$(R^C)_2NC(O)-$, halogen, or –H, provided at least one R^1 in formula (I) is a radical having formula (II), a radical having formula (III), or a radical having formula (IV); Q is (C_1-C_{12})alkylene or (C_1-C_{12})heteroalkylene ; one of z_1 and z_2 is sulfur, and the other of z_1 and z_2 is $-C(R^Z)-$, wherein R^Z is (C_1-C_8)alkyl or −H; R^{4a}, R^{5a}, R^{6a}, R^{7a}, R^{4b}, R^{5b}, R^{6b}, and R^{7b} are independently chosen from (C_1-C_{20})alkyl, (C_3-C_{20})cycloalkyl, (C_1-C_{20})heteroalkyl, (C_6-C_{50})aryl, (C_4-C_{50})heteroaryl, $-Si(R^C)_3$, $-OR^C$, –CN, $-CF_3$, halogen, and –H, in which optionally R^{4a} and R^{5a}, or R^{5a} and R^{6a}, or R^{6a} and R^{7a}, or R^{4b} and R^{5b}, or R^{5b} and R^{6b}, or R^{6b} and R^{7b} may be covalently connected to form an aromatic ring or a non-aromatic ring; each R^C, R^N, and R^P in formula (I) is independently selected from the group consisting of (C_1-C_{20})hydrocarbyl, (C_1-C_{20})heterohydrocarbyl, and –H.

BRIEF DESCRIPTION OF FIGURES

[0013] FIG. 1 dipicts Ligand 1 to Ligand 10.

[0014] FIG. 2 dipicts Ligand 11 to Ligand 19.

[0015] FIG. 3 dipicts Ligand 20 to Ligand 25.

[0016] FIG. 4 depicts a three step synthetic scheme to synthesize the precursors to the ligands.

[0017] FIG. 5 depicts a three step synthetic scheme to synthesize the precursors to the ligands.

DETAILED DESCRIPTION

[0018] 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.

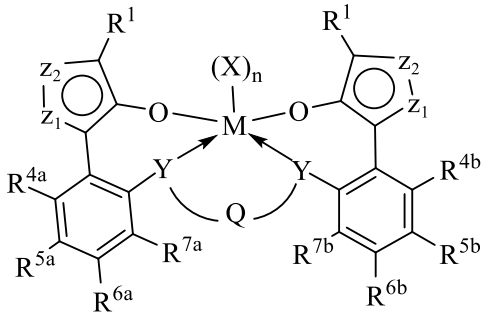
[0019] Common abbreviations are listed below:

[0020] **R, Z, M, X and n**: 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); **Tf** : trifluoromethane sulfonate; **CV** : column volume (used in column chromatography); **EtOAc** : ethyl acetate; **TEA :** triethylaluminum; **MAO** : methylaluminoxane; **MMAO** : modified methylaluminoxane; **$LiCH_2TMS$**: (trimethylsilyl)methyllithium; **TMS** : trimethylsilyl; **Pd(AmPhos)Cl_2:** Bis(di-tert-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II);

CLAIMS

1. A polymerization process comprising:

contacting propylene and one or more (C_4–C_{12})α-olefins in a reactor including a catalyst system, the catalyst system comprising a chain transfer or chain shuttling agent and a metal–ligand complex according to formula (I):



(I)

where:

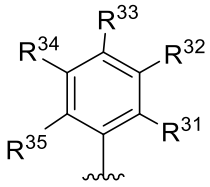
M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4;

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, −OR^C, –$N(R^N)_2$, and –$NCOR^C$;

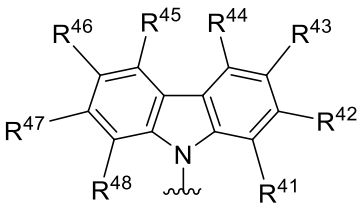
n is 1 or 2;

each Y is –O−;

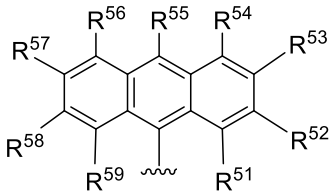
each R^1 is independently selected from the group consisting of –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −$Si(R^C)_3$, −$Ge(R^C)_3$, −$P(R^P)_2$, −$N(R^N)_2$, −OR^C, −SR^C, −NO_2, −CN, −CF_3, $R^CS(O)$−, $R^CS(O)_2$−, $(R^C)_2C$=N−, $R^CC(O)O$−, $R^COC(O)$−, $R^CC(O)N(R)$−, $(R^C)_2NC(O)$−, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $–N=CHR^C$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^N)-$, $(R^C)_2NC(O)-$, halogen, or –H,

provided at least one R^1 in formula (I) is a radical having formula (II), a radical having formula (III), or a radical having formula (IV);

