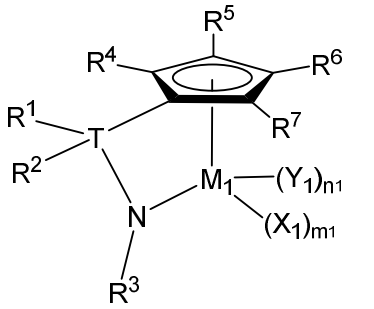
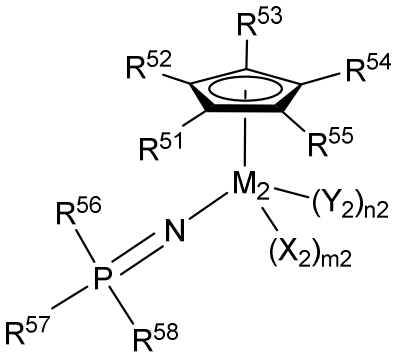
CLAIMS

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 and optionally hydrogen gas; 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 phosphinimine procatalyst according to formula (V):



(I)



(V)

where:

M_1 is titanium, zirconium, hafnium, or scandium;

each X_1 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_1 ligands can be connected to form a metallacycle ring;

each Y_1 is independently Lewis Base; optionally, X_1 and Y_1 can be linked to form a ring;

m_1 is 1 or 2;

n_1 is 0, 1 or 2;

the procatalysts (I) and (V) are overall charge-neutral;

N is nitrogen;

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

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 H, (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 one ring structure or a multi-ring structure;

M_2 is titanium, zirconium, or hafnium;

each X_2 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_2 ligands can be connected to form a metallacycle ring;

each Y_2 is independently Lewis Base; optionally, X_2 and Y_2 can be linked to form a ring.

m_2 is 1 or 2;

n_2 is 0, 1 and 2;

R^{51}, R^{52}, R^{53}, R^{54}, and R^{55} are independently H, (C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl wherein any of the R^{52}, R^{53}, R^{54}, and R^{55} optionally are connected to form one ring structure or a multi-ring structure;

R^{56}, R^{57}, and R^{58} are independently (C_1–C_{20})hydrocarbyl, (C_1–C_{20})heterohydrocarbyl, (C_6–C_{30})aryl, (C_5–C_{30})heteroaryl wherein two of R^{56}, R^{57}, and R^{58} are optionally connected to form a ring.

2. The polymerization process according to claim 1, wherein the ratio of hydrogen chain transfer constants for the procatalyst of formula (V) to the procatalyst of formula (I) is greater than or equal to 3 at 160 °C.

3. The polymerization process according to claim 1, wherein R^1 and R^2 are methyl, ethyl, propyl, isopropyl, isobutyl,phenyl, para-tolyl

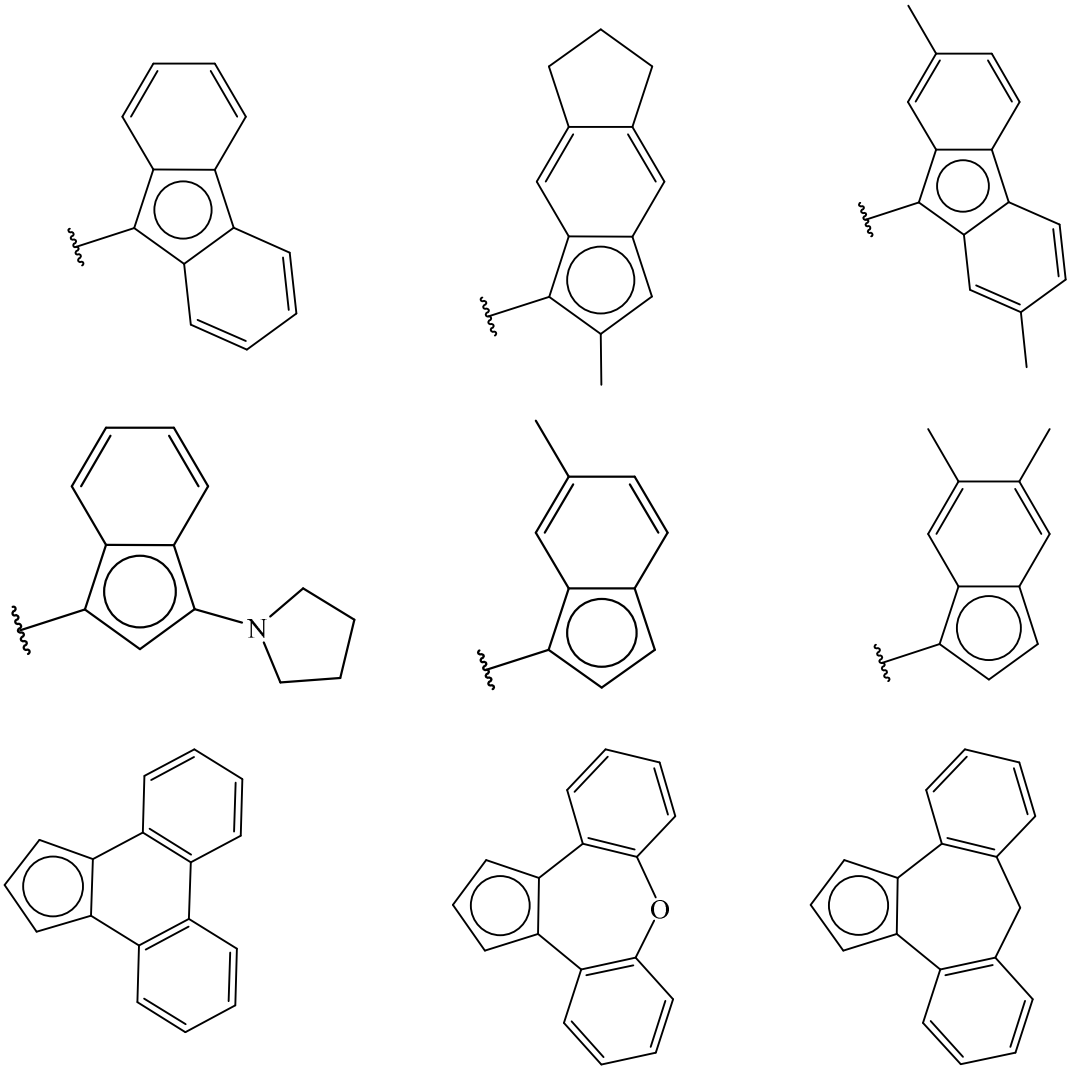
4. The polymerization process according to any one of claims 1 to 3, wherein R^3 is independently (C_1–C_{12})alkyl.

