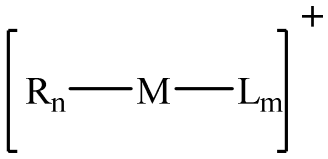
CLAIMS

1. A process of polymerizing olefins, the process comprising polymerizing ethylene and optionally one or more α-olefin monomers in the presence of a catalyst system, the catalyst system comprising a procatalyst and a metallic activator ionic complex, wherein the metallic activator ionic complex comprises a cation and a weakly coordinating anion, the cation having a structure according to formula (I):



(I)

where:

M is magnesium, boron, aluminum, gallium, zinc, silicon or germanium;

when M is zinc or magnesium, n is 1;

when M is boron, aluminum, or gallium, n is 2;

when M is silicon or germanium, n is 3;

m is 1, 2, or 3;

each R is a ligand independently selected from the group consisting of (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, –OR^C, –SiC^R, –$CH_2Si(OR^C)_wR^C{}_Y$, –$CH_2Si(NR^N)_wR^C{}_Y$, −NR^N, and −$NR^N{}_2$; where R^C is (C_1−C_{30})hydrocarbyl, R^N is (C_1−C_{30})hydrocarbyl or hydrogen, w is 1, 2, or 3, and y is 0, 1, or 2, provided that the sum of w plus y is 3; and

each L is a neutral Lewis base; and

provided that:

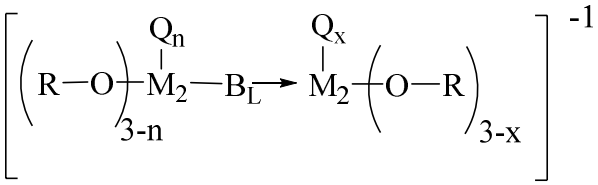
when n is 2 or 3, each R is optionally covalently connected to form a multidentate ligand; and

when m is 2 or 3, each L is optionally covalently connected to form a Lewis base having at least two coordinating atoms; and

wherein one of:

the anion is $[B(C_6F_5)_4]^-$;

the anion has a structure according to formula (II):



(II)

where:

each M_2 is independently aluminum, boron, or gallium;

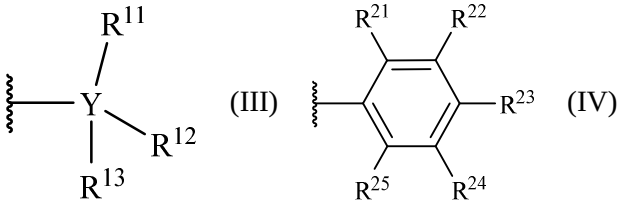
B_L is chosen from a species having at least two Lewis basic sites;

each Q is independently a monodentate ligand;

n is 0, 1, 2, or 3, wherein when n is 0, Q of Q_n is not present;

x is 0, 1, 2, or 3, wherein when x is 0, Q of Q_x is not present;

each R is independently selected from the group consisting of radicals having formula (III) and radicals having formula (IV):



(III) (IV)

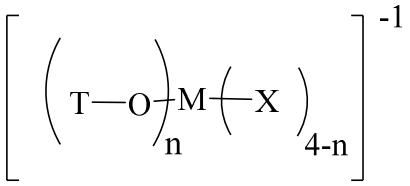
each Y is independently carbon or silicon;

each R^{11}, R^{12}, R^{13}, R^{21}, R^{22}, R^{23}, R^{24}, and R^{25}, is independently chosen from $(C_1–C_{40})$alkyl, $(C_6–C_{40})$aryl, –H, $–NR^N_2$, $–OR^C$, $–SR^C$, or halogen, wherein when R is a radical according to formula (III), at least one of R^{11}, R^{12}, or R^{13} is perhalogenated $(C_1–C_{40})$alkyl , perhalogenated $(C_6–C_{40})$aryl, or −F; and when R is a radical according to formula (IV), at least one of R^{21}, R^{22}, R^{23}, R^{24}, and R^{25} is perhalogenated $(C_1–C_{40})$alkyl , perhalogenated $(C_6–C_{40})$aryl, or −F;

optionally, when n is 0 or 1, two R groups in formula (II) are covalently connected; and

each R^N or R^C is independently $(C_1–C_{30})$hydrocarbyl or –H;

the anion has a structure according to formula (IX):



