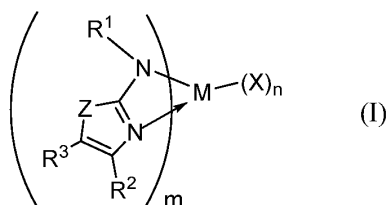


CLAIMS

1. A catalyst system comprising a procatalyst having a structure according to formula (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 (C₂–C₅₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₆–C₅₀)aryl, (C₆–C₅₀)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C₄–C₁₂)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 (C₁–C₄₀)hydrocarbyl or (C₁–C₄₀)heterohydrocarbyl;

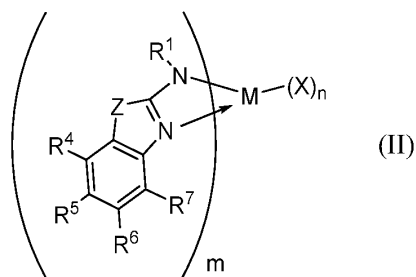
each R¹ is a (C₁–C₄₀)hydrocarbyl or (C₁–C₄₀)heterohydrocarbyl;

each R² and R³ is independently selected from the group consisting of (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, –Si(R^C)₃, halogen, and –H, wherein R^C is independently selected from the group consisting of (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, and –H; and

optionally, R² and R³ are covalently linked to form a ring.

2. The catalyst system of claim 1, wherein R³ is (2,4,6-triisopropyl)phenyl, 2,4,6-trimethylphenyl, 3,5-di-tert butylphenyl, naphthyl, carbozoyl, or cyclopropyl.

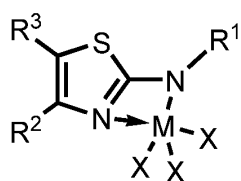
3. The catalyst system of claim 1, wherein R^2 and R^3 are covalently linked to form an aromatic ring, and the metal–ligand complex has a structure according to formula (II):



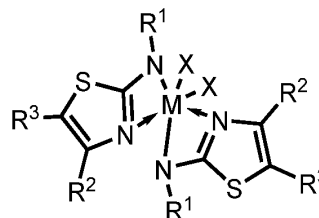
where each R^1 , Z, X, n, m, and M are defined as in formula (I); and each R^4 , R^5 , R^6 , and R^7 are independently (C_1-C_{40}) hydrocarbyl or (C_1-C_{40}) heterohydrocarbyl.

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, carbozoyl, or cyclopropyl.
6. The catalyst system of any one of claims 1 to 5, wherein each Z is NR^N , where R^N is (C_1-C_8) alkyl.
7. The catalyst system of any one of claims 1 to 5, wherein each Z is S.
8. The catalyst system of any one of claims 1 to 7, wherein m is 2.
9. The catalyst system of any one of claims 1 to 7, wherein m is 1.

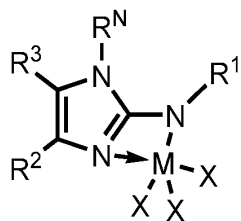
10. The catalyst system of any one of claims 1 to 5, wherein the metal–ligand complex has a structure according to formula (Ia), formula (Ib), formula (Ic), or formula (Id):



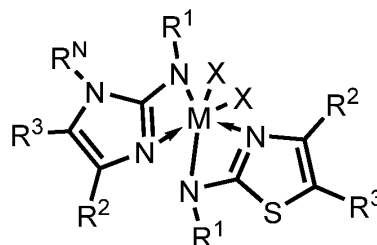
(Ia)



(Ib)



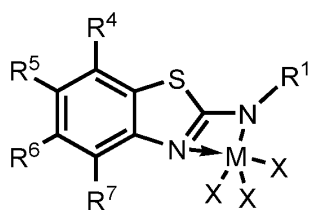
(Ic)



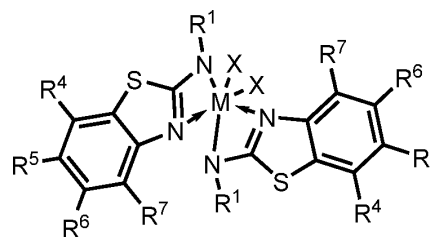
(Id)

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

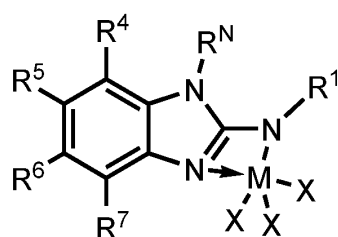
11. The catalyst system of any one of claims 3 to 5, wherein the metal–ligand complex has a structure according to formula (IIa), formula (IIb), formula (IIc), or formula (IId):



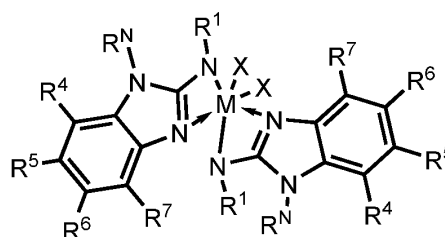
(IIa)



(IIb)



(IIc)



(IIId)

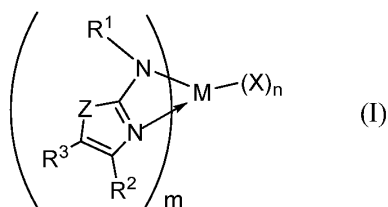
where each R^1 , R^4 , R^5 , R^6 , R^7 , R^N , X , and M are as defined in formula (II)

12. The catalyst system of any one of claims 1 to 11, 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 any one of claims 1 to 12, wherein each X is independently benzyl, phenyl, or chloro.

14. The catalyst system of any one of the preceding claims, further comprising a chain transfer agent and an activator mixed in solution with one or more metal–ligand complexes according to any one of claims 1 to 13.

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 (C₂–C₂₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₆–C₅₀)aryl, (C₆–C₅₀)heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C₄–C₁₂)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 (C₁–C₂₀)hydrocarbyl or (C₁–C₂₀)heterohydrocarbyl;

each R¹ is a (C₁–C₄₀)hydrocarbyl or (C₁–C₂₀)heterohydrocarbyl;

each R² and R³ is independently selected from the group consisting of (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, –Si(R^C)₃, halogen, and –H, wherein R^C is independently selected from the group consisting of (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, and –H; and

optionally, R² and R³ are covalently linked to form a ring.

16. The catalyst system of claim 15, wherein Z is NR^N, where R^N is (C₁–C₈)alkyl.
17. The catalyst system 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.