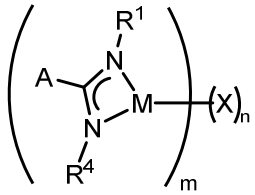
CLAIMS

1. A process for polymerizing polyolefin, the process comprising contacting ethylene and optionally one or more (C_3–C_{12})α-olefin in the presence of a catalyst system, wherein the catalyst systems comprises a metal–ligand 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;

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, (C_4–C_{12})diene, halogen, $-OR^C$, $-N(R^N)_2$, and $-NCOR^C$;

n is 1, 2, or 3;

m is 1 or 2;

m + n = 3 or 4;

each R^1 is R^{1a} or R^{1b};

each R^4 is R^{4a} or R^{4b};

R^{1a}, R^{1b}, R^{4a}, and R^{4b} are independently chosen from –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, (C_1-C_{40})aryl, (C_1-C_{40})heteroaryl, $-P(R^P)_2$, $-N(R^N)_2$, $R^CS(O)-$, $R^CS(O)_2-$, or $(R^C)_2C=N-$;

each A is independently $-NR^1R^2$; where each R^2 is R^{2a} or R^{2b}; each R^3 is R^{3a} or R^{3b}; and R^{2a}, R^{2b}, R^{3a}, and R^{3b} are independently –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, (C_1-C_{40})aryl, or (C_1-C_{40})heteroaryl;

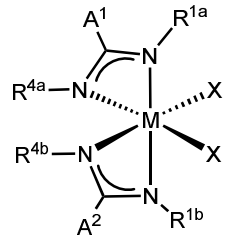
provided that

when (1) m is 2 and (2) all of R^{2a}, R^{2b}, R^{3a}, and R^{3b} are methyl, at least one of R^{1a}, R^{1b}, R^{4a}, and R^{4b} is not 2-propyl;

when m is 1, each X is identical; and

any of R^1 and R^2, or R^2 and R^3, or R^3 and R^4 optionally may be connected to form a ring.

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

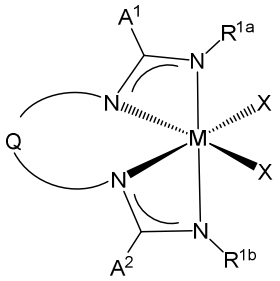


(II)

where:

R^{1a}, R^{1b}, R^{4a}, R^{4b}, M and X are as defined in formula (I), and A^1 and A^2 are independently A as defined in formula (I).

3. The process according to claim 2, wherein m is 2, n is 2, and R^{4a} and R^{4b} are covalently linked, whereby the metal–ligand complex comprises a divalent radical Q consisting of the two covalently linked groups R^{4a} and R^{4b} and the metal–ligand complex has a structure according to formula (III):



(III)

where:

Q is $(C_2–C_{12})$alkylene, $(C_2–C_{12})$heteroalkylene, $(C_6–C_{50})$arylene, $(C_4–C_{50})$heteroarylene, $(–CH_2Si(R^C)_2CH_2–)$, $(–CH_2CH_2Si(R^C)_2CH_2CH_2–)$, $(–CH_2Ge(R^C)_2CH_2–)$, or $(–CH_2CH_2Ge(R^C)_2CH_2CH_2–)$; and

R^{1a}, R^{1b}, R^{2a}, R^{2b}, R^{3a}, R^{3b} R^{4a}, R^{4b}, M, and X are as defined in formula (I) and A^1 and A^2 are as defined in formula (II).

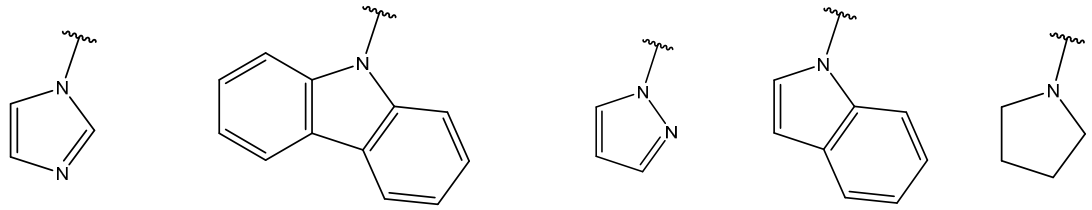
4. The process of any one of the preceding claims, wherein each X is benzyl, chloro, $-CH_2SiMe_3$, or phenyl.

5. The process of any one of the preceding claims, wherein each R^1, R^{1a}, or R^{1b} and each R^4, R^{4a}, or R^{4b} are independently (C_1-C_{20})alkyl or (C_1-C_{20})aryl.

6. The process of any one of the preceding claims, wherein each R^1 and each R^4 are independently benzyl, cyclohexyl, 2,6-dimethylphenyl, *tert*-butyl, or ethyl.

7. The process of claim 3, wherein R^{1a} and R^{1b} are 2-propyl.

8. The process of any one of the preceding claims, wherein each A has one of the following structures:



9. The process of any one of claims 1 to 8, wherein R^{2a}, R^{2b}, R^{3a}, and R^{3b} are (C_1-C_{12})alkyl.

10. The process of claim 9, wherein R^{2a}, R^{2b}, R^{3a}, and R^{3b} are methyl, ethyl, 1-propyl, 2-propyl, n-butyl, *tert*-butyl, 2-methylpropyl (*iso*-butyl), n-butyl, n-hexyl, cyclohexyl, *n*-octyl, or *tert*-octyl.

11. The process of any one of claims 1 to 4, wherein R^{1a}, R^{1b}, R^{4a}, and R^{4b} are independently chosen from 3,5-di-*tert*-butylphenyl; 2,4,6-trimethylphenyl; 2,6-dimethylphenyl; 2,4,6-triisopropylphenyl; 2,6-di-*iso*-propylphenyl; benzyl, cyclohexyl, or 2-propyl..

12. The catalyst system according to claim 3, wherein Q is chosen from $-(CH_2)_x-$, where x is from 2 to 5.

13. The catalyst system according to claim 3, wherein Q is $-(CH_2)_4-$.

14. The catalyst system of any one of the preceding claims, wherein the catalyst system further comprises a chain transfer agent.

15. The catalyst system according to claim 14, wherein the chain transfer agent is diethylzinc.