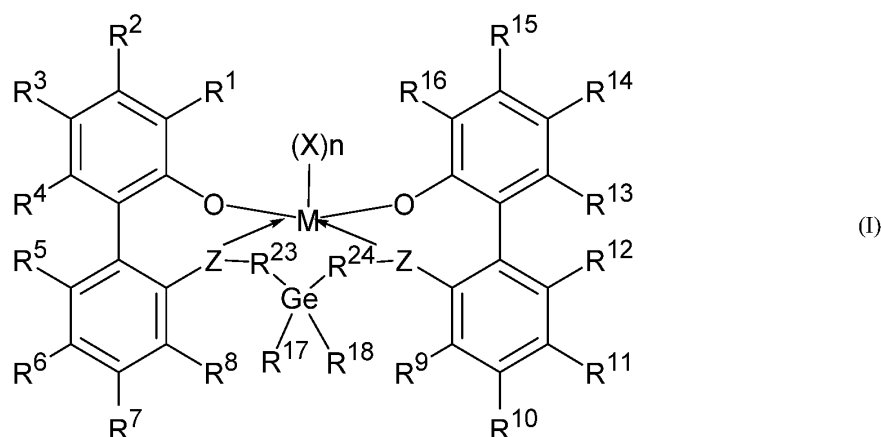


CLAIMS

1. A procatalyst comprising a metal-ligand complex disposed on one or more support materials, wherein the metal-ligand complex has a structure according to formula (I):



wherein:

M is titanium, zirconium, or hafnium;

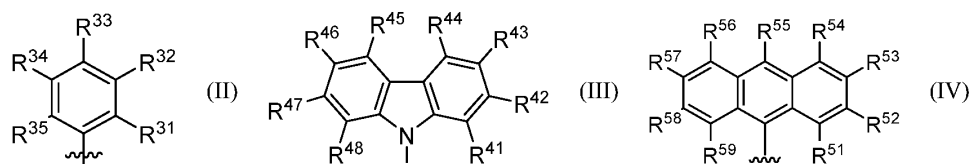
n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from unsaturated (C₂-C₅₀)hydrocarbon, unsaturated (C₂-C₅₀)heterohydrocarbon, (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)heterohydrocarbyl, (C₆-C₅₀)aryl, (C₄-C₅₀)heteroaryl, halogen, -N(R^N)₂, and -N(R^N)COR^C;

the metal-ligand complex is overall charge-neutral;

each Z is independently chosen from -O-, -S-, (C₆-C₅₀)aryl, (C₄-C₅₀)heteroaryl, N(C₁-C₅₀)hydrocarbyl, and P(C₁-C₅₀)hydrocarbyl;

R¹ and R¹⁶ are independently chosen from (C₆-C₅₀)aryl, (C₄-C₅₀)heteroaryl, (C₁-C₅₀)alkyl, (C₃-C₄₀)heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



wherein R³¹⁻³⁵, R⁴¹⁻⁴⁸, and R⁵¹⁻⁵⁹ are independently chosen from -H, (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-,

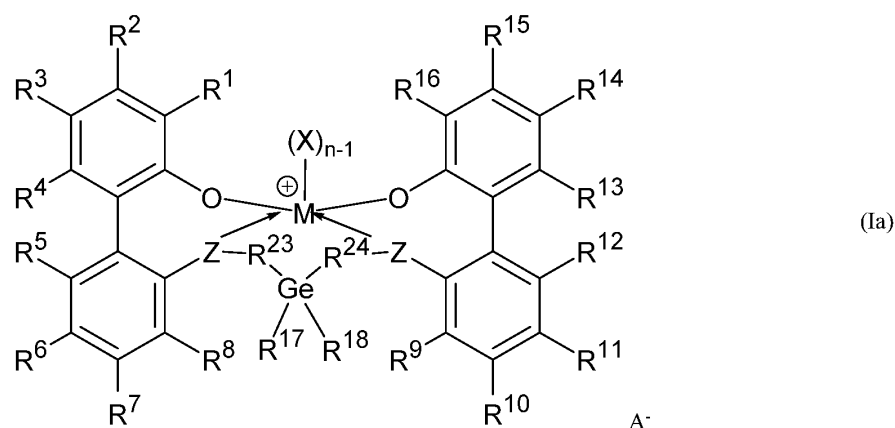
$(R^C)_2C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R^N)-$, $(R^C)_2NC(O)-$, or halogen;

R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently chosen from $-H$, (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^C S(O)-$, $R^C S(O)_2-$, $(R^C)_2C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R)-$, $(R^C)_2NC(O)-$, and halogen; R^{23} and R^{24} are independently chosen from $-(CR^C_2)_m-$, wherein subscript m is from 1 to 10;

R^{17} and R^{18} are independently chosen from linear or branched (C_1-C_{20}) alkyl; and each R^C , R^P , and R^N are independently chosen from $-H$, (C_1-C_{50}) hydrocarbyl, and (C_1-C_{50}) heterohydrocarbyl.

