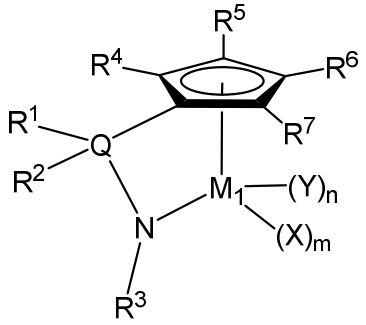
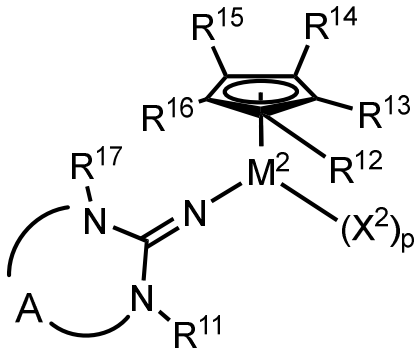
CLAIMS

1. A process of polymerizing olefin monomers to produce polyolefin, the process comprising reacting ethylene and optionally one or more olefin monomers in one or multiple reactors in the presence of a catalyst system; the catalyst system comprises two or more catalysts, at least one of which is derived from constrained geometry procatalyst according to formula (I) and at least one of which is derived from guanidine procatalyst according to formula (II):



(I)



(II)

where:

M_1 is titanium, zirconium, hafnium, or scandium;

each X is a monodentate ligand independently chosen from (C_1−C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, -$CH_2Si(R^C)_{3-Q}(OR^C)_Q$, −$Si(R^C)_{3-Q}(OR^C)_Q$, -$OSi(R^C)_{3-Q}(OR^C)_Q$, −$CH_2Ge(R^C)_{3-Q}(OR^C)_Q$, −$Ge(R^C)_{3-Q}(OR^C)_Q$, −$P(R^C)_{2-W}(OR^C)_W$, −$P(O)(R^C)_{2-W}(OR^C)_W$, −$N(R^C)_2$, −$NH(R^C)$, −$N(Si(R^C)_3)_2$, −$NR^CSi(R^C)_3$, −$NHSi(R^C)_3$, −$OR^C$, −$SR^C$, −$NO_2$, −CN, −$CF_3$, −$OCF_3$, −$S(O)R^C$, −$S(O)_2R^C$, −$OS(O)_2R^C$, −$N{=}C(R^C)_2$, −$N{=}CH(R^C)$, −$N{=}CH_2$, −$N{=}P(R^C)_3$, −$OC(O)R^C$, −$C(O)OR^C$, −$N(R^C)C(O)R^C$, −$N(R^C)C(O)H$, −$NHC(O)R^C$, −$C(O)N(R^C)_2$, −$C(O)NHR^C$, −$C(O)NH_2$, a halogen, $B(R^Y)_4$, $Al(R^Y)_4$, or $Ga(R^Y)_4$, or a hydrogen, wherein each R^C is independently a

(C_1−C_{30})hydrocarbyl, or (C_1−C_{30})heterohydrocarbyl, and each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; each R^Y is –H, (C_1−C_{30})hydrocarbyl, or halogen atom, wherein two X ligands can be connected to form a ring;

each Y is independently Lewis Base; optionally, X and Y can be linked to form a ring;

m is 1 or 2;

n is 0, 1, or 2;

p is 1, or 2

the metal–ligand complex is overall charge-neutral;

N is nitrogen;

Q is carbon, silicon, or germanium;

R^1 and R^2 are independently selected from −H, (C_1−C_{40})hydrocarbyl, and (C_1−C_{40})heterohydrocarbyl;

R^3 are independently selected from (C_1−C_{40})hydrocarbyl, and (C_1−C_{40})heterohydrocarbyl;

R^4, R^5, R^6, and R^7 are independently (C_1−C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl wherein any of the R^4, R^5, R^6, and R^7 optionally are connected to form a ring structure;

