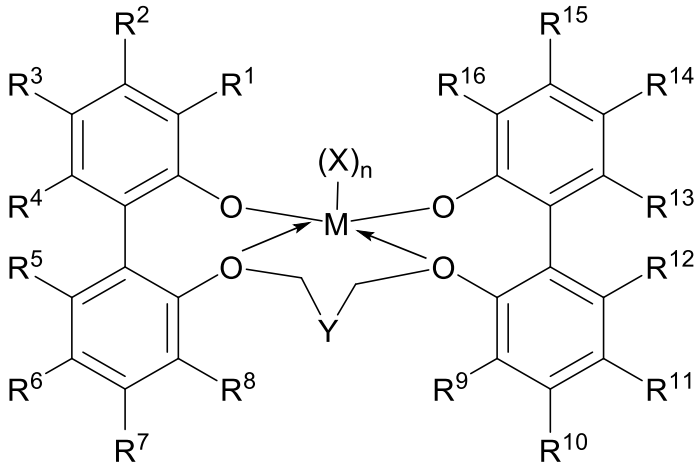
CLAIMS

1. A process of polymerizing olefin monomers, the process comprising reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system, wherein the catalyst system comprises:

modified-hydrocarbyl methylaluminoxane having less than 50 mole percent $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane, where R^{A1}, R^{B1}, and R^{C1} are independently linear $(C_1–C_{40})$alkyl, branched $(C_1–C_{40})$alkyl, or $(C_6–C_{40})$aryl; and

one or more metal–ligand complexes according to formula (I):



(I)

where:

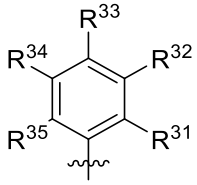
M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

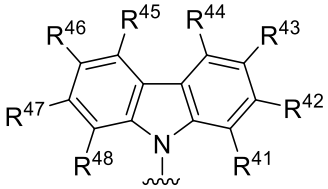
each X is a monodentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2–C_{50})$heterohydrocarbon, $(C_1–C_{50})$hydrocarbyl, $(C_6–C_{50})$aryl, $(C_6–C_{50})$heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, $(C_4–C_{12})$diene, halogen, $–N(R^N)_2$, and $–N(R^N)COR^C$;

the metal–ligand complex is overall charge-neutral;

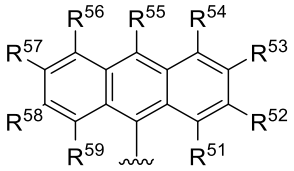
R^1 and R^{16} are independently selected from the group consisting of –H, $(C_6–C_{40})$aryl, $(C_5–C_{40})$heteroaryl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from –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)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R^N)−, (R^C)$_2$NC(O)−, or halogen;

R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, and R^{15} are independently selected from −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)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R)−, (R^C)$_2$NC(O)−, and halogen;

Y is CH_2, CHR^{21}, $CR^{21}R^{22}$, $SiR^{21}R^{22}$, or $GeR^{21}R^{22}$, where R^{21} and R^{22} are (C_1–C_{20})alkyl; provided that when:

(1) Y is CH_2, then at least one of R^8 and R^9 is not –H;

each R^C, R^P, and R^N in formula (I) is independently a (C_1–C_{30})hydrocarbyl, (C_1–C_{30})heterohydrocarbyl, or –H; and

wherein the catalysts system does not contain a borate activator.

2. The polymerization process according to claim 1, where the modified-hydrocarbyl methylaluminoxane contains less than 25 mole percent $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.

3. The polymerization process according to claim 1 or claim 2, where the modified-hydrocarbyl methylaluminoxane contains less than 15 mole percent $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane~~.~~

~~4. The polymerization process according to claim 1 or claim 2, where~~ or the modified-hydrocarbyl methylaluminoxane contains less than 10 mole percent $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.

~~5~~4. The polymerization process according to ~~any one of~~ claim 1 ~~to claim 4~~, where the modified-hydrocarbyl methylaluminoxane is modified methylaluminoxane.

~~6~~5. The polymerization process according to ~~any one of the preceding claims~~claim 1, wherein the aluminum to catalyst metal is less than 500:1.

~~7~~6. The polymerization process according to ~~any one of the preceding claims~~claim 1, wherein the aluminum to catalyst metal is less than 200:1 or is less than 50:1.

~~8~~7. The polymerization process according to ~~any one of the preceding claims~~claim 1, wherein at least one of R^8 and R^9 is (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, or halogen atom.

~~9~~8. The polymerization process according to ~~any one of the preceding claims~~claim 1, wherein at least one of R^8 and R^9 is (C_1-C_5)alkyl.

~~10.~~9. The polymerization process according to ~~any one of the preceding claims, wherein R^1 and R^{16} are identical.~~

~~11. The polymerization process according to any one of the preceding claims~~claim 1, wherein at least one of R^1 and R^{16} is a radical having formula (III).

~~12~~10. The polymerization process according to claim ~~7~~9, wherein R^{42} and R^{47} are (C_1-C_{20})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$~~.~~

~~13. The polymerization process according to claim 7, wherein~~ or R^{43} and R^{46} are (C_1-C_{20})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.

~~14~~11. The polymerization process according to ~~any one of claims~~claim 1 ~~to 5~~, wherein at least one of R^1 and R^{16} is a radical having formula (II).

~~15~~12. The polymerization process according to claim ~~10~~11, wherein R^{32} and R^{34} are (C_1-C_{12})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.

~~16~~13. The polymerization process according to ~~any one of claims~~claim 1 ~~to 5~~, wherein at least one of R^1 and R^{16} is a radical having formula (IV).

~~17~~14. The polymerization process according to claim 12, wherein at least two of R^{52}, R^{53}, R^{55}, R^{57}, and R^{58} are (C_1-C_{20})hydrocarbyl or $-Si[(C_1-C_{20})hydrocarbyl]_3$.

~~18~~15. The polymerization process according to ~~any one of claims~~claim 1 ~~to 13~~, wherein ~~R~~R^8 and ~~R~~R^9 are ~~independently selected from methyl, ethyl, 1-propyl, or 2-propyl~~(C_1-C_{20})alkyl.

~~19~~16. The polymerization process according to ~~any of the preceding claims~~claim 1, wherein ~~R~~$R^3$$R^6$ and ~~R~~$R^{14}$$R^{11}$ are ~~(C_1–C_{20})alkyl~~*tert*-butyl.

~~20~~17. The polymerization process according to ~~any one of the preceding claims, wherein R~~R^3 ~~and R~~R^{14} ~~are methyl, R~~R^6 ~~and R~~R^{11} ~~are halogen.~~

~~21. The polymerization process according to any one of claims~~claim 1~~–20, wherein R~~R^6 ~~and R~~R^{11} ~~are *tert*-butyl.~~

~~22. The polymerization process according to any one of claims 1 to 20~~, wherein R^3 and R^{14} are *tert*-octyl or *n*-octyl.

~~23~~18. The polymerization process according to ~~any one of the preceding claims, where M is zirconium.~~

~~24. The polymerization process according to any one of the preceding claims~~claim 1, wherein the olefin monomer is (C_3–C_{20})α-olefin.

~~25~~19. The polymerization process according to ~~any one of the preceding claims~~claim 1, wherein the olefin monomer is a cyclic olefin.

~~26~~20. The polymerization process according to ~~any one of the preceding claims~~claim 1, wherein the polymerization process is a solution polymerization reaction.