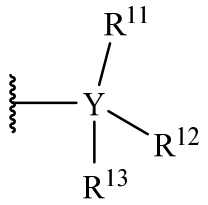
(IX)

where:

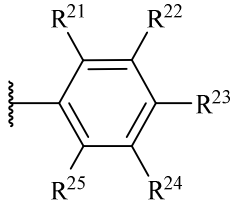
M is aluminum, boron, or gallium;

n is 1, 2, 3, or 4;

each T is independently selected from the group consisting of radicals having formula (XI) and radicals having formula (XI):



(X)

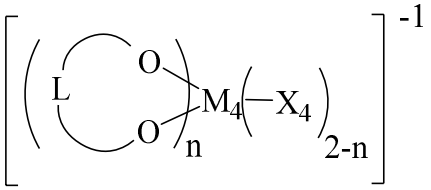


(XI)

where each Y, R^{11}, R^{12}, R^{13}, R^{21}, R^{22}, R^{23}, R^{24}, and R^{25} is defined in claim 10 and

each X is a monodentate ligand independently chosen from halogen-substituted $(C_1–C_{20})$alkyl, $(C_1–C_{20})$alkyl, halogen-substituted $(C_6–C_{40})$aryl, $(C_6–C_{40})$aryl, triflate, or $–S(O)_3R^C$;

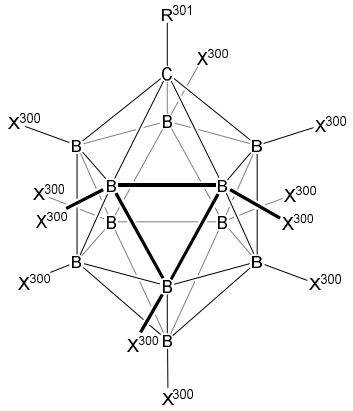
optionally, two groups T in formula (IX) are covalently connected and the anion has a structure according to formula (XII):



(XII)

each R^C is independently $(C_1–C_{30})$hydrocarbyl or –H; or

the anion has a structure according to formula the anion has a structure according to formula (XXX):



(XXX)

wherein R^{301} and each X^{300} are each independently selected from a halogen, a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, or a substituted or unsubstituted (C_1−C_{40})heterohydrocarbyl, $Si(R^C)_3$, $Si(N(R^C)_2)_3$, $Si(O(R^C)_2)_3$, $Ge(R^C)_3$, $Ge(N(R^C)_2)_3$, $Ge(O(R^C)_2)_3$, $P(R^C)_2$, $P(N(R^C)_2)_2$, $P(OR^C)_2$, $N(R^C)_2$, $NH(R^C)$, NH_2, OH, SH, OR^C, SR^C, NO_2, CN, $-CF_3$, $-CF_2R^C$, $-CF(R^C)_2$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R^C)-$, $(R^C)_2NC(O)-$, or hydrogen, wherein each R^C is independently a substituted or unsubstituted (C_1-C_{35})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{35})heterohydrocarbyl;

wherein:

two or more of X^{300} may optionally form one or more ring structures;

two or more of X^{300} and R^{301} may optionally form one or more ring structures; and

one or more hydrogen atoms may optionally be substituted with deuterium; and at least one of X^{300} or R^{301} is a halogen atom;

