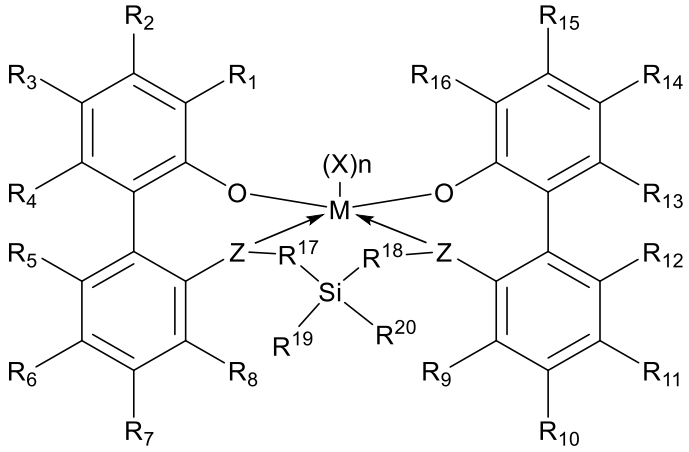
productivity when compared to similar catalyst systems including BPP metal-ligand complexes without silicon-containing bridges.

[0006] The present disclosure includes a procatalyst. The procatalyst includes a metal-ligand complex disposed on one or more support materials. The metal-ligand complex has a structure according to formula (I):

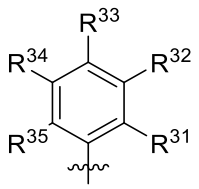


(I)

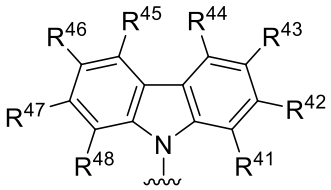
[0007] In formula (I), M is titanium, zirconium, or hafnium; subscript n of $(X)_n$ is 1, 2, or 3; each X is a monodentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2\text{-}C_{50})$heterohydrocarbon, $(C_1\text{-}C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, halogen, $–N(R^N)_2$, and $–N(R^N)COR^C$; and the metal-ligand complex of formula (I) is overall charge-neutral.

[0008] In formula (I), 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.

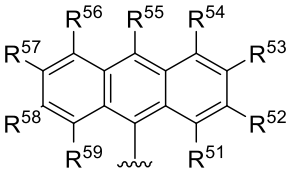
[0009] In formula (I), R^1 and R^{16} are independently chosen from $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, $(C_1–C_{40})$alkyl, $(C_3–C_{40})$heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

[0010] In formulas (II), (III), and (IV), $R^{31–35}$, $R^{41–48}$, 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, $−CF_3$, $R^CS(O)−$, $R^CS(O)_2−$, $(R^C)_2C=N−$, $R^CC(O)O−$, $R^COC(O)−$, $R^CC(O)N(R^N)−$, $(R^C)_2NC(O)−$, or halogen.

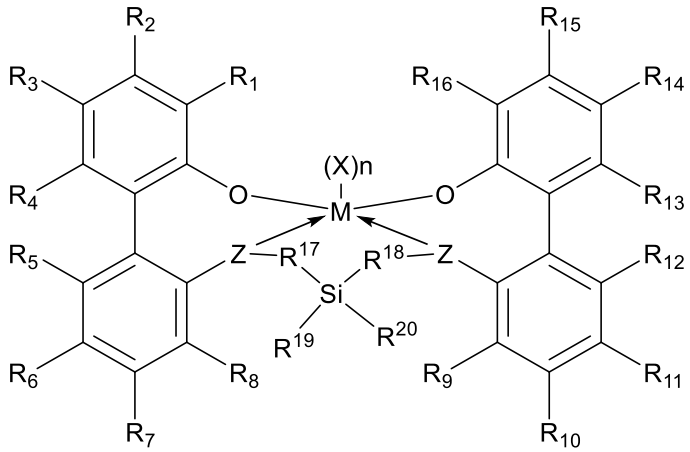
[0011] In formula (I), R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, and R^{15} are independently chosen from −H, (C_1−C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, −CN, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C{=}N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, and halogen.

[0012] In formula (I), R^{17} and R^{18} are independently chosen from $-(CR^C_2)_m-$, wherein subscript m is from 1 to 10.

[0013] In formula (I), R^{19} and R^{20} are independently chosen from linear or branched (C_1−C_{20})alkyl.

[0014] In formulas (I), (II), (III), and (IV), each R^C, R^P, and R^N are independently chosen from −H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})heterohydrocarbyl.

