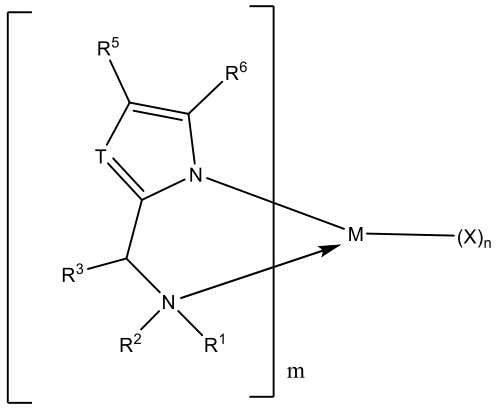
the polyethylene product from the diluent and the unreacted reactants, with the diluent and unreacted reactants typically being recycled back into the reactor. Alternatively, the reaction mixture may be sent to a second reactor, serially connected to the first reactor, where a second polyethylene fraction may be produced. Despite the research efforts in developing catalyst systems suitable for olefin polymerization, such as polyethylene or polypropylene polymerization, there is still a need to increase the efficiencies of catalyst systems that are capable of producing polymer with high molecular weights and a narrow molecular weight distribution.

SUMMARY

[0005] This disclosure includes a catalyst system comprising a metal–ligand complex according to formula (I):



(I)

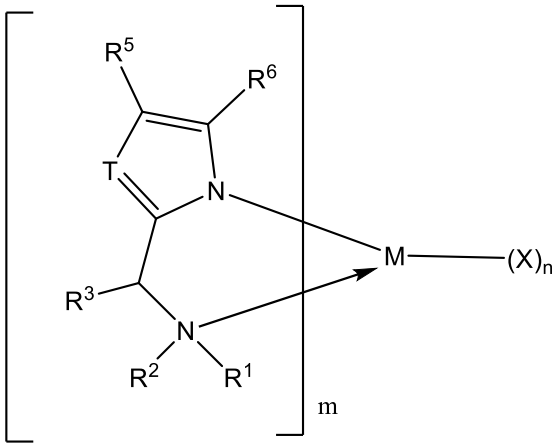
[0006] In formula (I), M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4. Each X is a monodentate or bidentate ligand independently chosen from unsaturated (C_2–C_{50})hydrocarbon, unsaturated (C_2–C_{50})heterohydrocarbon, (C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_6–C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4–C_{12})diene, halogen, –$N(R^N)_2$, and –$NCOR^C$; subscript n is 1, 2, or 3; and subscript m is 1 or 2. The metal–ligand complex has 6 or fewer metal–ligand bonds.

[0007] In formula (I), each T is nitrogen or CR^4, in which each R^4 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, halogen, or –H. Each R^1 is independently selected from the group consisting of an aliphatic (C_1–C_{50})hydrocarbyl, an aliphatic (C_1–C_{50})heterohydrocarbyl, – halogen, and –H, and, when m is 2, two R^1 are optionally

covalently linked. 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 $–Ge(R^C)_3$, and R^1 and R^2 are optionally covalently connected to form a ring structure.

[0008] In formula (I), each R^3 and each R^5 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^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, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $(R^C)_2C=N–$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, $(R^C)_2NC(O)–$, or halogen; R^5 and R^6 are optionally covalently connected to form a ring structure; and each R^C and R^N in formula (I) is independently a $(C_1–C_{50})$hydrocarbyl.

[0008a] In one aspect, there is provided 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, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, $(C_4–C_{12})$diene, halogen, $–N(R^N)_2$, or $–NCOR^C$;

n is 1, 2, or 3;

m is 1 or 2;

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

each T is nitrogen or CR^4, wherein each R^4 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, $–CF_3$, halogen, or –H;

each R^1 is independently selected from the group consisting of an aliphatic $(C_1–C_{50})$hydrocarbyl, an aliphatic $(C_1–C_{50})$heterohydrocarbyl, – halogen, and –H, and, when m is 2, two R^1 are covalently connected to each other;

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, $–Si(R^C)_3$, or $–Ge(R^C)_3$;

R^1 and R^2 are optionally covalently connected to form a ring structure;

each R^3 and each R^5 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^6 is independently chosen from $(C_6–C_{50})$aryl or $(C_4–C_{50})$heteroaryl;

R^5 and R^6 are optionally covalently connected to form a ring structure;

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

each R^P is unsubstituted $(C_1$-$C_{18})$hydrocarbyl or -H.

