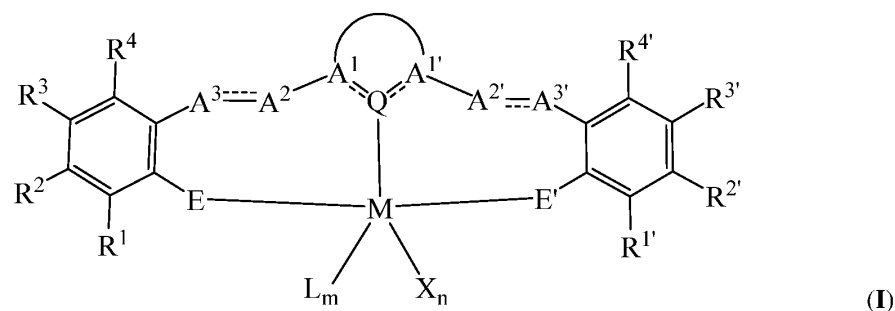


Claims

What is claimed is

1. A polymerization process comprising contacting in a homogeneous phase ethylene and an optional comonomer selected from C₃ to C₄₀ alpha olefins with a catalyst system comprising
- 5 activator and catalyst compound represented by the Formula (I):



wherein:

- M is a group 3, 4, 5, or 6 transition metal or a Lanthanide;
- E and E' are each independently O, S, or NR⁹ where R⁹ is independently hydrogen, a
- 10 C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl or a heteroatom-containing group;
- Q is group 14, 15, or 16 atom that forms a dative bond to metal M;
- A¹QA^{1'} are part of a heterocyclic Lewis base containing 4 to 40 non-hydrogen atoms that links A² to A^{2'} via a 3-atom bridge with Q being the central atom of the 3-atom bridge, A¹ and A^{1'} are independently C, N, or C(R²²), where R²² is selected from hydrogen, C₁-C₂₀
- 15 hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl;
- A³---A² is a divalent group containing 2 to 40 non-hydrogen atoms that links A¹ to the E-bonded aryl group via a 2-atom bridge;
- A^{2'}---A^{3'} is a divalent group containing 2 to 40 non-hydrogen atoms that links A^{1'} to the E'-bonded aryl group via a 2-atom bridge;
- 20 L is a Lewis base;
- X is an anionic ligand;
- n is 1, 2 or 3;
- m is 0, 1, or 2;
- n+m is not greater than 4;
- 25 each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, and one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be

joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings;

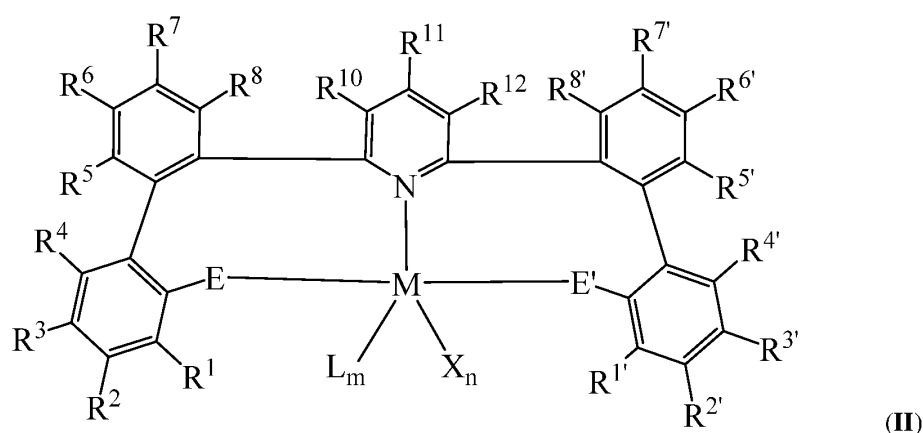
any two L groups may be joined together to form a bidentate Lewis base;

5 an X group may be joined to an L group to form a monoanionic bidentate group;

any two X groups may be joined together to form a dianionic ligand group;

and obtaining a polymer comprising greater than 35 mole% ethylene.