2. The process of claim 1, wherein n is 2 or 3 and at least two groups R in formula (I) are covalently connected.

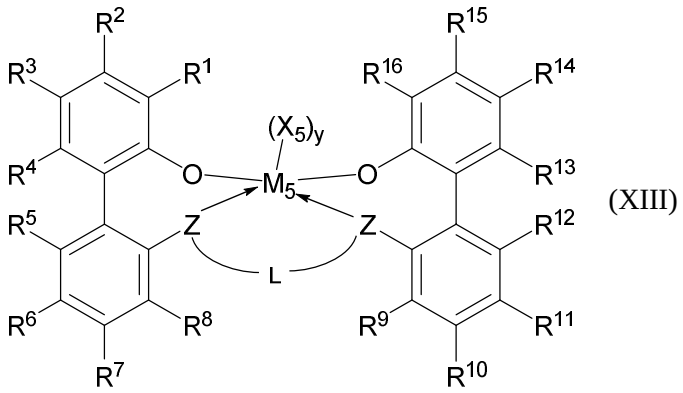
3. The process of claim 1 or claim 2, wherein m is 2 or 3 and at least two groups L in formula (I) are covalently connected.

4. The process of any previous claim, wherein R is (C_1–C_{10})alkyl, –OR^C, wherein R^C is (C_1–C_{10})alkyl, or –NR^N_2, where R^N is (C_6–C_{15})aryl.

5. The process of any previous claim, wherein L is tetrahydrofuran or trimethylamine or wherein m is 2 and each L is OEt_2.

6. The process of any previous claim, wherein each R is octyl, $–CH_3$, $–OCH_3$, or $–NPh_2$.

7. The process of any one previous claims, wherein the procatalyst has the structure according to formula (XIII):



(XIII)

where:

M_5 is titanium, zirconium, or hafnium;

y is 1, 2, or 3;

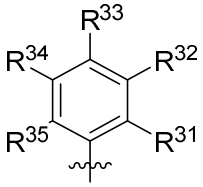
each X_5 is a monodentate ligand independently chosen from unsaturated (C_2–C_{50})hydrocarbon, unsaturated (C_2–C_{50})heterohydrocarbon, saturated (C_2–C_{50})heterohydrocarbon, (C_1–C_{50})hydrocarbyl, (C_6–C_{50})aryl, (C_6–C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4–C_{12})diene, halogen, –$N(R^N)_2$, and –$N(R^N)COR^C$;

the metal–ligand complex is overall charge-neutral;

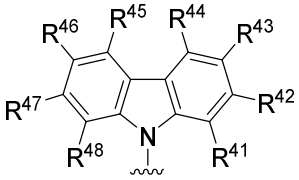
each Z is independently chosen from –O–, –S–, –$N(R^N)$–, or –$P(R^P)$–;

R^1 and R^{16} are independently selected from the group consisting of –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, –$Si(R^C)_3$, –$Ge(R^C)_3$, –$P(R^P)_2$,

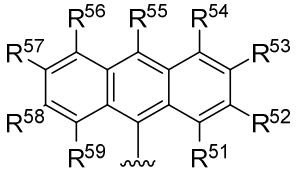
$-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $-N=C(R^C)_2$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, halogen, radicals having formula (XIV), radicals having formula (XV), and radicals having formula (XVI):



(XIV)



(XV)



(XVI)

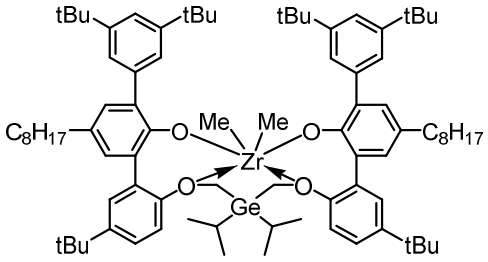
where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from –H, $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$,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

L is $(C_1–C_{40})$hydrocarbylene or $(C_2–C_{40})$heterohydrocarbylene; and

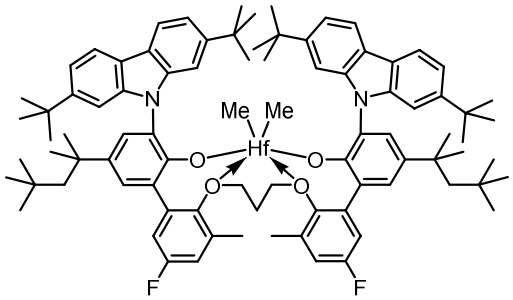
each R^C, R^P, and R^N in formula (I) is independently a $(C_1–C_{30})$hydrocarbyl, $(C_1–C_{30})$heterohydrocarbyl, or −H.

