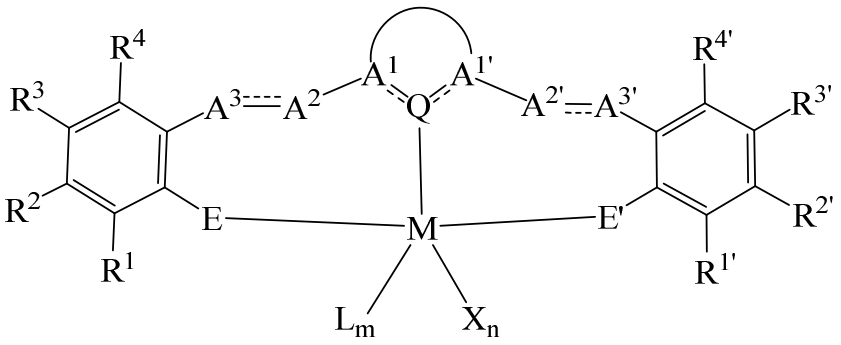
Claims

1. A polymerization process comprising contacting in a homogeneous phase ethylene and an optional comonomer selected from C_3 to C_{40} alpha olefins with a catalyst system comprising activator and catalyst compound represented by the Formula (**I**):



(**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 NR^9 where R^9 is independently hydrogen, a C_1-C_{40} hydrocarbyl, a C_1-C_{40} substituted hydrocarbyl or a heteroatom-containing group;

Q is group 14, 15, or 16 atom that forms a dative bond to metal M;

$A^1QA^{1'}$ are part of a heterocyclic Lewis base containing 4 to 40 non-hydrogen atoms that links A^2 to $A^{2'}$ via a 3-atom bridge with Q being the central atom of the 3-atom bridge, A^1 and $A^{1'}$ are independently C, N, or C(R^{22}), where R^{22} is selected from hydrogen, C_1-C_{20} hydrocarbyl, C_1-C_{20} substituted hydrocarbyl;

A^3----A^2 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;

$A^{2'}$---$A^{3'}$ 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;

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;

each of R^1, R^2, R^3, R^4, $R^{1'}$, $R^{2'}$, $R^{3'}$, and $R^{4'}$ is independently hydrogen, a C_1-C_{40} hydrocarbyl, a C_1-C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, and one or more of R^1 and R^2, R^2 and R^3, R^3 and R^4, $R^{1'}$ 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;

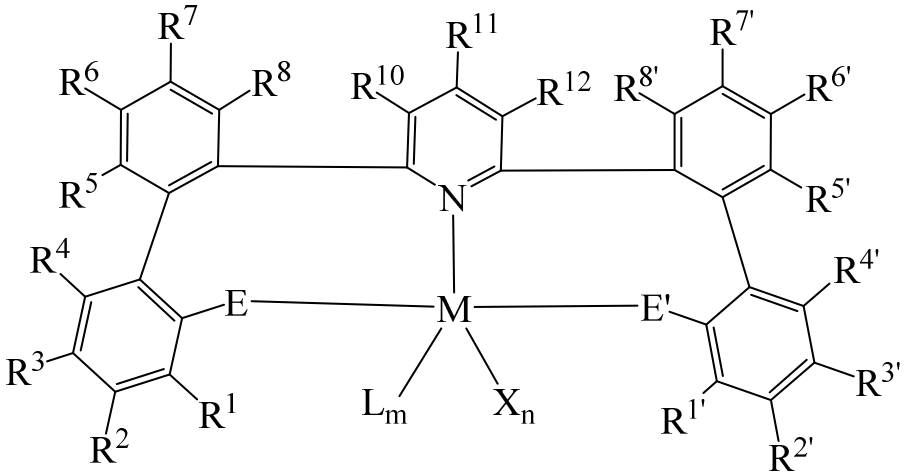
any two L groups may be joined together to form a bidentate Lewis base;

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;

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**):



