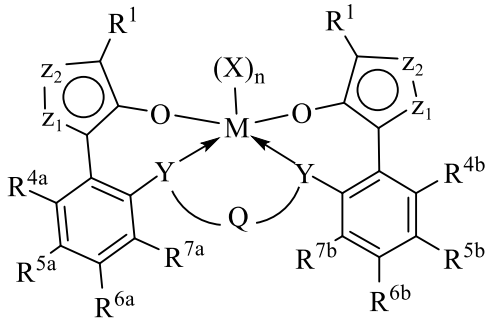
CLAIMS

1. A catalyst system comprising:

a metal–ligand complex according to formula (I):



(I)

where:

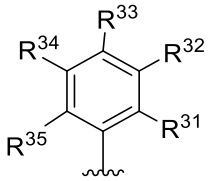
M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4;

each X is a monodentate or bidentate ligand independently chosen from unsaturated (C_2–C_{20})hydrocarbon, unsaturated (C_2–C_{50})heterohydrocarbon, (C_1–C_{50})hydrocarbyl, (C_6–C_{50})aryl, (C_6–C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4–C_{12})diene, halogen, −OR^C, –$N(R^N)_2$, and –$NCOR^C$;

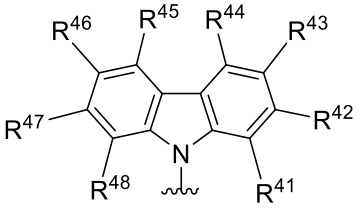
n is 1 or 2;

Y is oxygen, sulfur, or –$N(R^N)$−;

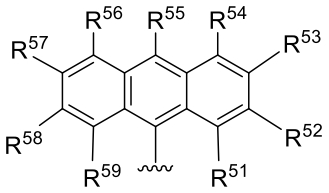
each R^1 is independently selected from the group consisting of –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −$Si(R^C)_3$, −$Ge(R^C)_3$, −$P(R^P)_2$, −$N(R^N)_2$, −OR^C, −SR^C, −NO_2, −CN, −CF_3, $R^CS(O)$−, $R^CS(O)_2$−, $(R^C)_2C$=N−, $R^CC(O)O$−, $R^COC(O)$−, $R^CC(O)N(R)$−, $(R^C)_2NC(O)$−, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −Si(R^C)$_3$, −Ge(R^C)$_3$, −P(R^P)$_2$, −N(R^N)$_2$, –N=CHR^C, −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^N)−, (R^C)$_2$NC(O)−, halogen, or –H, provided at least one R^1 in formula (I) is a radical having formula (II), a radical having formula (III), or a radical having formula (IV);

Q is (C_1–C_{12})alkylene, (C_1–C_{12})heteroalkylene, (–CH_2Si(R_Q)$_2$$CH_2$–), (–$CH_2CH_2$Si($R_Q$)$_2$$CH_2CH_2$–), (–$CH_2$Ge($R_Q$)$_2$$CH_2$–), or (–$CH_2CH_2$Ge($R_Q$)$_2$$CH_2CH_2$–), where R_Q is (C_1–C_{20})hydrocarbyl;

each z_1 and z_2 is independently selected from the group consisting of sulfur, oxygen, −N(R^C)−, and −C(R^C)−, provided at least one of z_1 and z_2 in each individual ring containing groups z_1 and z_2 is sulfur;

R^{4a}, R^{5a}, R^{6a}, R^{7a}, R^{4b}, R^{5b}, R^{6b}, and R^{7b} are independently chosen from (C_1−C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, (C_6−C_{50})aryl, (C_4−C_{50})heteroaryl, –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)–, –P(O)(R^P)$_2$, 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)–, halogen, and –H, in which optionally R^{4a} and R^{5a}, or R^{5a} and R^{6a}, or R^{6a} and R^{7a}, or R^{4b} and R^{5b}, or R^{5b} and R^{6b}, or R^{6b} and R^{7b} are covalently connected to form an aromatic ring or a non-aromatic ring;

each R^C, R^N, and R^P in formula (I) is independently selected from the group consisting of (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl, and –H; and

provided that when Q is –$CH_2CH_2CH_2CH_2$−:

(1) when each R^1 is 3,6-di-*tert*-butylcarbazol-9-yl and z_2 is sulfur and each X is benzyl, R^{5a} and R^{5b} are not –OMe, fluorine, or *tert*-octyl; or

(2) at least one of R^{4a}, R^{5a}, R^{6a}, and R^{7a} is halogen, and at least one of R^{4b}, R^{5b}, R^{6b}, and R^{7b} is halogen; or

(3) at least one of R^{4a}, R^{5a}, R^{6a}, R^{7a}, R^{4b}, R^{5b}, R^{6b}, and R^{7b} is selected from the group consisting of $(C_1–C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, $–Si(R^C)_3$, $–Ge(R^C)_3$, $–P(R^P)_2$, $–N(R^N)_2$, $–OR^C$, $–SR^C$, $–NO_2$, –CN, $–CF_3$, $R^CS(O)–$, $–P(O)(R^P)_2$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, and $(R^C)_2NC(O)–$.

2. The catalyst system of claim 1, wherein each z_1 is sulfur.

3. The catalyst system of claim 1, wherein each z_2 is sulfur.

4. The catalyst system of claim 1, wherein each Y is oxygen.

5. The catalyst system of claim 1, further comprising one or more cocatalysts.

6. The catalyst system of claim 1, wherein each R^1 is a radical having formula (III), in which at least one of $R^{41–48}$ is chosen from $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $–Si(R^C)_3$, $–OR^C$, $–SR^C$, $–NO_2$, –CN, $–CF_3$, or halogen.

7. The catalyst system of claim 1, wherein each R^1 is a radical having formula (III), in which:

(1) R^{42} and R^{47} are independently chosen from $(C_1–C_{20})$alkyl, $–Si(R^C)_3$, $–CF_3$, or halogen and R^{43} and R^{46} are –H; or

(2) R^{43} and R^{46} are independently chosen from $(C_1–C_{20})$alkyl, $–Si(R^C)_3$, $–CF_3$, or halogen and R^{42} and R^{47} are –H.

8. The catalyst system of claim 1, wherein each R^1 is a radical having formula (IV), in which at least one of $R^{51–59}$ is chosen from $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $–Si(R^C)_3$, $–OR^C$, $–SR^C$, $–NO_2$, –CN, $–CF_3$, or halogen

9. The catalyst system of claim 1, wherein each R^1 is a radical having formula (IV), in which $R^{51–59}$ are –H.

10. The catalyst system of claim 1, wherein when Q is $(C_3–C_4)$alkylene, at least two of R^{4a}, R^{5a}, R^{6a}, R^{7a}, R^{4b}, R^{5b}, R^{6b}, and R^{7b} are selected from the group consisting of $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, $–Si(R^C)_3$, $–Ge(R^C)_3$, $–P(R^P)_2$, $–N(R^N)_2$, $–OR^C$, $–SR^C$, $–NO_2$, –CN, $–CF_3$, $R^CS(O)–$, $–P(O)(R^P)_2$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R^N)–$, $(R^C)_2NC(O)–$, and halogen.

11. The catalyst system of claim 1, wherein at least one of R^{4a}, R^{5a}, R^{6a}, R^{7a} is halogen and at least one of R^{4b}, R^{5b}, R^{6b}, and R^{7b} is halogen.

12. The catalyst system of claim 1, wherein at least two of R^{4a}, R^{5a}, R^{6a}, R^{7a} are halogen and at least two of R^{4b}, R^{5b}, R^{6b}, and R^{7b} are halogen.

13. The catalyst system of claim 1, wherein Q is $(–CH_2Si(R_Q)_2CH_2–)$, $(–CH_2CH_2Si(R_Q)_2CH_2CH_2–)$, $(–CH_2Ge(R_Q)_2CH_2–)$, or $(–CH_2CH_2Ge(R_Q)_2CH_2CH_2–)$, where R_Q is $(C_1–C_5)$alkyl.

14. The catalyst system of claim 1, wherein Q is benzene-1,2-diyl or cyclohexane-1,2-diyl.

15. The catalyst system of claim 1, wherein Q is $(–CH_2Si(R_Q)_2CH_2–)$ or $(–CH_2Si(R_Q)_2CH_2–)$, where R_Q is ethyl or 2-propyl.