Q is $(C_1–C_{12})$alkylene or $(C_1–C_{12})$heteroalkylene;

one of z_1 and z_2 is sulfur, and the other of z_1 and z_2 is $-C(R^Z)-$, wherein R^Z is $(C_1–C_8)$alkyl or −H;

R^{4a}, R^{5a}, R^{6a}, R^{7a}, R^{4b}, R^{5b}, R^{6b}, and R^{7b} are independently chosen from $(C_1–C_{20})$alkyl, $(C_3–C_{20})$cycloalkyl, $(C_1–C_{20})$heteroalkyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, $–Si(R^C)_3$, $–OR^C$, –CN, $–CF_3$, halogen, and –H, in which optionally R^{4a} and R^{5a}, or R^{5a} and R^{6a}, or R^{6a} and R^{7a}, or R^{4b} and R^{5b}, or R^{5b} and R^{6b}, or R^{6b} and R^{7b} may be covalently connected to form an aromatic ring or a non-aromatic ring;

each R^C, R^N, and R^P in formula (I) is independently selected from the group consisting of $(C_1–C_{20})$hydrocarbyl, $(C_1–C_{20})$heterohydrocarbyl, and –H.

2. The polymerization process of claim 1, wherein each z_1 is sulfur and each z_2 is $-C(R^Z)-$, wherein R^Z is $(C_1–C_8)$alkyl or −H.

3. The polymerization process of claim 1, wherein each z_2 is sulfur and each z_1 is $-C(R^Z)-$, wherein R^Z is $(C_1–C_8)$alkyl or −H.

4. The polymerization process of any one of the preceding claims, wherein the catalyst system further comprises one or more cocatalysts.

5. The polymerization process of any one of claims 1 to 4, wherein each R^1 is a radical having formula (III), in which:

(1) R^{42} and R^{47} are independently chosen from $(C_1–C_{20})$alkyl, $–Si(R^C)_3$, $–CF_3$, or halogen, and R^{43} and R^{46} are –H; or

(2) R^{43} and R^{46} are independently chosen from $(C_1–C_{20})$alkyl, $(C_6–C_{40})$aryl, $(C_5–C_{40})$heteroaryl, $–Si(R^C)_3$, $–CF_3$, or halogen, and R^{42} and R^{47} are –H.

6. The polymerization process of any one of claims 1 to 4, wherein each R^1 is a radical having formula (IV), in which at least one of $R^{51–59}$ is chosen from $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $–Si(R^C)_3$, $–OR^C$, $–SR^C$, $–NO_2$, $–CN$, $–CF_3$, or halogen.

7. The polymerization process of any one of claims 1 to 4, wherein each R^1 is a radical having formula (IV), in which at least one of R^{53}, R^{55}, and R^{57} is $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $–Si(R^C)_3$, $–OR^C$, $–SR^C$, $–NO_2$, $–CN$, $–CF_3$, or halogen.

8. The polymerization process of any one of claims 1 to 4, wherein each R^1 is a radical having formula (II).

9. The polymerization process of any one of claims 1 to 4, wherein each R^1 is a radical having formula (II), and wherein R^{32} and R^{34} are independently $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $–Si(R^C)_3$, $–OR^C$, $–SR^C$, $–NO_2$, $–CN$, $–CF_3$, or halogen.

10. The polymerization process of any one of claims 1 to 4, wherein each R^1 is a radical having formula (II), and wherein R^{32} and R^{34} are independently $(C_1–C_{20})$alkyl, substituted $(C_6–C_{20})$aryl, or unsubstituted $(C_6–C_{20})$aryl.

11. The polymerization process of any one of claims 1 to 4, wherein each R^1 is a radical having formula (II), and wherein R^{32} and R^{34} are independently *tert*-butyl, phenyl, 3,5-di(*tert*-butyl)phenyl, 2,4,6-trimethylphenyl, or 2,4,6-tri(*iso*-propyl)phenyl.

12. The polymerization process of any one of claims 1 – 11, wherein Q is $(–CH_2Si(R_Q)_2CH_2–)$, $(–CH_2CH_2Si(R_Q)_2CH_2CH_2–)$, $(–CH_2Ge(R_Q)_2CH_2–)$, or $(–CH_2CH_2Ge(R_Q)_2CH_2CH_2–)$, where R_Q is $(C_1–C_5)$alkyl.

13. The polymerization process of any one of the preceding claims, wherein the reactor has a reactor temperature of 140 °C or greater.

14. The polymerization process of any one of the preceding claims, wherein the polymer process further comprises a solution polymerization, and the solution polymerization takes place at a pressure from 10 psi to 2000 psi.

15. The polymerization process of claim 1, wherein the chain transfer or chain shuttling agent is diethyl zinc.