(**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 NR^9, where R^9 is independently hydrogen, a C_1-C_{40} hydrocarbyl, a C_1-C_{40} substituted hydrocarbyl, or a heteroatom-containing group;

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;

each of R^1, R^2, R^3, R^4, $R^{1'}$, $R^{2'}$, $R^{3'}$, and $R^{4'}$ is independently hydrogen, C_1-C_{40} hydrocarbyl, C_1-C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R^1 and R^2, R^2 and R^3, R^3 and R^4, $R^{1'}$ 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 R^5, R^6, R^7, R^8, $R^{5'}$, $R^{6'}$, $R^{7'}$, $R^{8'}$, R^{10}, R^{11}, and R^{12} is independently hydrogen, a C_1-C_{40} hydrocarbyl, a C_1-C_{40} substituted hydrocarbyl, a heteroatom or a heteroatom-containing group, or one or more of R^5 and R^6, R^6 and R^7, R^7 and R^8, $R^{5'}$ and $R^{6'}$, $R^{6'}$ and $R^{7'}$, $R^{7'}$ and $R^{8'}$, R^{10} and R^{11}, or R^{11} and R^{12} 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.

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.

5. The process of claim 1, 2, 3, or 4 wherein R^1 and $R^{1'}$ is independently a C_4-C_{40} tertiary hydrocarbyl group.

6. The process of claim 1, 2, 3, or 4 wherein R^1 and $R^{1'}$ is independently a C_4-C_{40} cyclic tertiary hydrocarbyl group.

7. The process of claim 1, 2, 3, or 4 wherein R^1 and $R^{1'}$ is independently a C_4-C_{40} polycyclic tertiary hydrocarbyl group.

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).

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.

10. The process of claim 1, wherein M is Zr or Hf, Q is nitrogen, both A^1 and $A^{1'}$ are carbon, both E and $E^{'}$ are oxygen, and both R^1 and $R^{1'}$ are C_4-C_{20} cyclic tertiary alkyls.

11. The process of claim 1, wherein M is Zr or Hf, Q is nitrogen, both A^1 and $A^{1'}$ are carbon, both E and E' are oxygen, and both R^1 and $R^{1'}$ are adamantan-1-yl or substituted adamantan -1-yl.

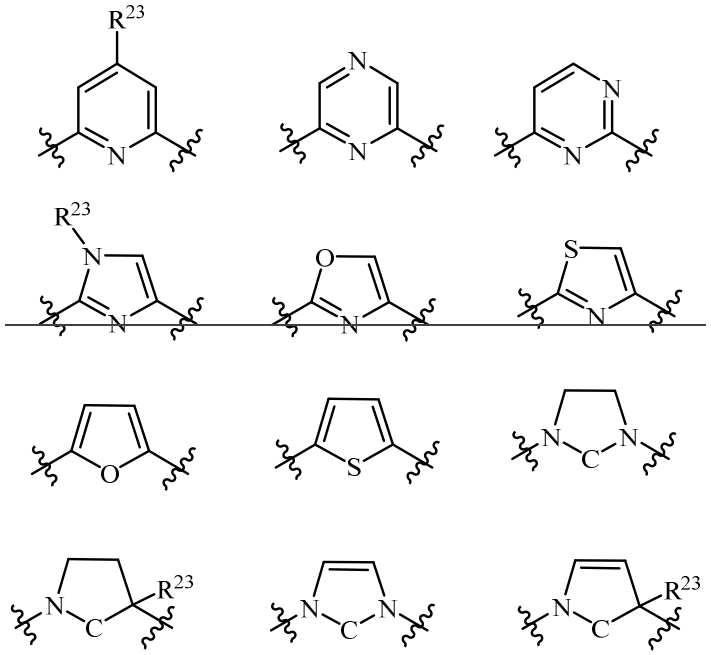
12. The process of claim 1, wherein M is Zr or Hf, Q is nitrogen, both A^1 and $A^{1'}$ are carbon, both E and E' are oxygen, and X is methyl or chloro, and n is 2.