2. The process of claim 1 where the catalyst compound represented by the Formula (II):



wherein:

M is a group 3, 4, 5, or 6 transition metal or a Lanthanide;

E and E' are each independently O, S, or NR⁹, where R⁹ is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group;

15 each L is independently a Lewis base;

each X is independently an anionic ligand;

n is 1, 2 or 3;

m is 0, 1, or 2;

n+m is not greater than 4;

20 each of R¹, R², R³, R⁴, R^{1'}, R^{2'}, R^{3'}, and R^{4'} is independently hydrogen, C₁-C₄₀ hydrocarbyl, C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R¹ and R², R² and R³, R³ and R⁴, R^{1'} and R^{2'}, R^{2'} and R^{3'}, R^{3'} and R^{4'} may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings; any two L groups may be joined together to form a bidentate Lewis base;

an X group may be joined to an L group to form a monoanionic bidentate group;

any two X groups may be joined together to form a dianionic ligand group;

each of R⁵, R⁶, R⁷, R⁸, R^{5'}, R^{6'}, R^{7'}, R^{8'}, R¹⁰, R¹¹, and R¹² is independently hydrogen, a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R⁵ and R⁶, R⁶ and R⁷, R⁷ and R⁸, R^{5'} and R^{6'}, R^{6'} and R^{7'}, R^{7'} and R^{8'}, R¹⁰ and R¹¹, or R¹¹ and R¹² may be joined to form one or more substituted hydrocarbyl rings, unsubstituted hydrocarbyl rings, substituted heterocyclic rings, or unsubstituted heterocyclic rings each having 5, 6, 7, or 8 ring atoms, and where substitutions on the ring can join to form additional rings.

10

3. The process of claim 1 or 2 wherein the M is Hf, Zr or Ti.

4. The process of claim 1, 2 or 3 wherein E and E' are each O.

15

5. The process of claim 1, 2, 3, or 4 wherein R¹ and R^{1'} is independently a C₄-C₄₀ tertiary hydrocarbyl group.

6. The process of claim 1, 2, 3, or 4 wherein R¹ and R^{1'} is independently a C₄-C₄₀ cyclic tertiary hydrocarbyl group.

20

7. The process of claim 1, 2, 3, or 4 wherein R¹ and R^{1'} is independently a C₄-C₄₀ polycyclic tertiary hydrocarbyl group.

25

8. The process any of claims 1 to 7 wherein each X is, independently, selected from the group consisting of substituted or unsubstituted hydrocarbyl radicals having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, and a combination thereof, (two X's may form a part of a fused ring or a ring system).

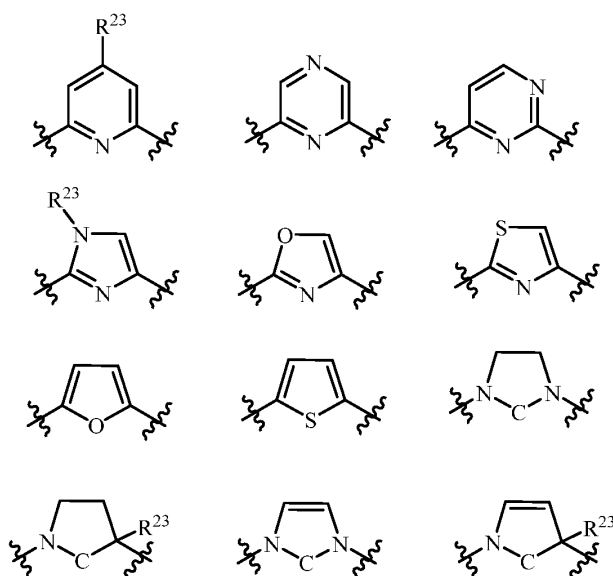
30

9. The process any of claims 1 to 8 wherein each L is, independently, selected from the group consisting of: ethers, thioethers, amines, phosphines, ethyl ether, tetrahydrofuran, dimethylsulfide, triethylamine, pyridine, alkenes, alkynes, allenes, and carbenes and a combinations thereof, optionally two or more L's may form a part of a fused ring or a ring system).