[0014a] In an aspect, the present disclosure includes 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):



(I)

wherein:

M is titanium, zirconium, or hafnium;

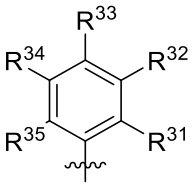
n is 1, 2, or 3;

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 $-N(R^N)COR^C$;

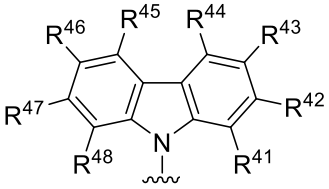
the metal-ligand complex is overall charge-neutral;

each Z is–O−;

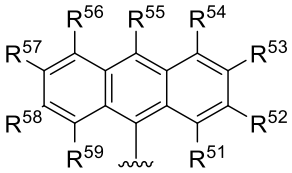
R^1 and R^{16} are independently chosen from (C_1−C_{50})alkyl, (C_3−C_{40})heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(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, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R^N)–$, $(R^C)_2NC(O)–$, 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, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, $(R^C)_2NC(O)–$, and halogen;

R^{17} and R^{18} are independently chosen from $–(CR^C_2)_m–$, wherein subscript m is from 1 to 10;

R^{19} and R^{20} are independently chosen from linear or branched $(C_1–C_{20})$alkyl; and

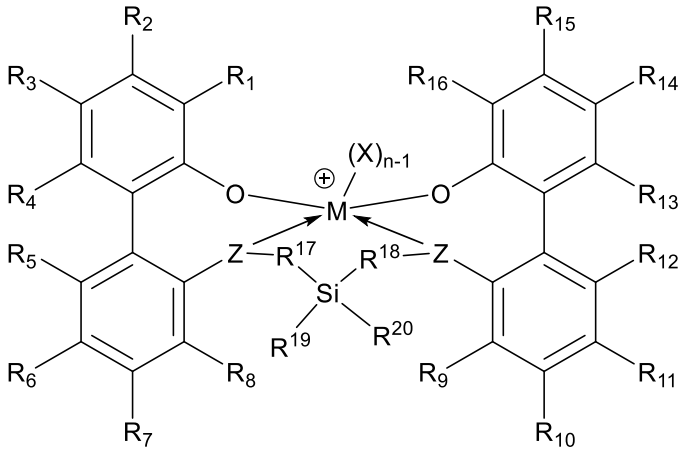
each R^C, R^P, and R^N are independently chosen from −H, $(C_1–C_{50})$hydrocarbyl, and $(C_1–C_{50})$heterohydrocarbyl.

[0014b] In another aspect, the present disclosure includes a catalyst system comprising the procatalyst as defined herein and one or more activators.

[0015] The present disclosure also includes methods for producing a catalyst system. The method includes 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.

[0015a] In another aspect, the present disclosure includes 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):



(Ia)

wherein:

A^- is an anion;

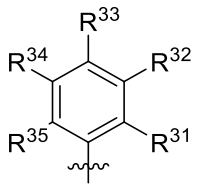
M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

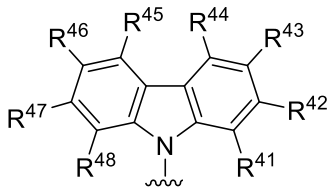
each X is a monodentate ligand independently chosen from unsaturated (C_2–C_{50})hydrocarbon, unsaturated (C_2-C_{50})heterohydrocarbon, (C_1-C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, halogen, –$N(R^N)_2$, and –$N(R^N)COR^C$;

each Z is–O–;

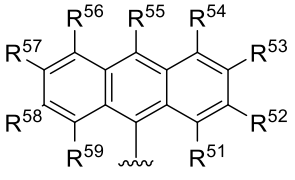
R^1 and R^{16} are independently chosen from (C_1–C_{40})alkyl, (C_3–C_{40})heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(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, $R^CS(O)$–, $R^CS(O)_2$–, $(R^C)_2C{=}N$–, $R^CC(O)O$–, $R^COC(O)$–, $R^CC(O)N(R^N)$–, $(R^C)_2NC(O)$–, 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, $R^CS(O)$–, $R^CS(O)_2$–, $(R^C)_2C{=}N$–, $R^CC(O)O$–, $R^COC(O)$–, $R^CC(O)N(R)$–, $(R^C)_2NC(O)$–, and halogen;