13. The process of claim 1, wherein Q is nitrogen, A^1 and $A^{1'}$ are both carbon, both R^1 and $R^{1'}$ are hydrogen, both E and E' are NR^9, where R^9 is selected from a C_1-C_{40} hydrocarbyl, a C_1-C_{40} substituted hydrocarbyl, or a heteroatom-containing group.

14. The process of claim 1, wherein Q is carbon, A^1 and $A^{1'}$ are both nitrogen, and both E and E' are oxygen.

15. The process of claim 1, wherein Q is carbon, A^1 is nitrogen, $A^{1'}$ is $C(R^{22})$, and both E and E' are oxygen, where R^{22} is selected from hydrogen, C_1-C_{20} hydrocarbyl, C_1-C_{20} substituted hydrocarbyl.

~~16. The process of claim 1, wherein the heterocyclic Lewis base is selected from the groups represented by the following formulas:~~



~~where each R^{23} is independently selected from hydrogen, C_1-C_{20} alkyls, and C_1-C_{20} substituted alkyls.~~

~~17. The process of claim 2, wherein M is Zr or Hf, both E and E' are oxygen, and both R^1 and $R^{1'}$ are C_4-C_{20} cyclic tertiary alkyls.~~

~~18. The process of claim 2, wherein M is Zr or Hf, both E and E' are oxygen, and both R^1 and $R^{1'}$ are adamantan-1-yl or substituted adamantan-1-yl.~~

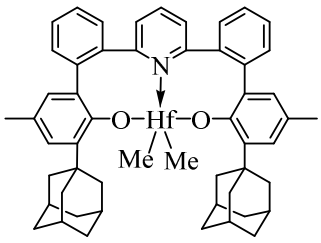
~~19. The process of claim 2, wherein M is Zr or Hf, both E and E' are oxygen, and each of R^1, $R^{1'}$, R^3 and $R^{3'}$ are adamantan-1-yl or substituted adamantan-1-yl.~~

~~20. The process of claim 2, wherein M is Zr or Hf, both E and E' are oxygen, both R^1 and $R^{1'}$ are C_4-C_{20} cyclic tertiary alkyls, and both R^7 and $R^{7'}$ are C_1-C_{20} alkyls.~~

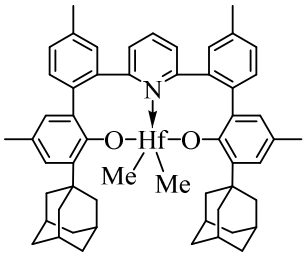
~~21. The process of claim 2, wherein M is Zr or Hf, both E and E' are O, both R^1 and $R^{1'}$ are C_4-C_{20} cyclic tertiary alkyls, and both R^7 and $R^{7'}$ are C_1-C_{20} alkyls.~~

~~22. The process of claim 2, wherein M is Zr or Hf, both E and E' are O, both R^1 and $R^{1'}$ are C_4-C_{20} cyclic tertiary alkyls, and both R^7 and $R^{7'}$ are C_1-C_3 alkyls.~~

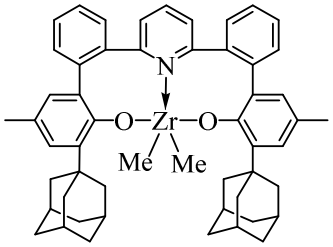
~~23~~16. The process of claim 1 wherein the catalyst compound is represented by one or more of the following formulas:



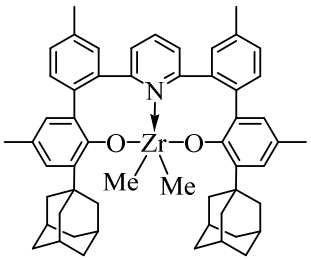
Complex 1



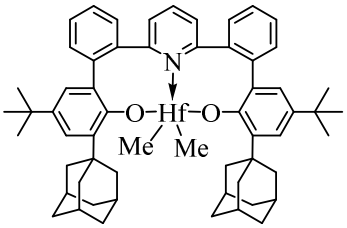
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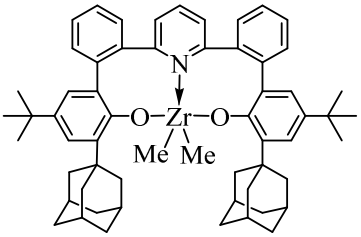
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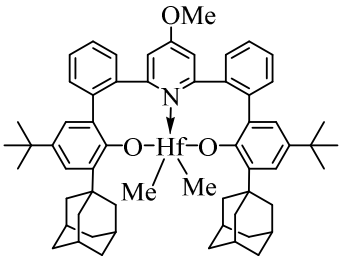
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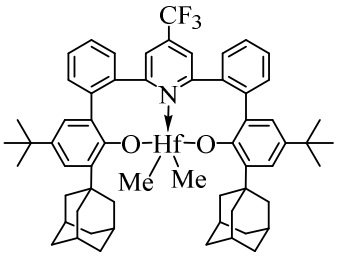
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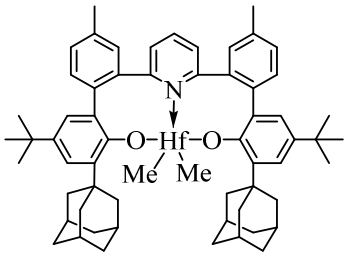
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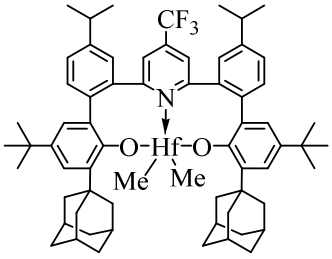
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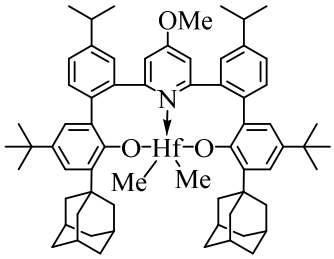
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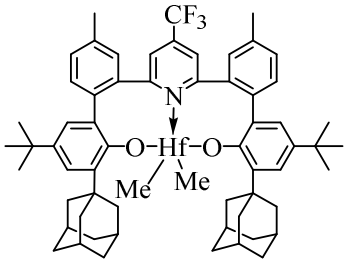
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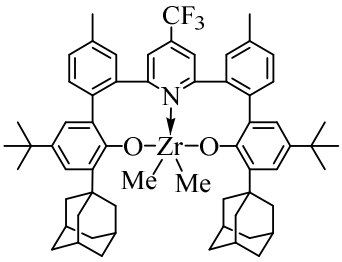
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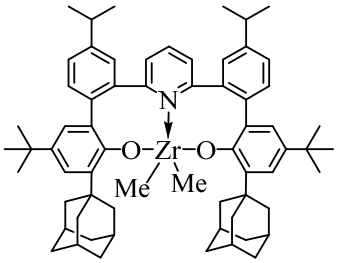
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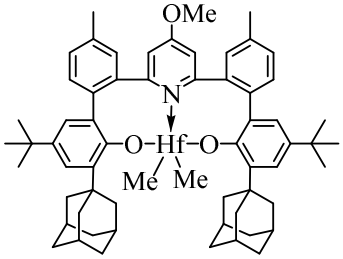
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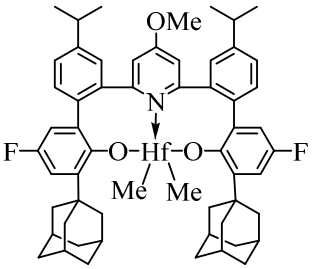
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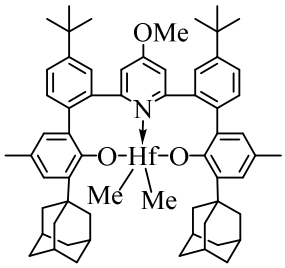
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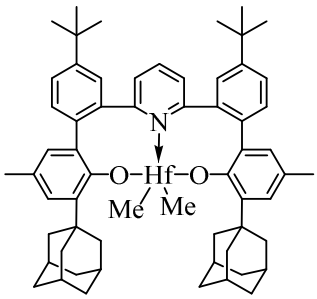