35

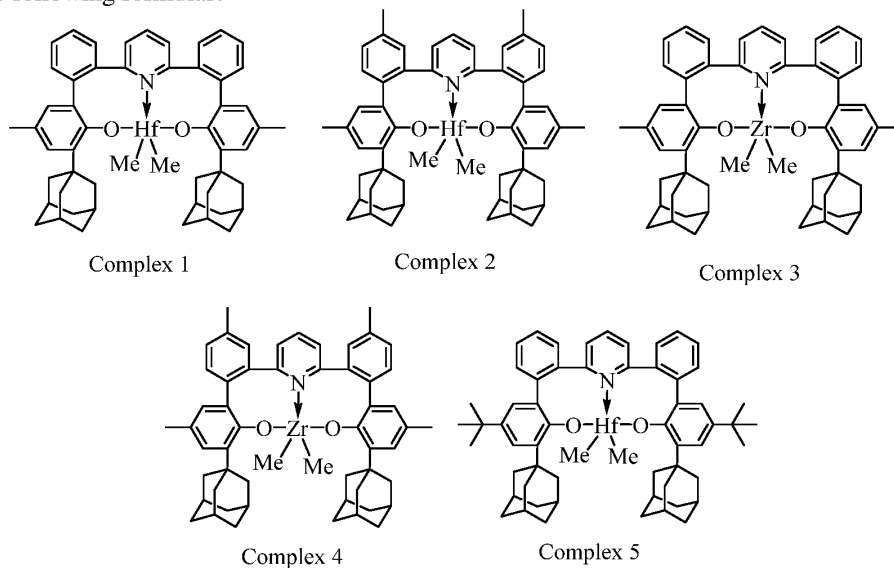
10. The process of claim 1, wherein M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls.

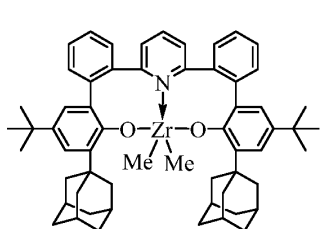
11. The process of claim 1, wherein M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and both R¹ and R^{1'} are adamantan-1-yl or substituted adamantan-1-yl.
- 5 12. The process of claim 1, wherein M is Zr or Hf, Q is nitrogen, both A¹ and A^{1'} are carbon, both E and E' are oxygen, and X is methyl or chloro, and n is 2.
13. The process of claim 1, wherein Q is nitrogen, A¹ and A^{1'} are both carbon, both R¹ and R^{1'} are hydrogen, both E and E' are NR⁹, where R⁹ is selected from a C₁-C₄₀ hydrocarbyl, a C₁-C₄₀ substituted hydrocarbyl, or a heteroatom-containing group.
- 10 14. The process of claim 1, wherein Q is carbon, A¹ and A^{1'} are both nitrogen, and both E and E' are oxygen.
- 15 15. The process of claim 1, wherein Q is carbon, A¹ is nitrogen, A^{1'} is C(R²²), and both E and E' are oxygen, where R²² is selected from hydrogen, C₁-C₂₀ hydrocarbyl, C₁-C₂₀ substituted hydrocarbyl.
16. The process of claim 1, wherein the heterocyclic Lewis base is selected from the groups represented by the following formulas:
- 20



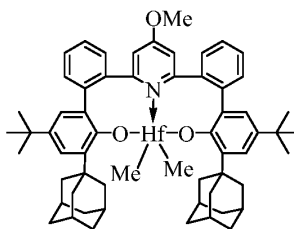
where each R²³ is independently selected from hydrogen, C₁-C₂₀ alkyls, and C₁-C₂₀ substituted alkyls.

17. The process of claim 2, wherein M is Zr or Hf, both E and E' are oxygen, and both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls.
18. The process of claim 2, wherein M is Zr or Hf, both E and E' are oxygen, and both R¹ and R^{1'} are adamantan-1-yl or substituted adamantan-1-yl.
19. The process of claim 2, wherein M is Zr or Hf, both E and E' are oxygen, and each of R¹, R^{1'}, R³ and R^{3'} are adamantan-1-yl or substituted adamantan-1-yl.
20. The process of claim 2, wherein M is Zr or Hf, both E and E' are oxygen, both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls, and both R⁷ and R^{7'} are C₁-C₂₀ alkyls.
21. The process of claim 2, wherein M is Zr or Hf, both E and E' are O, both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls, and both R⁷ and R^{7'} are C₁-C₂₀ alkyls.
22. The process of claim 2, wherein M is Zr or Hf, both E and E' are O, both R¹ and R^{1'} are C₄-C₂₀ cyclic tertiary alkyls, and both R⁷ and R^{7'} are C₁-C₃ alkyls.
23. The process of claim 1 wherein the catalyst compound is represented by one or more of the following formulas:

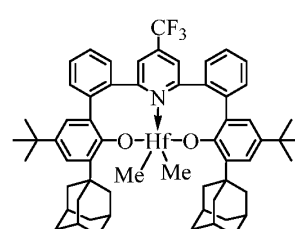




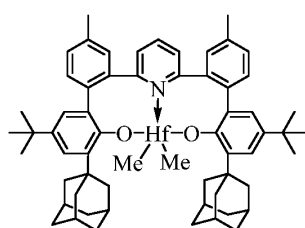
Complex 6



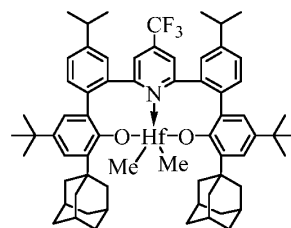
Complex 7



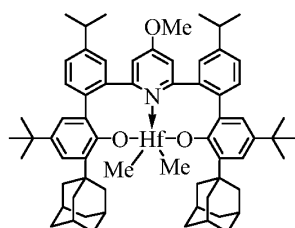
Complex 8



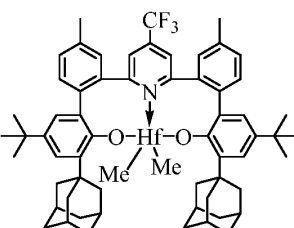
Complex 9



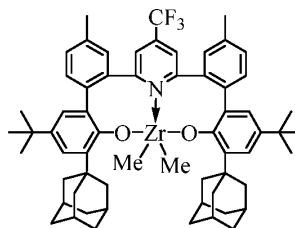
Complex 10



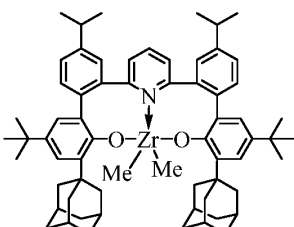
Complex 11



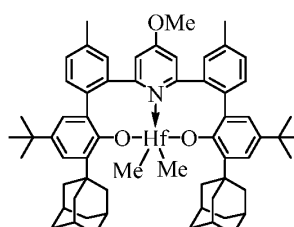
Complex 12



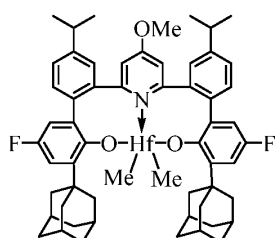
Complex 13



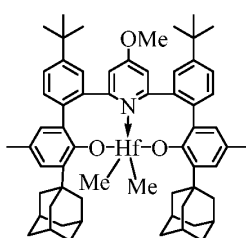
Complex 14



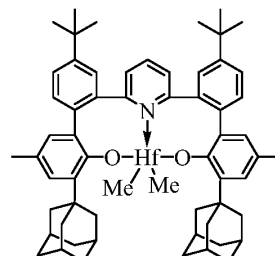
Complex 15



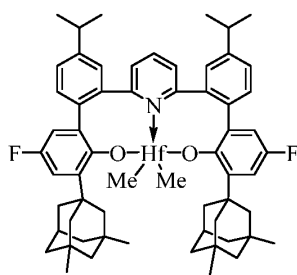
Complex 16



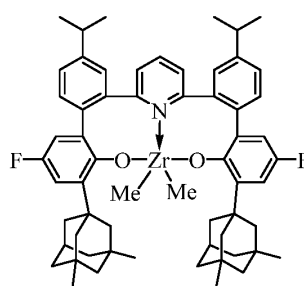
Complex 17



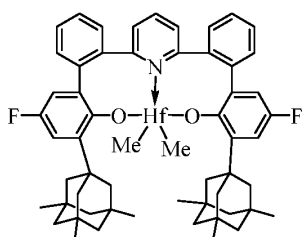
Complex 18



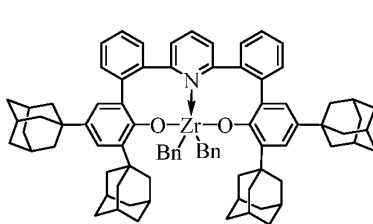
Complex 19



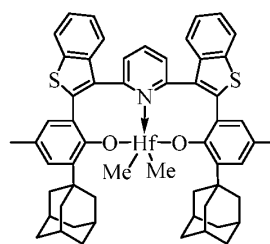
Complex 20



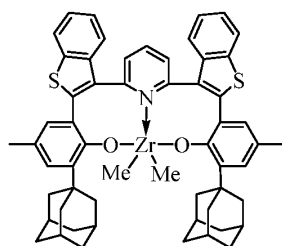
Complex 21



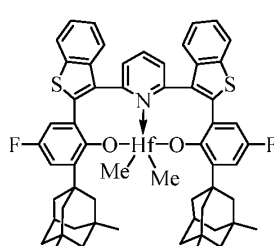
Complex 22



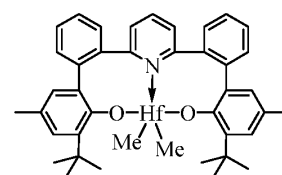
Complex 23



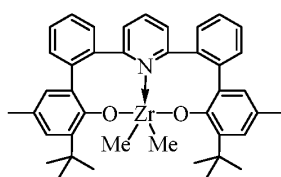
Complex 24



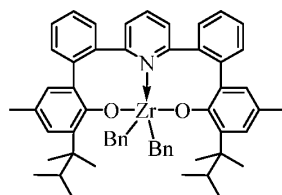
Complex 25



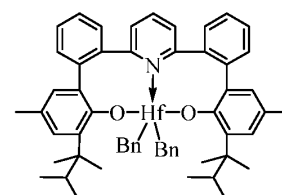
Complex 26



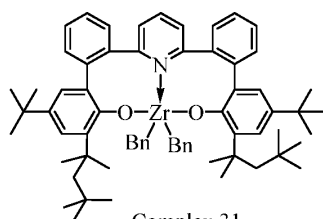
Complex 27



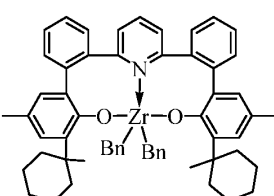
Complex 29



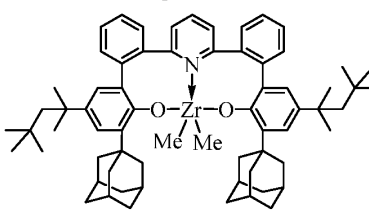
Complex 30



Complex 31

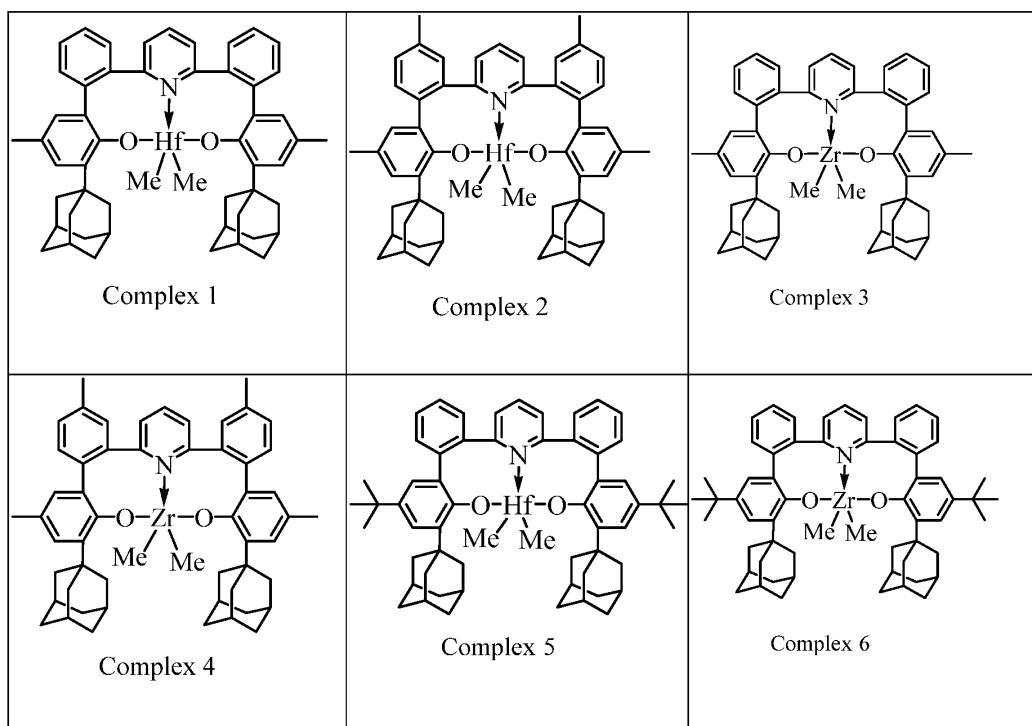


Complex 32

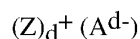


Complex 33

24. The process of claim 1 wherein the catalyst compound is one or more of

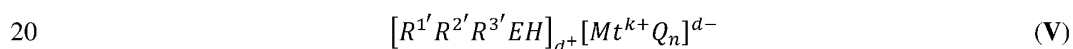


25. The process of any of claims 1 to 24, wherein the activator comprises an alumoxane or a non-coordinating anion.
26. The process of any of claims 1 to 24, wherein the activator is soluble in non-aromatic-hydrocarbon solvent.
27. The process of any of claims 1 to 24, wherein the catalyst system is free of aromatic solvent.