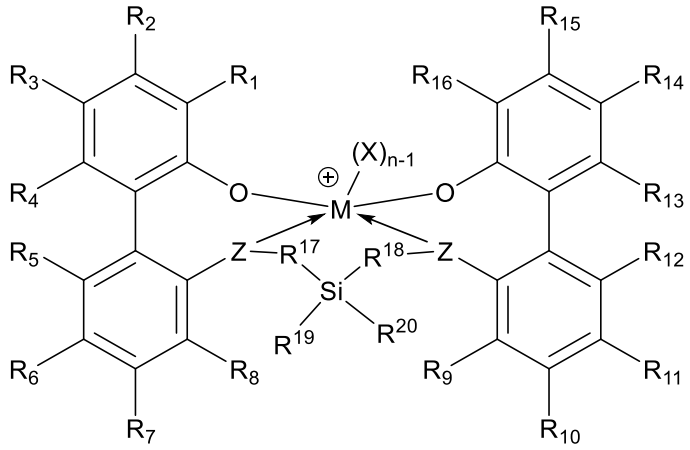
R^{17} and R^{18} are independently chosen from $–(CR^C_2)_m–$, wherein subscript m is from 1 to 10;

R^{19} and R^{20} 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.

[0016] The present disclosure also includes a process for producing polyethylene. The process includes contacting ethylene and, optionally, one or more $(C_3–C_{12})$α-olefin comonomers with a catalyst system in a gas-phase polymerization reactor. The catalyst system comprises a metal-ligand complex disposed on one or more support materials.

[0016a] In another aspect, the present disclosure includes a process for producing polyethylene, the process comprising contacting ethylene and, optionally, one or more $(C_3–C_{12})$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):



(Ia)

wherein:

A^- is an anion;

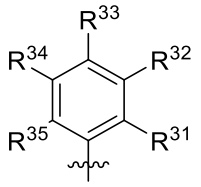
M is titanium, zirconium, or hafnium;

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

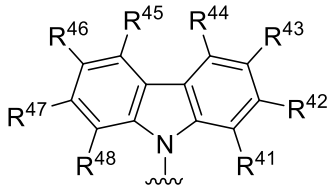
each X is a monodentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2$-$C_{50})$heterohydrocarbon, $(C_1$-$C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, halogen, $–N(R^N)_2$, and $–N(R^N)COR^C$;

each Z is–O−;

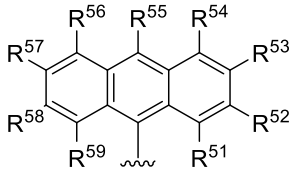
R^1 and R^{16} are independently chosen from $(C_1–C_{40})$alkyl, $(C_3–C_{40})$heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(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, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R^N)–$, $(R^C)_2NC(O)–$, 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, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, $(R^C)_2NC(O)–$, and halogen;

R^{17} and R^{18} are independently chosen from $–(CR^C_2)_m–$, wherein subscript m is from 1 to 10;

R^{19} and R^{20} 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.

[0017] These and additional features provided by the present disclosure will be more fully understood in view of the following detailed description.

DETAILED DESCRIPTION

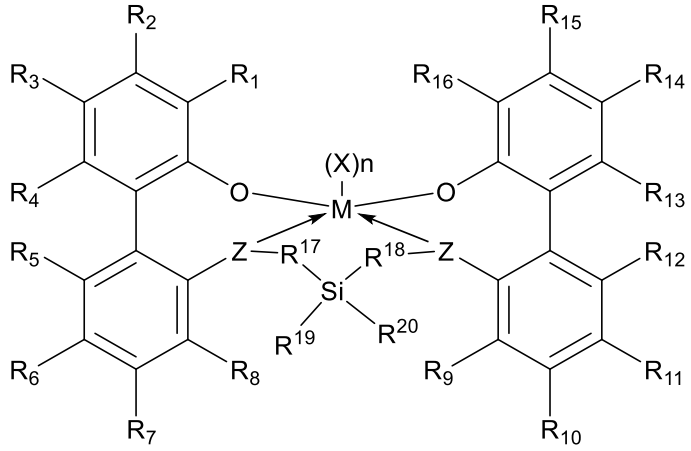
[0018] Specific embodiments of procatalysts, catalyst systems, methods of producing catalyst systems, and processes for producing polyethylene will now be described. However, it should be understood that the systems, methods, and processes of the present disclosure may be embodied in different forms, and should not be construed as limited to the specific embodiments set forth in the present disclosure. Rather, embodiments are provided so that the present disclosure will be thorough and complete, and will fully convey the scope of the disclosed subject matter to those skilled in the art.