5. The polymerization process according to any one of claims 1 to 4, wherein R^4, R^5, R^6, and R^7 are 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, heptyl, dimethylamino, pyrrolidino, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

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

7. 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; or
(B) R^6 and R^7 are connect and form ring optionally substituted by one or more R^S; 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:



8. The polymerization process according to any one of claims 1 to 7, wherein one of R^{51}, R^{52}, R^{53}, R^{54}, and R^{55} is selected from –OMe and–NMe_2.

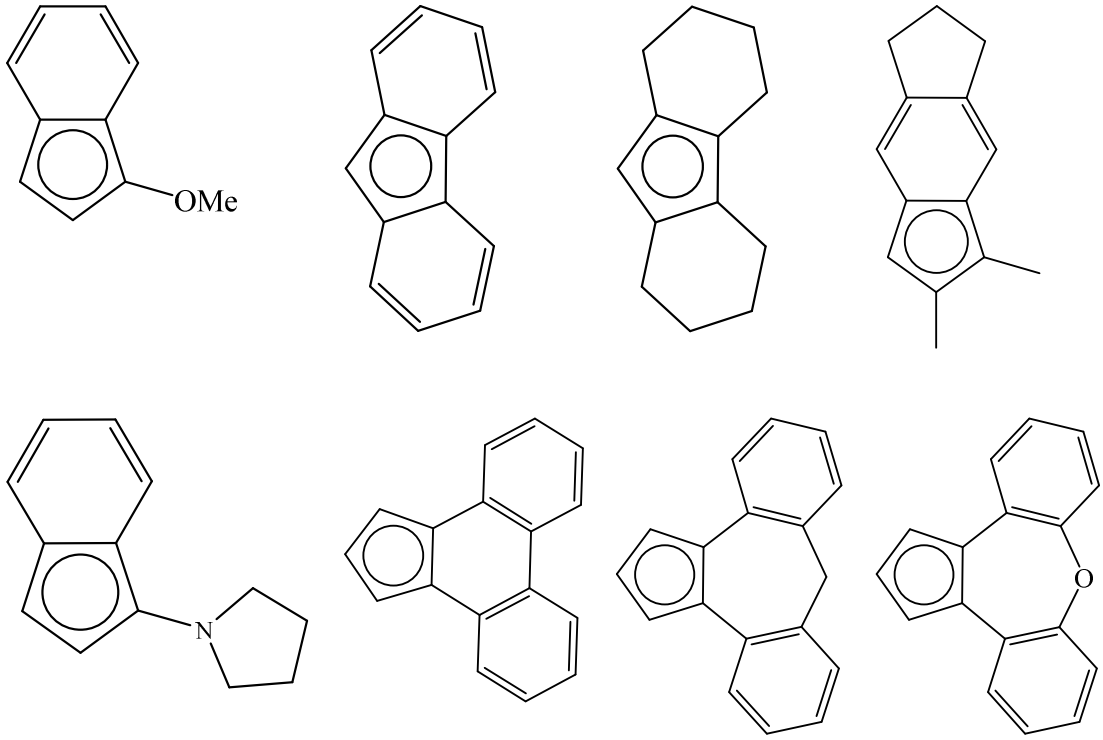
9. The polymerization process according to any one of claims 1 to 7, wherein:

(A) R^{51} and R^{52} are connected and form a ring and are optionally substituted by one or more R^S; or

(B) R^{53} and R^{54} are connected and form a ring and are optionally substituted by one or more R^S; or

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

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



10. The polymerization process according to any one of claims 1–9, wherein R^{56}, R^{57}, R^{58} are independently (C_1–C_{20})alkyl.

11. The polymerization process according to any one of claims 1–10, wherein R^{56}, R^{57}, R^{58} are 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, 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 to 11, wherein R^{51}, R^{52}, R^{53}, R^{54}, and R^{55} are 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, heptyl, dimethylamino, pyrrolidino, *n*-octyl, *tert*-octyl (also called 2,4,4-trimethylpentan-2-yl), nonyl, and decyl.

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