M^2 is titanium, zirconium, or hafnium;

each X^2 is independently selected from (C_1−C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, $-CH_2Si(R^C)_{3-J}(OR^C)_J$, $-Si(R^C)_{3-J}(OR^C)_Q$, $-OSi(R^C)_{3-J}(OR^C)_J$, $-CH_2Ge(R^C)_{3-J}(OR^C)_J$, $-Ge(R^C)_{3-J}(OR^C)_J$, $-P(R^C)_{2-K}(OR^C)_K$, $-P(O)(R^C)_{2-K}(OR^C)_K$, $-N(R^C)_2$, $-NH(R^C)$, $-N(Si(R^C)_3)_2$, $-NR^CSi(R^C)_3$, $-NHSi(R^C)_3$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-OS(O)_2R^C$, $-N=C(R^C)_2$, $-N=CH(R^C)$, $-N=CH_2$, $-N=P(R^C)_3$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R^C)C(O)R^C$, $-N(R^C)C(O)H$, $-NHC(O)R^C$, $-C(O)N(R^C)_2$, $-C(O)NHR^C$, $-C(O)NH_2$, a halogen, $B(R^Y)_4$, $Al(R^Y)_4$, or $Ga(R^Y)_4$, or a hydrogen, wherein each R^C is independently a (C_1−C_{30})hydrocarbyl, or (C_1−C_{30})heterohydrocarbyl, and each J is 0, 1, 2 or 3, and each K is 0, 1, or 2; each R^Y is –H, (C_1−C_{30})hydrocarbyl, or halogen atom, wherein two X^2 ligands can be connected to form a ring;

A is $–C(R^8)C(R^9)–$, $−CH(R^8)CH(R^9)−$, or $−CH(R^8)CH(R^9)CH(R^{10})−$, and optionally:

R^{17} and R^8 may be connected to form an aromatic or non-aromatic ring; or R^8 and R^9 may be connected to form an aromatic or non-aromatic ring; or when A is $–C(R^8)C(R^9)C(R^{10})–$, R^9 and R^{10} may be connected to form an aromatic or non-aromatic ring, or R^{10} and R^{11} may be connected to form an aromatic or non-aromatic ring; or

when A is $–C(R^8)C(R^9)–$, R^9 and R^{11} may be connected to form an aromatic or non-aromatic ring;

R8 and R9 are independently (C1-C50)hydrocarbyl, (C1-C50)heterohydrocarbyl, (C6-C30)aryl, (C5-C30)heteroaryl, or H;

R^{10}, R^{11}, and R^{17} are independently $(C_1–C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{30})$aryl, $(C_5–C_{30})$heteroaryl; and

R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} are each independently $(C_1–C_{12})$alkyl, halogen substituted $(C_1–C_{12})$ alkyl, halogen substituted $(C_6–C_{18})$ aryl, halogen substituted $(C_3–C_{50})$ cycloalkyl, or –H.

2. The polymerization process according to claim 1, wherein the polymerization process occurs in the presence of hydrogen feed.

3. The polymerization process according to claim 1, wherein the polymerization process occurs in the absence of hydrogen feed.

4. The polymerization process according to claim 1, wherein R^1 and R^2 are methyl, ethyl, propyl, isopropyl, isobutyl or phenyl.

5. The polymerization process according to any one of claims 1-4, wherein R^3 is independently $(C_1–C_{12})$alkyl.

6. The polymerization process according to any one claims 1-5, wherein R^4, R^5, R^6, and R^7 are methyl; or R^4 and R^7 are methyl, or R^5 and R^6 are methyl or R^6 and R^7 are methyl.