[0019] Common abbreviations used in the present disclosure are listed below:

[0020] **Me**: methyl; **Et**: ethyl; **Ph**: phenyl; **Bn**: benzyl; ***i*-Pr**: *iso*-propyl; ***t*-Bu**: *tert*-butyl; ***t*-Oct**: *tert*-octyl (2,4,4-trimethylpentan-2-yl); **Tf**: trifluoromethane sulfonate; **THF**: tetrahydrofuran; **Et_2O**: diethyl ether; **CH_2Cl_2**: dichloromethane; **CV**: column volume (used in column chromatography); **EtOAc**: ethyl acetate; **C_6D_6**: deuterated benzene or benzene-*d*6; **$CDCl_3$**: deuterated chloroform; **Na_2SO_4**: sodium sulfate; **$MgSO_4$**: magnesium sulfate; **HCl**:

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):



(I)

wherein:

M is titanium, zirconium, or hafnium;

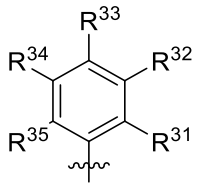
n is 1, 2, or 3;

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 –$N(R^N)COR^C$;

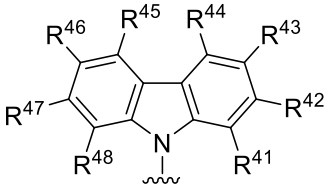
the metal-ligand complex is overall charge-neutral;

each Z is–O−;

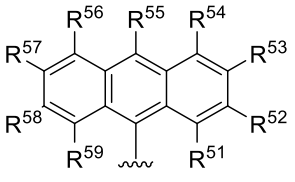
R^1 and R^{16} are independently chosen from (C_1−C_{50})alkyl, (C_3−C_{40})heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(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−, $R^CC(O)O$−, $R^COC(O)$−, $R^CC(O)N(R^N)$−, $(R^C)_2NC(O)$−, 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^CS(O)−, R^CS(O)$_2$−, (R^C)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R)−, (R^C)$_2$NC(O)−, and halogen;

R^{17} and R^{18} are independently chosen from –(CR^C_2)$_m$ – , wherein subscript m is from 1 to 10;

R^{19} and R^{20} 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 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.

3. The procatalyst of claim 1, wherein at least one of R^1 and R^{16} is a radical having formula (III).

4. The procatalyst of claim 3, wherein at least one of R^{42}, R^{43}, R^{46}, and R^{47} is *tert*-butyl.

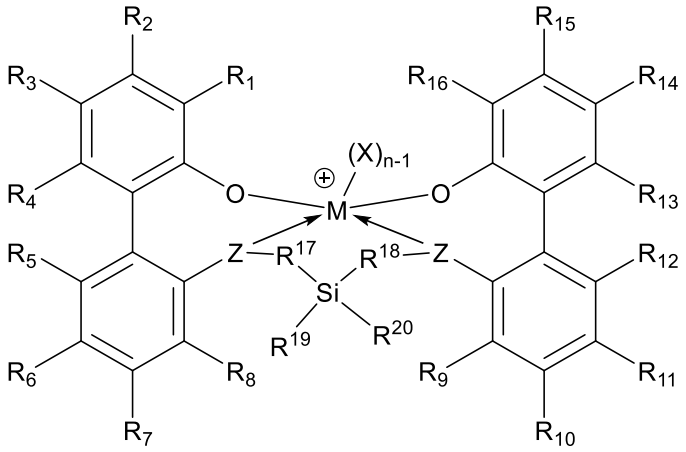
5. The procatalyst of any of claims 1-4, wherein the one or more support materials comprise fumed silica.

6. A catalyst system comprising the procatalyst of any of claims 1-4 and one or more activators.

7. The catalyst system of claim 5, wherein the activator comprises methylalumoxane (MAO).

8. 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):



(Ia)

wherein:

A^- is an anion;

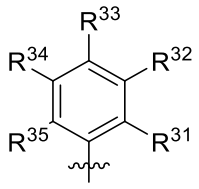
M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

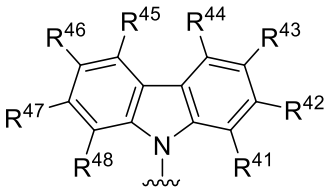
each X is a monodentate ligand independently chosen from unsaturated (C_2–C_{50})hydrocarbon, unsaturated (C_2-C_{50})heterohydrocarbon, (C_1-C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, halogen, –$N(R^N)_2$, and –$N(R^N)COR^C$;

each Z is–O–;