[0008b] In another aspect, there is provided 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 as defined herein and at least one activator to form a polymer.

DETAILED DESCRIPTION

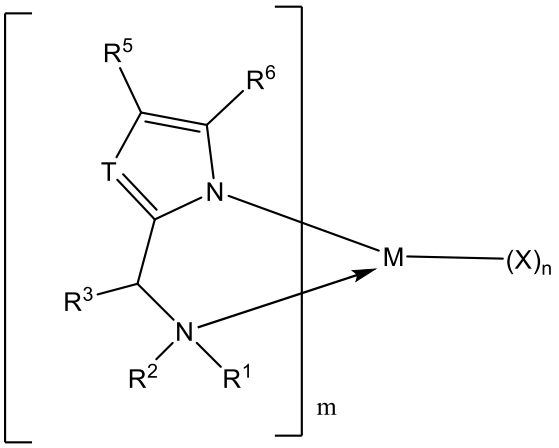
[0009] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

[0010] Common abbreviations are listed below:

[0011] **R^C, R^Z, R^1, R^2, R^3, R^4, Z_1, Z_2, Z_3, X, Y, Q, and W**: as defined above; **Me** : methyl; **Et** : ethyl; **Ph** : phenyl; **Bn**: benzyl; ***i*-Pr** : *iso*-propyl; ***t*-Bu** : *tert*-butyl; ***t*-Oct** : *tert*-octyl (2,4,4-trimethylpentan-2-yl); **THF** : tetrahydrofuran; **Et_2O** : diethyl ether; **CH_2Cl_2** : dichloromethane; **EtOAc** : ethyl acetate; **C_6D_6 :** deuterated benzene or benzene-*d*6 : **$CDCl_3$** : deuterated chloroform; **Na_2SO_4** : sodium sulfate; **$MgSO_4$** : magnesium sulfate; **HCl** : hydrogen chloride; ***n*-BuLi:** butyllithium; ***t*-BuLi** : *tert*-butyllithium; **K_2CO_3:** potassium carbonate; **N_2** : nitrogen gas; **PhMe**: toluene; **PPR** : parallel pressure reactor; **MAO** : methylaluminoxane; **MMAO** : modified methylaluminoxane; **GC** : gas chromatography; **LC** : liquid chromatography; **NMR** : nuclear magnetic resonance; **MS**: mass spectrometry; **mmol** : millimoles; **mL** : milliliters; **M** : molar;

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_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4–C_{12})diene, halogen, –$N(R^N)_2$, or –$NCOR^C$;

n is 1, 2, or 3;

m is 1 or 2;

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

each T is nitrogen or CR^4, wherein each R^4 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, halogen, or –H;

each R^1 is independently selected from the group consisting of an aliphatic (C_1–C_{50})hydrocarbyl, an aliphatic (C_1–C_{50})heterohydrocarbyl, – halogen, and –H, and, when m is 2, two R^1 are covalently connected to each other;

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, –$Si(R^C)_3$, or –$Ge(R^C)_3$;

R^1 and R^2 are optionally covalently connected to form a ring structure;

each R^3 and each R^5 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^6 is independently chosen from $(C_6–C_{50})$aryl or $(C_4–C_{50})$heteroaryl;

R^5 and R^6 are optionally covalently connected to form a ring structure;

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

each R^P is unsubstituted $(C_1$-$C_{18})$hydrocarbyl or -H.