28. The process of any of claims 1 to 27, wherein the activator is represented by the formula:



- wherein Z is (L-H) or a reducible Lewis Acid, L is a neutral Lewis base; H is hydrogen; (L-H)⁺ is a Bronsted acid; A^{d-} is a non-coordinating anion having the charge d⁻; and d is an integer from 1 to 3.

29. The process of any of claims 1 to 27, wherein the activator is represented by the formula:



wherein:

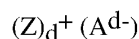
E is nitrogen or phosphorous;

d is 1, 2 or 3; k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6; $n - k = d$;

- R^1 , R^2 , and R^3 are independently a C_1 to C_{50} hydrocarbyl group optionally substituted
 5 with one or more alkoxy groups, silyl groups, a halogen atoms, or halogen containing groups,
 wherein R^1 , R^2 , and R^3 together comprise 15 or more carbon atoms;

Mt is an element selected from group 13 of the Periodic Table of the Elements; and
 each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide,
 aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or
 10 halosubstituted-hydrocarbyl radical.

30. The process of any of claims 1 to 27, wherein the activator is represented by the formula:



wherein A^{d-} is a non-coordinating anion having the charge d^- ; and d is an integer from 1 to 3

- 15 and $(Z)_d^+$ is represented by one or more of:

10		11		12	
13		14		15	
16		17		18	
19		20		21	

22		23		24	
25		26		27	
29		28		30	
31		32		33	
34		35		36	

31. The process of any of claims 1 to 27, wherein the activator is one or more of:
- N-methyl-4-nonadecyl-N-octadecylbenzenaminium tetrakis(pentafluorophenyl)borate,
N-methyl-4-nonadecyl-N-octadecylbenzenaminium tetrakis(perfluoronaphthalenyl)borate,
- 5 dioctadecylmethylammonium tetrakis(pentafluorophenyl)borate,
dioctadecylmethylammonium tetrakis(perfluoronaphthalenyl)borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate,
trimethylammonium tetrakis(perfluoronaphthalenyl)borate,