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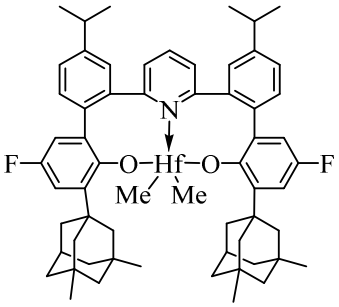
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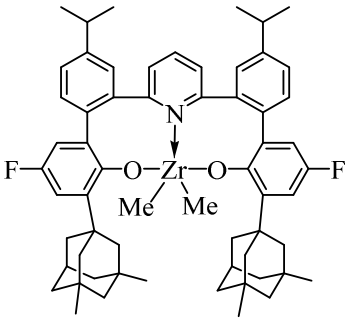
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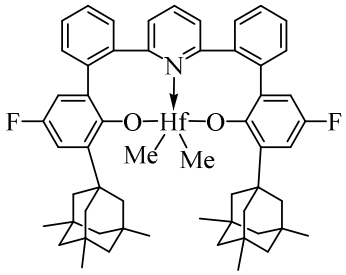
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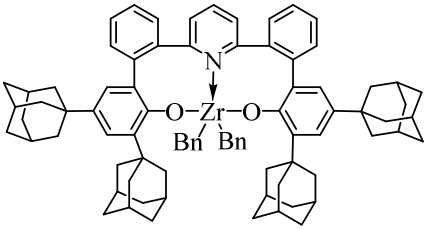
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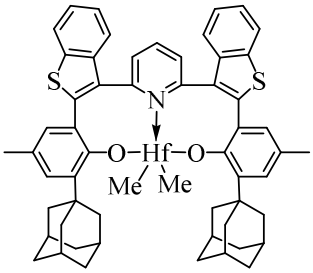
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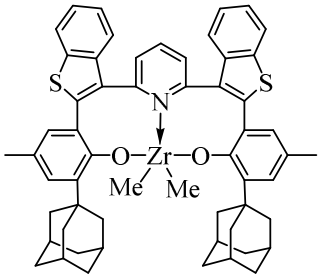
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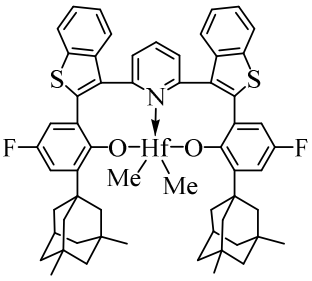
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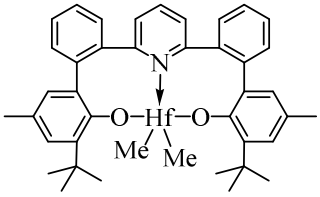
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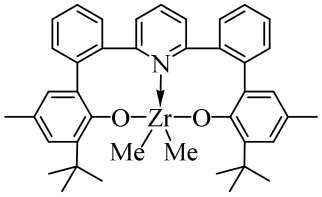
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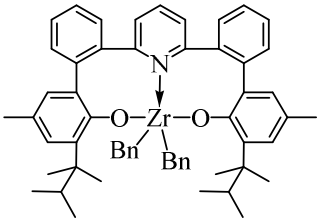
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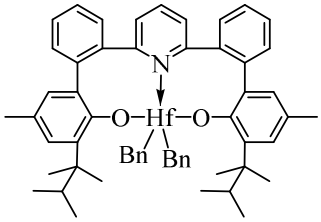
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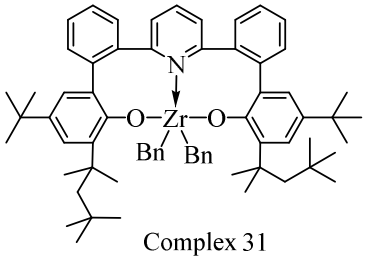
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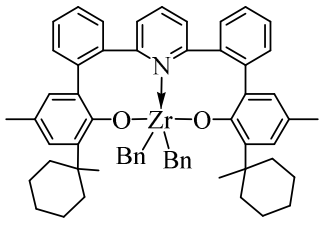
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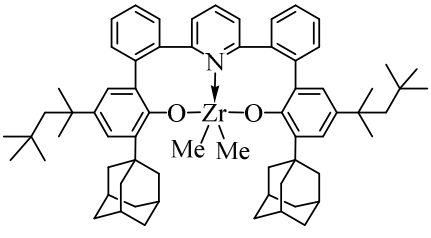
Complex 30