2. The procatalyst of claim 1, wherein R^1 and R^{16} are the same.
3. The procatalyst of either claim 1 or 2, wherein at least one of R^1 and R^{16} is a radical having formula (II) and at least one of R^{32} and R^{34} is *tert*-butyl.
4. The procatalyst of either claim 1 or 2, wherein at least one of R^1 and R^{16} is a radical having formula (III).
5. The procatalyst of claim 4, wherein at least one of R^{42} , R^{43} , R^{46} , and R^{47} is *tert*-butyl.
6. The procatalyst of claim 5, wherein R^{41-48} are $-H$.
7. The procatalyst of any of claims 1-7, wherein the one or more support materials comprise fumed silica.
8. A catalyst system comprising the procatalyst of any of claims 1-6 and one or more activators.
9. The catalyst system of claim 7, wherein the activator comprises methylalumoxane (MAO).

10. A method for producing a catalyst system, the method comprising:
 contacting one or more support materials, one or more activators, and a metal-ligand complex in an inert hydrocarbon solvent to produce the catalyst system, wherein the metal-ligand complex has a structure according to formula (Ia):



wherein:

A^- is an anion;

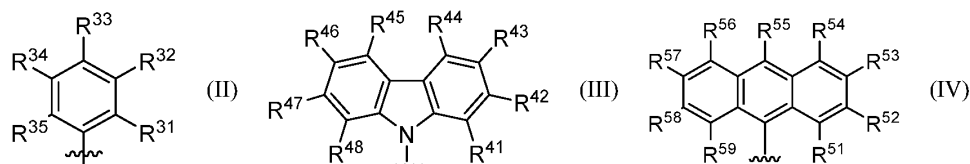
M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from unsaturated (C_2-C_{50}) hydrocarbon, unsaturated (C_2-C_{50}) heterohydrocarbon, (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, (C_6-C_{50}) aryl, (C_4-C_{50}) heteroaryl, halogen, $-N(R^N)_2$, and $-N(R^N)COR^C$;

each Z is independently chosen from $-O-$, $-S-$, (C_6-C_{50}) aryl, (C_4-C_{50}) heteroaryl, $N(C_1-C_{40})$ hydrocarbyl, and $P(C_1-C_{40})$ hydrocarbyl;

R^1 and R^{16} are independently chosen from (C_6-C_{50}) aryl, (C_4-C_{50}) heteroaryl, (C_1-C_{40}) alkyl, (C_3-C_{40}) heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



wherein R^{31-35} , R^{41-48} , and R^{51-59} are independently chosen from $-H$, (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$,

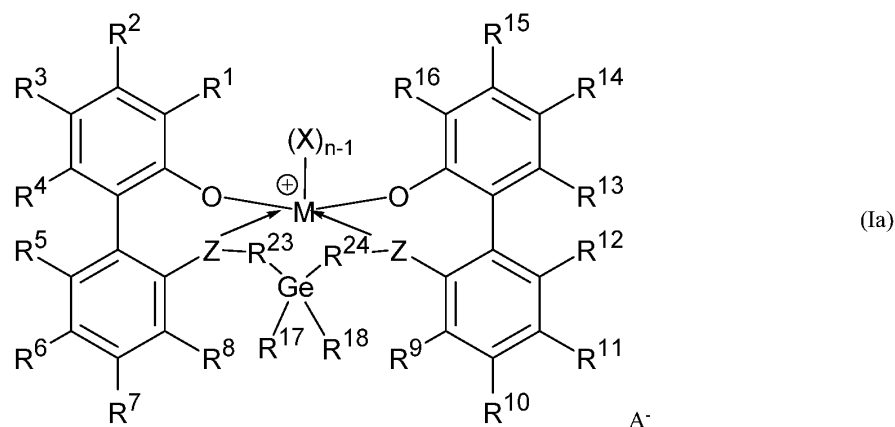
$(R^C)_2C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R^N)-$, $(R^C)_2NC(O)-$, or halogen;