- 10 triethylammonium tetrakis(perfluoronaphthalenyl)borate,
tripropylammonium tetrakis(perfluoronaphthalenyl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthalenyl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthalenyl)borate,
N,N-dimethylanilinium tetrakis(perfluoronaphthalenyl)borate,
- 15 N,N-diethylanilinium tetrakis(perfluoronaphthalenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthalenyl)borate,
trollium tetrakis(perfluoronaphthalenyl)borate,

- triphenylcarbenium tetrakis(perfluoronaphthalenyl)borate,
triphenylphosphonium tetrakis(perfluoronaphthalenyl)borate,
triethylsilylium tetrakis(perfluoronaphthalenyl)borate,
benzene(diazonium) tetrakis(perfluoronaphthalenyl)borate,
5 trimethylammonium tetrakis(perfluorobiphenyl)borate,
triethylammonium tetrakis(perfluorobiphenyl)borate,
tripropylammonium tetrakis(perfluorobiphenyl)borate,
tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
tri(t-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
10 N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate,
tropillium tetrakis(perfluorobiphenyl)borate,
triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
15 triphenylphosphonium tetrakis(perfluorobiphenyl)borate,
triethylsilylium tetrakis(perfluorobiphenyl)borate,
benzene(diazonium) tetrakis(perfluorobiphenyl)borate,
[4-t-butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B],
trimethylammonium tetraphenylborate,
20 triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,
N,N-dimethylanilinium tetraphenylborate,
25 N,N-diethylanilinium tetraphenylborate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate,
tropillium tetraphenylborate,
triphenylcarbenium tetraphenylborate,
triphenylphosphonium tetraphenylborate,
30 triethylsilylium tetraphenylborate,
benzene(diazonium)tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl)borate,
triethylammonium tetrakis(pentafluorophenyl)borate,
tripropylammonium tetrakis(pentafluorophenyl)borate,

- tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl)borate,
- 5 N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate,
tropillium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate,
triphenylphosphonium tetrakis(pentafluorophenyl)borate,
triethylsilylium tetrakis(pentafluorophenyl)borate,
- 10 benzene(diazonium) tetrakis(pentafluorophenyl)borate,
trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate,
triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate,
- 15 dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
- 20 triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
- 25 triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(t-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
- 30 N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,

- triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
dicyclohexylammonium tetrakis(pentafluorophenyl)borate,
5 tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate,
tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(perfluorophenyl)borate,
1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium,
tetrakis(pentafluorophenyl)borate,
10 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine, and
triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).
32. The process of any of claims 1 to 31, wherein the process is a solution process.
- 15 33. The process of any of claims 1 to 32 wherein the process occurs at a temperature of from about 80°C to about 300°C, at a pressure in the range of from about 0.35 MPa to about 10 MPa, and at a residence time up to 300 minutes.
34. The process of any of claims 1 to 33 wherein the process is a continuous process.
- 20 35. The process of any of claims 1 to 34 further comprising obtaining a polyethylene composition with at least 20 mol% ethylene content.
36. The process of any of claims 1 to 34 further comprising obtaining an ethylene
25 copolymer wherein the copolymer has a composition of at least 20 mol% ethylene, and a shear thinning ratio that is greater than 30, and an I_{21}/I_2 greater than 10.
37. A polymer comprising ethylene and comonomer selected from propylene, butene, hexene and octene, where the copolymer has a composition of at least 20 mol% ethylene and a
30 melt index of 400 g/10min or less.
38. A polymer produced by the process of any of claims 1 to 36 comprising ethylene and one or more comonomer selected from propylene, butene, hexene and octene, where the copolymer has 30 to 50 mol% ethylene content.
- 35 39. A polymer produced by the process of any of claims 1 to 36 comprising ethylene and one or more comonomer selected from propylene, butene, hexene and octene, where the

copolymer has 50 to 70 mol% ethylene content.

40. A polymer produced by the process of any of claims 1 to 36 comprising ethylene and one or more comonomer selected from propylene, butene, hexene and octene, where the
5 copolymer has 70 to 90 mol% ethylene content.

41. A polymer produced by the process of any of claims 1 to 36 comprising ethylene and one or more comonomer selected from propylene, butene, hexene and octene, where the copolymer has 90 mol% or higher ethylene content.

10 42. A polymer produced by process of any of claims 1 to 34 comprising ethylene and one or more comonomer selected from propylene, butene, hexene and octene, where the copolymer has a branching index of 0.98 or less.

15 43. A copolymer produced by a polymerization process comprising contacting in a homogeneous phase ethylene and propylene with a catalyst system comprising an activator and group 4 bis(phenolate) catalyst compound, wherein the polymerization process takes place at a temperature of 90°C or higher in the absence of added hydrogen, to produce a polymer having:

- 20 (i) 65 to 80 mol% ethylene;
(ii) a shear thinning ratio (measured at 125°) of 70-150;
(iii) a phase angle (measured at 125°C) @ complex modulus $G^* = 500$ kPa of less than 50°;
(iv) a Mooney Large viscosity (measured at 125°C) of 80 to 120 mu; and
25 (v) a Mooney relaxation area (measured at 125°) of 550 to 3200 mu.sec.

44. A copolymer produced by a polymerization process comprising contacting in a homogeneous phase ethylene and propylene with a catalyst system comprising an activator and group 4 bis(phenolate) catalyst compound, wherein the polymerization process takes place at
30 a temperature of 120°C or higher in the presence of added hydrogen, to produce a polymer having:

- (i) 50 to 65 mol% ethylene;
(ii) a g'_{vis} of from 0.8 to 0.9;
(iii) a Mooney Large viscosity (measured at 125°C) of 35 to 40 mu;
35 (iv) a Mooney relaxation area (measured at 125°C) of 300-400 mu.sec.