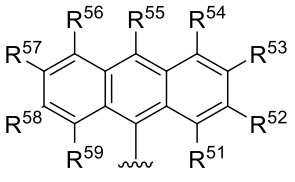
R^1 and R^{16} are independently chosen from (C_1–C_{40})alkyl, (C_3–C_{40})heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(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–, $R^CC(O)O$–, $R^COC(O)$–, $R^CC(O)N(R^N)$–, $(R^C)_2NC(O)$–, 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, $R^CS(O)$–, $R^CS(O)_2$–, $(R^C)_2C$=N–, $R^CC(O)O$–, $R^COC(O)$–, $R^CC(O)N(R)$–, $(R^C)_2NC(O)$–, and halogen;

R^{17} and R^{18} are independently chosen from $-(CR^{C}{}_{2})_{m}-$, wherein subscript m is from 1 to 10;

R^{19} and R^{20} 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.

9. The method of claim 8, 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.

10. The method of claim 9, wherein the catalyst system precursor is spray dried to produce the catalyst system; and the catalyst system comprises spray-dried particles.

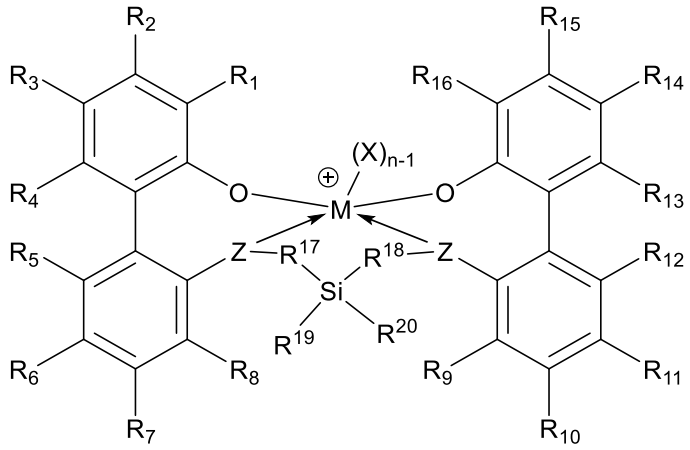
11. The method of claim 8, wherein the method further comprises:

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.

12. The method of claim 11, wherein disposing the one or more activators on the one or more support materials comprises spray drying to produce a spray-dried supported activator.

13. A process for producing polyethylene, the process comprising contacting ethylene and, optionally, one or more (C_3-C_{12})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):



(Ia)

wherein:

A^- is an anion;

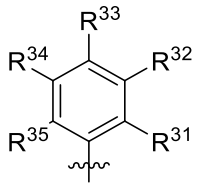
M is titanium, zirconium, or hafnium;

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

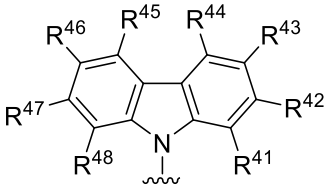
each X is a monodentate ligand independently chosen from unsaturated (C_2−C_{50})hydrocarbon, unsaturated (C_2-C_{50})heterohydrocarbon, (C_1-C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, (C_6−C_{50})aryl, (C_4−C_{50})heteroaryl, halogen, –$N(R^N)_2$, and –$N(R^N)COR^C$;

each Z is–O−;

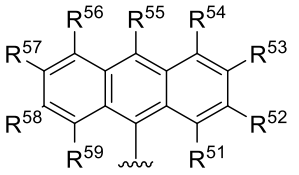
R^1 and R^{16} are independently chosen from (C_1−C_{40})alkyl, (C_3−C_{40})heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(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−, $R^CC(O)O$−, $R^COC(O)$−, $R^CC(O)N(R^N)$−, $(R^C)_2NC(O)$−, 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, $R^CS(O)$−, $R^CS(O)_2$−, $(R^C)_2C$=N−, $R^CC(O)O$−, $R^COC(O)$−, $R^CC(O)N(R)$−, $(R^C)_2NC(O)$−, and halogen;

R^{17} and R^{18} are independently chosen from $-(CR^{C}{}_{2})_{m}-$, wherein subscript m is from 1 to 10;

R^{19} and R^{20} 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.

14. The process of claim 13, wherein the catalyst system further comprises an activator.

15. The process of either claim 13 or claim 14, wherein the catalyst system is fed to the gas-phase polymerization reactor in neat form, as a solution, or as a slurry.