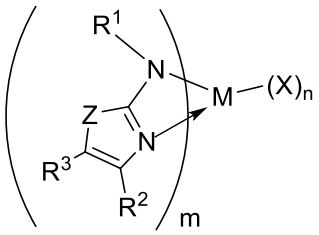
Claims:

1. A catalyst system comprising a procatalyst having a structure 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_6−C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4−C_{12})diene, halogen, −$N(R^N)_2$, and −$NCOR^C$;

m is 1 or 2;

n is 2 or 3, provided m + n = 4;

each Z is NR^N or S, wherein R^N is (C_1−C_{40})hydrocarbyl or (C_1−C_{40})heterohydrocarbyl;

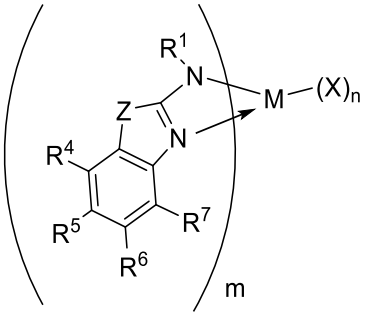
each R^1 is a (C_1−C_{40})hydrocarbyl or (C_1−C_{40})heterohydrocarbyl;

each R^2 and R^3 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, −$Si(R^C)_3$, halogen, and –H, wherein R^C is independently selected from the group consisting of (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl, and –H; and

optionally, R^2 and R^3 are covalently linked to form a ring.

2. The catalyst system of claim 1, wherein R^3 is (2,4,6-triisopropyl)phenyl, 2,4,6-trimethylphenyl, 3,5-di-tert butylphenyl, naphthyl, carbozolyl, or cyclopropyl.

3. The catalyst system of claim 1, wherein R^2 and R^3 are covalently linked to form an aromatic ring, and the metal−ligand complex has a structure according to formula (II):



(II)

where each R^1, Z, X, n, m, and M are defined as in formula (I); and
each R^4, R^5, R^6, and R^7 are independently $(C_1–C_{40})$hydrocarbyl or $(C_1–C_{40})$heterohydrocarbyl.

4. The catalyst system of claim 3, wherein each R^7 is $(C_6–C_{40})$aryl or $(C_6–C_{40})$heteroaryl.

5. The catalyst system of claim 3, wherein each R^7 is phenyl, (2,4,6-triisopropyl)phenyl, 2,4,6-trimethylphenyl, 3,5-di-*tert*-butylphenyl, naphthyl, carbozolyl, or cyclopropyl.

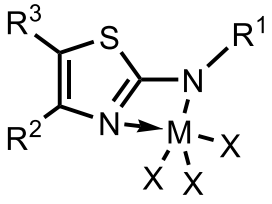
6. The catalyst system of claim 1, wherein each Z is NR^N, where R^N is $(C_1–C_8)$alkyl.

7. The catalyst system of claim 1, wherein each Z is S.

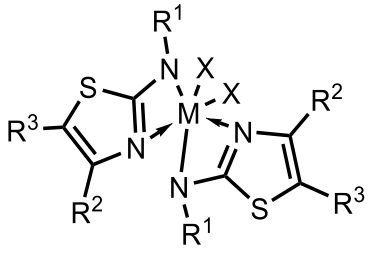
8. The catalyst system of claim 1, wherein m is 2.

9. The catalyst system of claim 1, wherein m is 1.

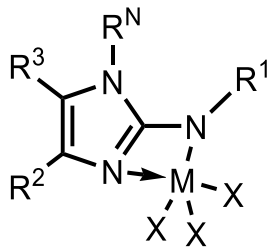
10. The catalyst system of claim 1, wherein the metal−ligand complex has a structure according to formula (Ia), formula (Ib), formula (Ic), or formula (Id):



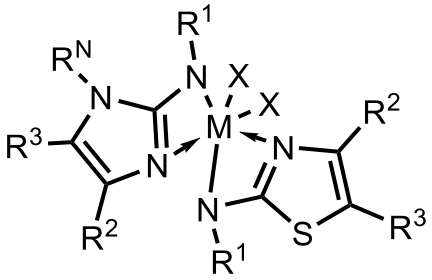
(Ia)