Complex 31

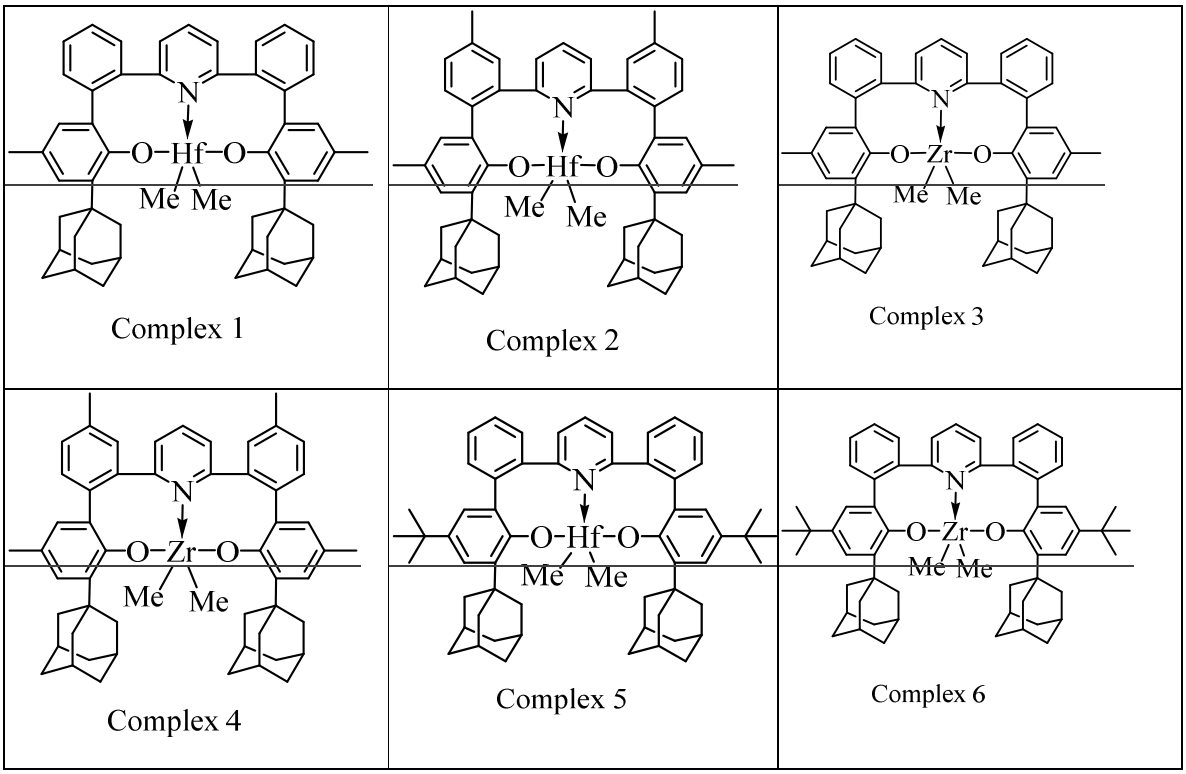


Complex 32



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:~~

$$(Z)_d^+ (A^{d-})$$

~~wherein Z is (L-H) or a reducible Lewis Acid, L is an neutral Lewis base; H is hydrogen; $(L\text{-}H)^+$ 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:~~