R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently chosen from $-H$, (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^C S(O)-$, $R^C S(O)_2-$, $(R^C)_2C=N-$, $R^C C(O)O-$, $R^C OC(O)-$, $R^C C(O)N(R)-$, $(R^C)_2NC(O)-$, and halogen; R^{23} and R^{24} are independently chosen from $-(CR^C_2)_m-$, wherein subscript m is from 1 to 10;

R^{17} and R^{18} are independently chosen from linear or branched (C_1-C_{20}) alkyl; and each R^C , R^P , and R^N are independently chosen from $-H$, (C_1-C_{50}) hydrocarbyl, and (C_1-C_{50}) heterohydrocarbyl.

11. The method of claim 10, wherein the activator comprises methylalumoxane (MAO).
12. The method of either claim 10 or 11, wherein the method further comprises:
mixing the one or more support materials, the one or more activators, and the metal-ligand complex in the inert hydrocarbon solvent to produce a catalyst system precursor;
and
drying the catalyst system precursor to produce the catalyst system.
13. The method of claim 12, wherein the catalyst system precursor is spray dried to produce the catalyst system; and the catalyst system comprises spray-dried particles.
14. The method of either claim 10 or 11, wherein the method further comprises:
disposing the one or more activators on the one or more support materials to produce a supported activator; and
contacting the supported activator with a solution of the metal-ligand complex in the inert hydrocarbon solvent.
15. The method of claim 14, wherein disposing the one or more activators on the one or more support materials comprises spray drying to produce a spray-dried supported activator.

16. A process for producing polyethylene, the process comprising contacting ethylene and, optionally, one or more (C₃–C₁₂) α -olefin comonomers with a catalyst system in a gas-phase polymerization reactor, wherein the catalyst system comprises a metal-ligand complex disposed on one or more support materials; and the metal-ligand complex has a structure according to formula (Ia):



wherein:

A⁻ is an anion;

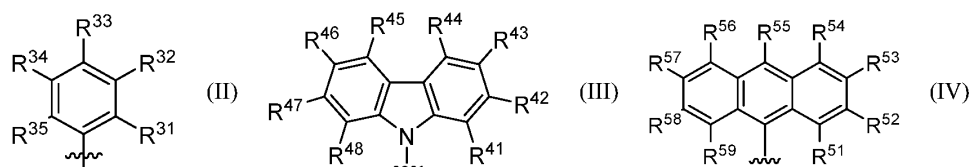
M is titanium, zirconium, or hafnium;

subscript n of (X)_n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from unsaturated (C₂–C₅₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, halogen, –N(R^N)₂, and –N(R^N)COR^C;

each Z is independently chosen from –O–, –S–, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, N(C₁–C₄₀)hydrocarbyl, and P(C₁–C₄₀)hydrocarbyl;

R¹ and R¹⁶ are independently chosen from (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, (C₁–C₄₀)alkyl, (C₃–C₄₀)heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



wherein R^{31–35}, R^{41–48}, and R^{51–59} are independently chosen from –H, (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃,

$-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R}^{\text{N}})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, or halogen;

R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently chosen from $-\text{H}$, $(\text{C}_1-\text{C}_{50})\text{hydrocarbyl}$, $(\text{C}_1-\text{C}_{50})\text{heterohydrocarbyl}$, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, and halogen; R^{23} and R^{24} are independently chosen from $-(\text{CR}^{\text{C}}_2)_m-$, wherein subscript m is from 1 to 10;

R^{17} and R^{18} are independently chosen from linear or branched $(\text{C}_1-\text{C}_{20})\text{alkyl}$; and each R^{C} , R^{P} , and R^{N} are independently chosen from $-\text{H}$, $(\text{C}_1-\text{C}_{50})\text{hydrocarbyl}$, and $(\text{C}_1-\text{C}_{50})\text{heterohydrocarbyl}$.

17. The process of claim 16, wherein the catalyst system further comprises an activator.
18. The process of claim 17, wherein the activator comprises methylalumoxane (MAO).
19. The process of any of claims 16-18, wherein the catalyst system is fed to the gas-phase polymerization reactor in neat form, as a solution, or as a slurry.
20. The process of any of claims 16-19, wherein the catalyst system comprises spray-dried particles.