8. The process of any previous claim, wherein the procatalyst has the structure according to formula (XVII):



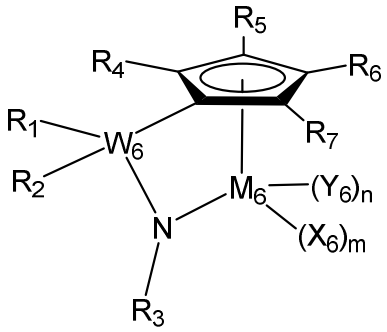
(XVII)

9. The process of any one of claims 1 to 7, wherein the procatalyst has the structure according to formula (XVIII):



(XVIII)

10. The process of any one of claims 1 to 7, wherein the procatalyst has the structure according to formula (XX):



(XX)

where

M_6 is hafnium, titanium or zirconium; n is 0, 1, or 2; m is 0, 1, or 2, provided that when m is 2, n is 0 and when n is 2, m is 0; and

each X_6 is a monodentate ligand independently chosen from (C_1–C_{50})hydrocarbon, (C_1–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, hydrogen, –$N(R^N)_2$, and –$NCOR^C$. The metal–ligand complex is overall charge-neutral;

each Y_6 is independently a Lewis base;

N is nitrogen; W_6 is carbon or silicon and is covalently bonded to cyclopentadiene; and 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; and

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.

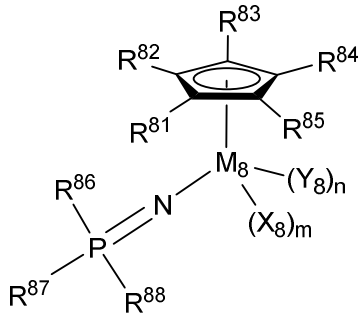
11. The process according to any previous claim, wherein the process further comprises a reactor at a reaction temperature.

12. The process of claim 11, wherein the reactor is a solution reactor comprising one or more solvents.

13. The process of claim 12, wherein the solvent is a hydrocarbon, an aliphatic hydrocarbon, a non-halogenated hydrocarbon, a non-aromatic hydrocarbon or combinations thereof.

14. The process according to any one of claims 11 to 13, wherein the reaction temperature is 120 °C-225 °C.

15. The process of any one of claims 1 to 7 and 11 to 14, wherein the procatalyst has the structure according to formula (XXVI):



(XXVI)

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, −$CF_3$, −$OCF_3$, a halogen, wherein each Q is 0, 1, 2 or 3, and each W is 0, 1, or 2; wherein two X ligands can be connected to form a ring, wherein one member of the ring is M_8;

each Y_8 is independently Lewis Base; optionally, X and Y can be linked to form a ring. Each subscript m is 1 and 2; and each subscript n is 0, 1 and 2. The metal–ligand complex is overall charge-neutral;

M_8 is titanium, zirconium, or hafnium; R^{81}, R^{82}, R^{83}, R^{84}, and R^{85} are independently $(C_1–C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl wherein any of the R^{82}, R^{83}, R^{84}, and R^{85} optionally are connected to form a ring structure; R^{86}, R^{87}, and R^{88} 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^{86}, R^{87}, and R^{88} are optionally connected to form a ring; and

R^{81}, R^{82}, R^{83}, R^{84}, and R^{85} are independently $(C_1–C_{50})$hydrocarbyl, wherein R^{81} and R^{82} are optionally connected to form a ring, or R^{82} and R^{83} are optionally connected to form a ring, R^{83} and R^{84} are optionally connected to form a ring, R^{84} and R^{55} optionally are connected to form a ring. In various embodiments, R^{86}, R^{87}, and R^{88} 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; and

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