$$\left[R^{1'}R^{2'}R^{3'}EH\right]_{d^+}[Mt^{k+}Q_n]^{d-} \quad \text{(V)}$$

~~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^{1t}, R^{2t}, and R^{3t} are independently a C_1 to C_{50} hydrocarbyl group optionally substituted with one or more alkoxy groups, silyl groups, a halogen atoms, or halogen containing groups,~~

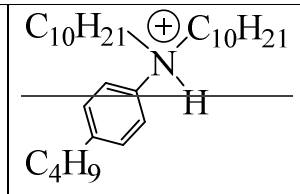
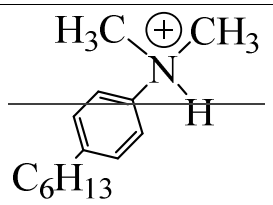
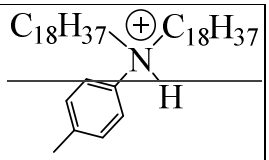
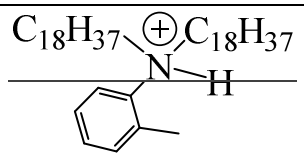
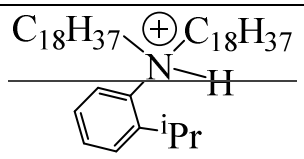
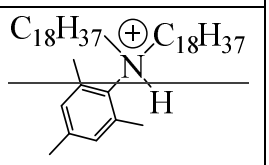
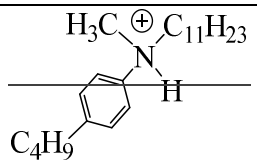
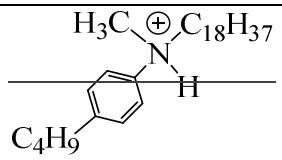
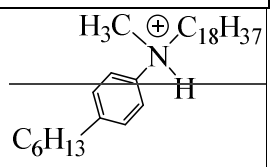
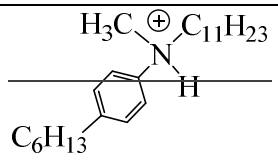
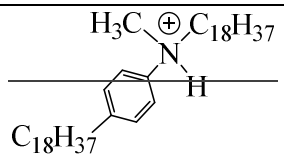
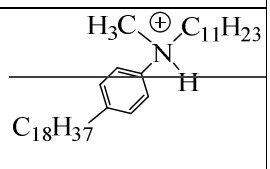
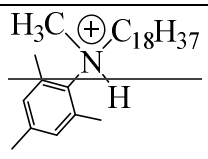
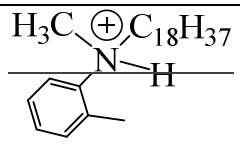
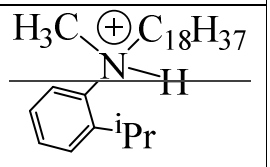
~~wherein R^{1t}, R^{2t}, and R^{3t} together comprise 15 or more carbon atoms;~~