(Ib)



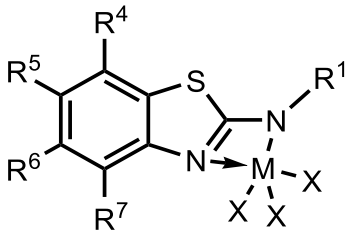
(Ic)



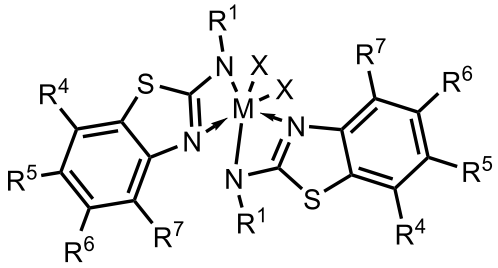
(Id)

where each R^1, R^2, R^3, R^N, X, and M are as defined in formula (I).

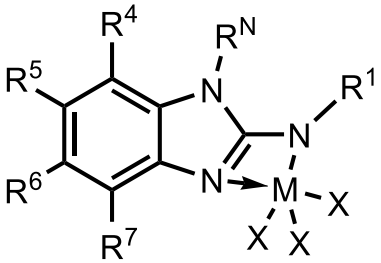
11. The catalyst system of claim 1, wherein the metal−ligand complex has a structure according to formula (IIa), formula (IIb), formula (IIc), or formula (IId):



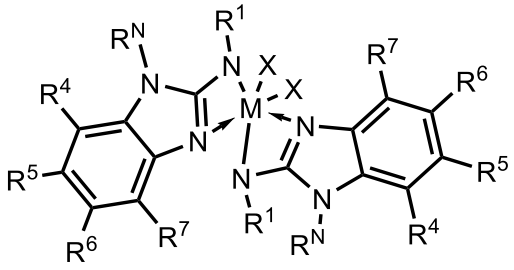
(IIa)



(IIb)



(IIc)



(IId)

where each R^1, R^4, R^5, R^6, R^7, R^N, X, and M are as defined in formula (II)

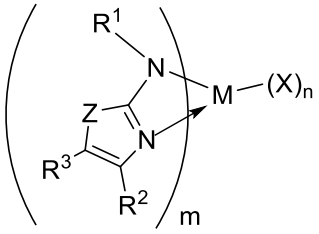
12. The catalyst system of claim 1, wherein each R^1 is chosen from a linear (C_1−C_{12})alkyl, branched (C_1−C_{12})alkyl, (C_1−C_{12})cycloalkyl, trimethylsilyl methyl, benzyl, and 1-adamantyl.

13. The catalyst system of claim 1, wherein each X is independently benzyl, phenyl, or chloro.

14. The catalyst system of claim 1, further comprising a chain transfer agent and an activator mixed in solution with one or more metal−ligand complexes according to claim 1.

15. A polymerization process comprising:

polymerizing ethylene and one or more olefins in the presence of a catalyst system under olefin polymerization conditions to form an ethylene-based polymer, the 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, −$N(R^N)_2$, and −$NCOR^C$;

m is 1 or 2;

n is 2 or 3, provided m+n=4;

each Z is NR^N or S, wherein R^N is (C_1−C_{20})hydrocarbyl or (C_1−C_{20})heterohydrocarbyl;

each R^1 is a (C_1−C_{40})hydrocarbyl or (C_1−C_{20})heterohydrocarbyl;

each R^2 and R^3 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, −$Si(R^C)_3$, halogen, and –H, wherein R^C is independently selected from the group consisting of (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl, and –H; and

optionally, R^2 and R^3 are covalently linked to form a ring.

16. The polymerization process of claim 15, wherein Z is NR^N, where R^N is (C_1−C_8)alkyl.

17. The polymerization process of claim 15, wherein Z is S.

18. The polymerization process of claim 15, wherein the catalyst system is a catalyst system according to claim 14, the process further comprising mixing the chain transfer agent and the activator in solution with the one or more metal−ligand complexes.