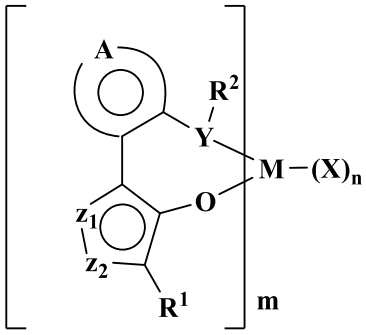
CLAIMS

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_{50})hydrocarbon, unsaturated (C_2–C_{50})heterohydrocarbon, (C_1–C_{50})hydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4–C_{12})diene, halogen, –$N(R^N)_2$, and –$NCOR^C$;

n is 1, 2, or 3;

m is 1 or 2;

the metal–ligand complex has 6 or fewer metal–ligand bonds;

each Y is independently selected from oxygen or sulfur;

each R^1 is independently 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, $R^CS(O)$–, –$P(O)(R^P)_2$, $R^CS(O)_2$–, $(R^C)_2C{=}N$–, $R^CC(O)O$–, $R^COC(O)$–, $R^CC(O)N(R)$–, $(R^C)_2NC(O)$–, halogen, and −H;

each R^2 is independently chosen from (C_1−C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, (C_6−C_{50})aryl, (C_4−C_{50})heteroaryl, –$Si(R^C)_3$, and –$Ge(R^C)_3$;

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

each A is independently chosen from $-z_3-z_4-z_5-$ or $-C(R^3)C(R^4)C(R^5)C(R^6)-$,

where:

each of z_3, z_4, and z_5 is selected from the group consisting of sulfur, oxygen, $-N(R^R)-$, and $-C(R^R)-$, provided that exactly one of z_3, z_4, or z_5 is $-C(R^R)-$ or that exactly two of z_3, z_4, or z_5 are $-C(R^R)-$; and

each R^3, R^4, R^5, and R^6 is independently chosen from (C_1-C_{50})hydrocarbyl, (C_1-C_{50})heterohydrocarbyl, (C_6-C_{50})aryl, (C_4-C_{50})heteroaryl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, halogen, or $-H$;

each R^C, R^N, and R^P in formula (I) is independently a (C_1-C_{50})hydrocarbyl; and

each R^R is independently chosen from (C_1-C_{50})hydrocarbyl, (C_1-C_{50})heterohydrocarbyl, (C_6-C_{50})aryl, (C_4-C_{50})heteroaryl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, halogen, or $-H$, wherein any two R^R groups bonded to neighboring atoms are optionally linked.

2. The catalyst system according to claim 1, wherein:

M is zirconium or hafnium;

each X is independently chosen from (C_6-C_{20})aryl, (C_4-C_{20})heteroaryl, (C_4-C_{12})diene, or a halogen;

each Y is oxygen; and

each R^1 is independently chosen from (C_6-C_{50})aryl or (C_4-C_{50})heteroaryl.

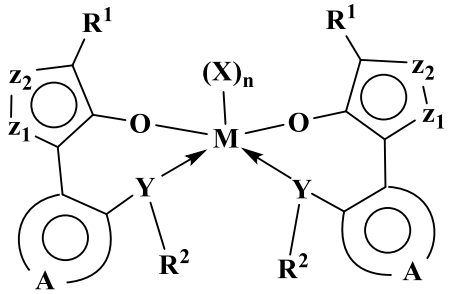
3. The catalyst system according to claim 1, wherein for each individual ring containing groups z_1 and z_2, one of z_1 and z_2 is sulfur, and the other is $-C(H)-$.

4. The catalyst system according to claim 1, wherein each A is $-C(R^3)C(R^4)C(R^5)C(R^6)-$ each R^3, R^4, R^5, and R^6 is –H.

5. The catalyst system according to claim 1, wherein each R^1 is carbazolyl and each R^2 is methyl.

6. The catalyst system according to claim 1, wherein each R^1 is phenyl or a substituted phenyl.

7. The catalyst system according to claim 1, wherein m is 2 and the metal–ligand complex has a structure according to formula (II):



(II)

where R^1, R^2, z_1, z_2, A, Y, and X are as defined in formula (I); and n is 1 or 2.

8. The catalyst system according to claim 7, wherein:

M is zirconium or hafnium;

each X is independently chosen from $(C_6–C_{50})$aryl, $(C_6–C_{50})$heteroaryl, $(C_4–C_{12})$diene, or halogen;

each Y is oxygen;

each R^1 and R^2 is independently chosen from $(C_1–C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, halogen, and hydrogen.

9. The catalyst system according to claim 7, wherein for each individual ring containing groups z_1 and z_2, one of z_1 and z_2 is sulfur, and the other is –C(H)–.

10. The catalyst system according to claim 7, wherein each R^1 is carbazolyl and each R^2 is methyl.

11. The catalyst system according to claim 7, wherein each R^1 is independently 3,6-di-*tert*-butylcarbazol-9-yl or 2,7-di-tert-butylcarbazol-9-yl.

12. The catalyst system according to claim 7, wherein each R^1 is 3,5-di-*tert*-butylphenyl.

13. The catalyst system according to claim 7, wherein each R^1 is 2,4,6-trimethylphenyl.

14. A polymerization process for producing an ethylene-based polymer, the polymerization process comprising:

polymerizing ethylene and at least one additional α-olefin in the presence of a catalyst system according to claim 1 and at least one activator to form a polymer.

15. A polymerization process for producing a propylene-based polymer, the polymerization process comprising:

polymerizing propylene with or without an additional α-olefin in the presence of a catalyst system according to claim 1and at least one activator to form a polymer.

16. The polymerization process according to claim 15, wherein the activator comprises MMAO, bis(hydrogenated tallow alkyl)methylammonium, tetrakis(pentafluorophenyl)borate, or tris(pentafluorophenyl)borane.