7. The polymerization process according to any one claims 1-6, wherein R^6 is –OMe; or R^5 is $–NMe_2$.

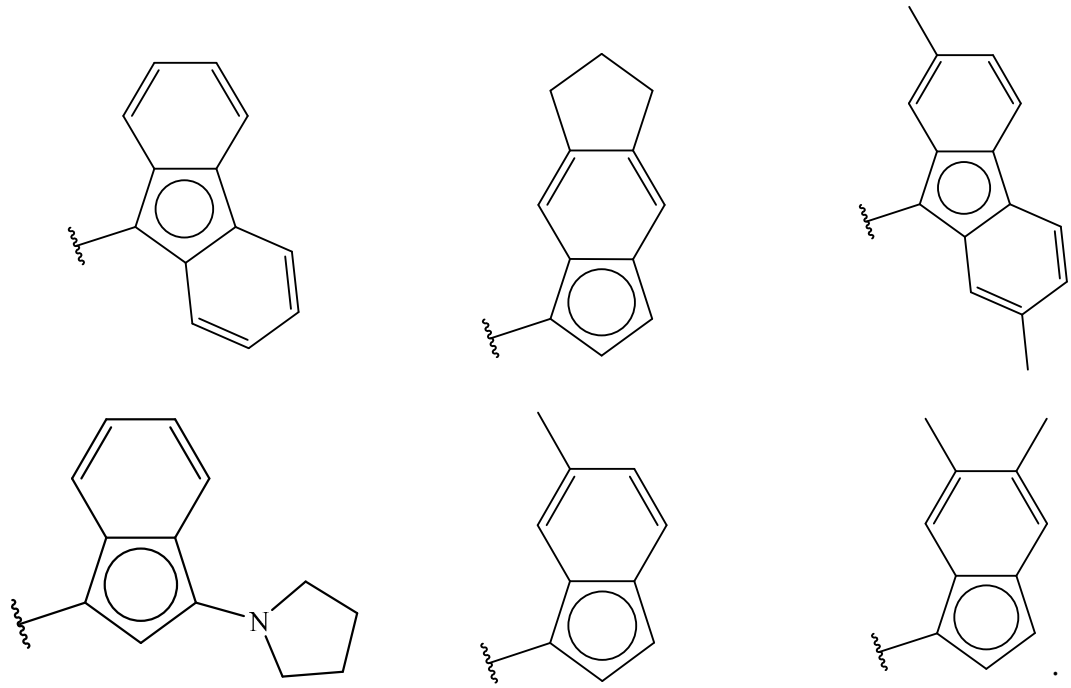
8. The polymerization process according to any one of claims 1 to 4, wherein:

(A) R^4 and R^5 are connected and form a ring optionally substituted by one or more R^S wherein R^S is selected from the group consisting of $(C_1–C_{30})$hydrocarbyl; or

(B) R^6 and R^7 are connect and form ring optionally substituted by one or more R^S wherein R^S is selected from the group consisting of $(C_1–C_{30})$hydrocarbyl; or

(C) both (A) and (B);

wherein (A), (B), or (C) and the cyclopentadienyl of formula (I) have a structure selected from the group consisting of:



9. The polymerization process according to any one of claims 1-8, wherein A is $-C(R^8)C(R^9)-$ or $-C(R^8)C(R^9)C(R^{10})-$.

10. The polymerization process according to any one of claims 1-9, wherein R^8 and R^9 are (C_1-C_{20})alkyl or –H, and R^{11} and R^{17} are substituted (C_6-C_{18})aryl.

11. The polymerization process according to any one of claims 1-10, wherein R^8, R^9, and R^{10} are independently selected independently selected from the group consisting of: methyl, ethyl, 1-propyl, 2-propyl (also called *iso*-propyl), 1,1-dimethylethyl (also called *tert*-butyl), cyclopentyl, cyclohexyl, 1-butyl, pentyl, 3-methylbutyl, hexyl, 4-methylpentyl, methoxy, dimethylamino, heptyl, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

12. The polymerization process according to any one of claims 1-11, wherein the polymerization process is a solution polymerization reaction.

13. An ethylene-based polymer produced from the polymerization process of any one of claims 1-12.

14. The ethylene-based polymer of claim 13, wherein the ethylene-based polymer is a bimodal polymer.