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

M is zirconium or hafnium; and

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

3. The catalyst system according to claim 1, wherein R^5 and R^6 are covalently connected to form a six-member aromatic ring.

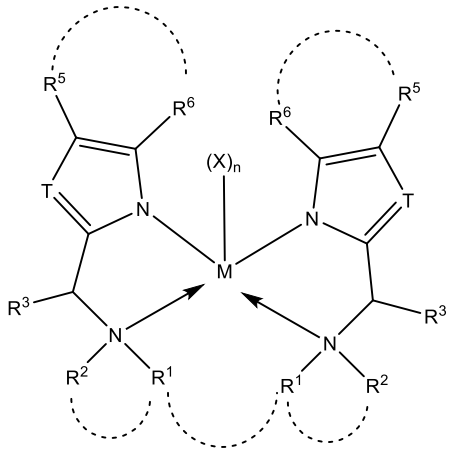
4. The catalyst system according to claim 1, wherein R^5 and R^6 are covalently connected to form a six-member aromatic ring; R^3 is –H; and R^2 is methyl.

5. The catalyst system according to claim 1, wherein each R^6 is anthracenyl, di-substituted anthracenyl, or tri-substituted anthracenyl.

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

7. The catalyst system according to claim 1, wherein each R^6 is a substituted phenyl chosen from 2,4,6-trimethylphenyl; 2,6-di(*iso*-propyl)phenyl; 3,5-di-*tert*-butylphenyl, or 3,5-diphenylphenyl.

8. 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 M, T, R^1, R^2, R^3, R^4, R^5, R^6, and X are as defined in formula (I); n is 1 or 2; and the dotted lines indicate optional covalent connections.

9. The catalyst system according to claim 8, 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;

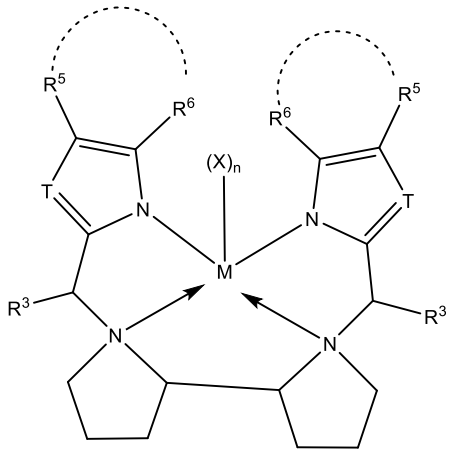
each R^1 is independently chosen from (C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, or halogen, and

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

10. The catalyst system according to claim 8, wherein the two R^1 are covalently connected to each other; and each R^2 is independently (C_1−C_{10})alkyl.

11. The catalyst system according to claim 1, wherein the two R^1 are covalently connected as an alkylene chosen from –CH_2CH_2−, –$CH_2CH_2CH_2$−, or −$CH_2CH_2CH_2CH_2$−.

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



(III)

where M, T, R^3, R^4, R^5, R^6, and X are as defined in formula (I); n is 1 or 2; and the dotted lines indicate optional covalent connections.

13. The catalyst system according to claim 12, wherein each R^6 is independently chosen from carbazolyl, 3,5-di-*tert*-butylphenyl; 2,4,6-trimethylphenyl; 2,6-di-*iso*-propylphenyl; or 3,5-di-*iso*-propylphenyl.

14. The catalyst system according to claim 12, wherein each R^6 is 2,6-di-*iso*-propylphenyl.

15. The catalyst system according to claim 12, wherein each R^6 is 2,4,6-trimethylphenyl.

16. The catalyst system according to claim 1, wherein T is N.

17. The catalyst system according to claim 1, wherein T is CR^4, and R^4 is –H.

18. 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.

19. The polymerization process according to claim 18, wherein the activator comprises MMAO, bis(hydrogenated tallow alkyl)methylammonium tetrakis(pentafluorophenyl)borate, or tris(pentafluorophenyl)borane.