16. The catalyst system of claim 1, wherein Q is benzene-1,2-diyldimethyl.

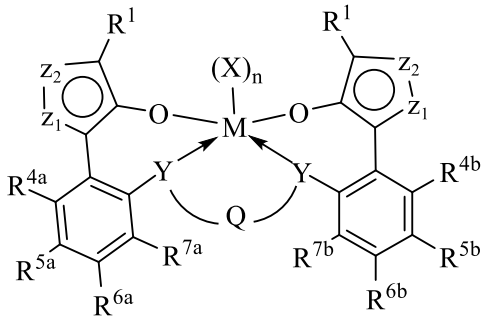
17. The catalyst system of claim 1, wherein the catalyst system further comprises a chain transfer agent.

18. A process for polymerizing olefins, the process comprising: contacting ethylene, or a combination of ethylene and one or more $(C_3–C_{12})$α-olefins with a catalyst system according to claim 1.

19. The process of claim 18, wherein the catalyst system further comprises a chain transfer agent.

20. A catalyst system comprising:

a metal–ligand complex according to formula (I):



(I)

where:

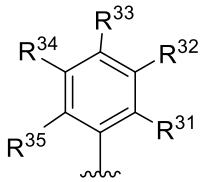
M is a metal chosen from zirconium or hafnium, the metal having a formal oxidation state of +2, +3, or +4;

each X is a monodentate or bidentate ligand independently chosen from (C_1–C_{50})hydrocarbyl;

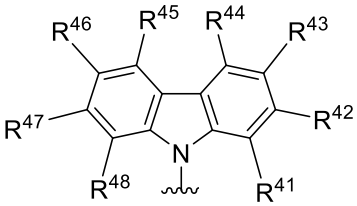
n is 1 or 2;

Y is oxygen or sulfur;

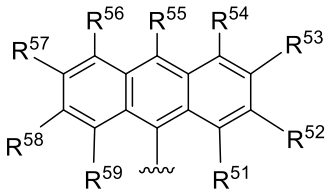
each R^1 is independently selected from the group consisting of radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from (C_1–C_{20}) hydrocarbyl, (C_1–C_{20}) heterohydrocarbyl, −CN, $-CF_3$, halogen, or –H, provided at least one R^1 in formula (I) is a radical having formula (II), a radical having formula (III), or a radical having formula (IV);

Q is $-CH_2CH_2CH_2CH_2-$, benzene-1,2-diyl, benzene-1,2-diyldimethyl, cyclohexane-1,2-diyl, or cyclohexane-1,2-diyldimethyl;

each z_1 and z_2 is independently selected from the group consisting of sulfur and −C(R^C)−, provided at least one of z_1 and z_2 in each individual ring containing groups z_1 and z_2 is sulfur;

R^{4a}, R^{5a}, R^{6a}, R^{7a}, R^{4b}, R^{5b}, R^{6b}, and R^{7b} are independently chosen from (C_1−C_{50})hydrocarbyl, –CF_3, halogen, and –H, in which optionally R^{4a} and R^{5a}, or R^{5a} and R^{6a}, or R^{6a} and R^{7a}, or R^{4b} and R^{5b}, or R^{5b} and R^{6b}, or R^{6b} and R^{7b} are covalently connected to form an aromatic ring or a non-aromatic ring;

each R^C in formula (I) is independently selected from the group consisting of (C_1−C_{20})hydrocarbyl and –H; and

provided that when Q is –$CH_2CH_2CH_2CH_2$−:

(1) when each R^1 is 3,6-di-*tert*-butylcarbazol-9-yl and z_2 is sulfur and each X is benzyl, R^{5a} and R^{5b} are not –OMe, fluorine, or *tert*-octyl; or

(2) at least one of R^{4a}, R^{5a}, R^{6a}, and R^{7a} is halogen, and at least one of R^{4b}, R^{5b}, R^{6b}, and R^{7b} is halogen; or

(3) at least one of R^{4a}, R^{5a}, R^{6a}, R^{7a}, R^{4b}, R^{5b}, R^{6b}, and R^{7b} is selected from the group consisting of (C_1−C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, (C_6−C_{50})aryl, (C_4−C_{50})heteroaryl, –Si(R^C)$_3$, –CN, and –CF_3.