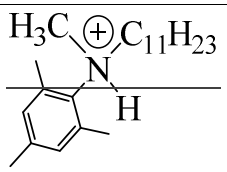
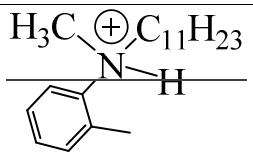
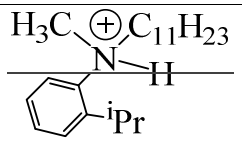
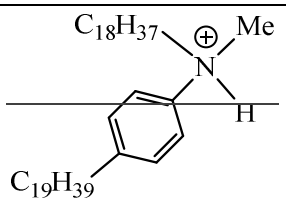
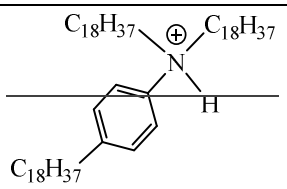
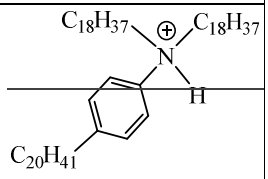
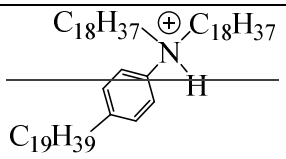
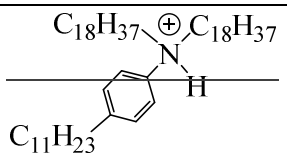
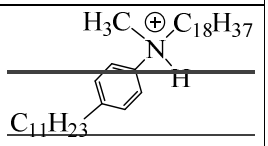
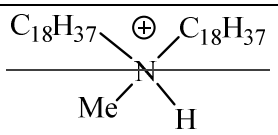
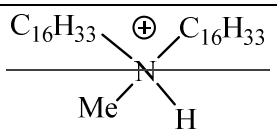
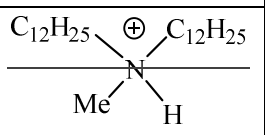
~~Mt is an element selected from group 13 of the Periodic Table of the Elements; and each Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted hydrocarbyl radical.~~

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

~~$(Z)_d^+ (A^{d-})$~~

~~wherein A^{d-} is a non-coordinating anion having the charge d ; and d is an integer from 1 to 3 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,~~
~~dioctadecylmethylammonium tetrakis(pentafluorophenyl)borate,~~
~~dioctadecylmethylammonium tetrakis(perfluoronaphthalenyl)borate,~~
~~N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,~~
~~triphenylcarbenium tetrakis(pentafluorophenyl)borate,~~
~~trimethylammonium tetrakis(perfluoronaphthalenyl)borate,~~
~~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,~~
~~N,N-diethylanilinium tetrakis(perfluoronaphthalenyl)borate,~~
~~N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthalenyl)borate,~~
~~tropillium tetrakis(perfluoronaphthalenyl)borate,~~
~~triphenylcarbenium tetrakis(perfluoronaphthalenyl)borate,~~
~~triphenylphosphonium tetrakis(perfluoronaphthalenyl)borate,~~
~~triethylsilylium tetrakis(perfluoronaphthalenyl)borate,~~
~~benzene(diazonium) tetrakis(perfluoronaphthalenyl)borate,~~

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,
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,
triphenylphosphonium tetrakis(perfluorobiphenyl)borate,
triethylsilylium tetrakis(perfluorobiphenyl)borate,
benzene(diazonium) tetrakis(perfluorobiphenyl)borate,
[4-t-butyl-PhNMe$_2$H][$(C_6F_3(C_6F_5)_2)_4B$],
trimethylammonium tetraphenylborate,
triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,
N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate,
tropillium tetraphenylborate,
triphenylcarbenium tetraphenylborate,
triphenylphosphonium tetraphenylborate,
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,

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,
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,
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,
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,
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,
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,

~~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,~~
~~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.~~

~~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.~~

~~35~~17. The process of any of claims 1 to ~~34~~ 16 further comprising obtaining a polyethylene composition with at least 20 mol% ethylene content.

~~36~~18. The process of any of claims 1 to ~~34~~ 16 further comprising obtaining an ethylene 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 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.~~

~~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~~

~~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.~~

~~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~~.

~~43~~19. 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:

(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

(v) a Mooney relaxation area (measured at 125°) of 550 to 3200 mu.sec.

~~44~~20. 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 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;

(iv) a Mooney relaxation area (measured at 125°C) of 300-400 mu.sec.