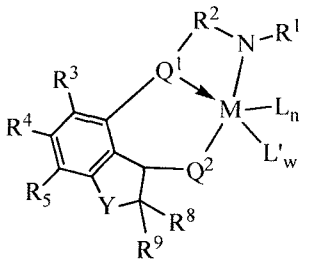
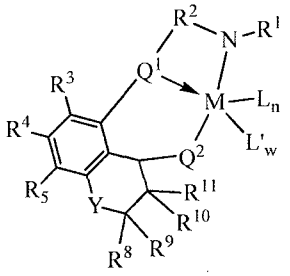
CLAIMS

What is claimed is:

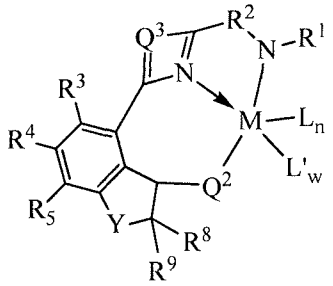
1. A process to polymerize ethylene and one or more C3 to C20 comonomers comprising contacting ethylene, one or more C3 to C20 comonomers, an activator, a chain transfer agent, and a pyridyldiamido transition metal complex represented by the formula: (A), (B), (C), or (D):



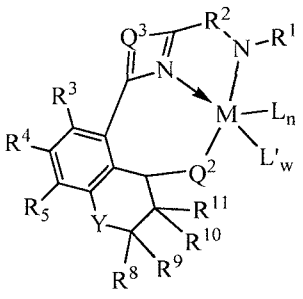
(A)



(B)



(C)



(D)

wherein:

M is a Group 3 or 4 metal;

Q^1 is a three atom bridge with the central of the three atoms being a group 15 or 16 element (said group 15 element may or may not be substituted with an R^{30} group) represented by the formula: $-G^1-G^2-G^3-$ where G^2 is a group 15 or 16 atom (said group 15 element may be substituted with a R^{30} group), G^1 and G^3 are each a group 14, 15 or 16 atom (each group 14, 15 and 16 element may or may not be substituted with one or more R^{30} groups), where G^1, G^2 and G^3, or G^1 and G^2, or G^1 and G^3, or G^2 and G^3 may form a singular or multi ring system;

each R^{30} group is, independently, hydrogen or a C_1 to C_{100} hydrocarbyl group or a silyl group;

Q^2 is $-NR^{17}$ or $-PR^{17}$, where R^{17} is selected from hydrocarbyls, substituted hydrocarbyls, silyls, ~~and~~ or germyls;

Q^3 is -(TT)- or -(TTT)- where each T is carbon or a heteroatom, and said carbon or heteroatom may be unsubstituted or substituted with one or more R^{30} groups that together with the "-C-Q^3=C-" fragment, forms a 5- or 6-membered cyclic group or a polycyclic group including the 5 or 6 membered cyclic group;

R^1 is selected from the group consisting of hydrocarbyls, ~~and~~ substituted hydrocarbyls, ~~or~~ and silyl groups;

R^3, R^4, and R^5 are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R^3 & R^4 and/or R^4 & R^5) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

R^2 is -E(R^{12})(R^{13})- with E being carbon, silicon, or germanium;

Y is selected from oxygen, sulfur, ~~and~~ or -E*(R^6)(R^7)-, with E* being carbon, silicon, or germanium;

R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R^6 & R^7, and/or R^8 & R^9, and/or R^9 & R^{10}, and/or R^{10} & R^{11} and/or R^{12} & R^{13}) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

n is 1 or 2;

L' is a neutral Lewis base; and

w is 0, 1, 2, 3 or 4.

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

3. The process of claim 1, wherein R^2 is selected from CH_2, CH(aryl), CH(2-isopropylphenyl), CH(2,6-dimethylphenyl), CH(2,4-6-trimethylphenyl), CH(alkyl),

CMe_2, $SiMe_2$, $SiEt_2$, ~~and~~ or $SiPh_2$.

4. The process of claim 1, wherein T is C, O, S, or N.

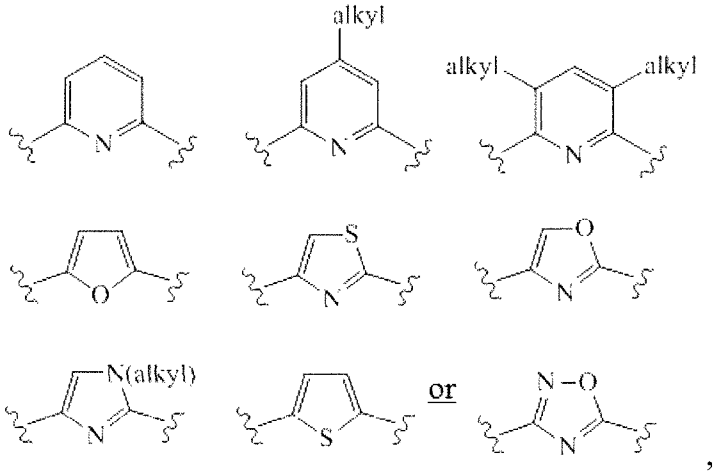
5. The process of claim 1, wherein E and E* are carbon and each R^6, R^7, R^{12}, and R^{13} are a C_1 to C_{30} substituted or unsubstituted hydrocarbyl group.

6. The process of claim 1, wherein E and E* are carbon and each R^6, R^7, R^{12}, and R^{13} are a C_6 to C_{30} substituted or unsubstituted aryl group.

7. The process of claim 1, wherein Q^2 is $-NR^{17}$.

8. The process of claim 1, wherein E and E* are carbon and R^1 and R^{17} are independently selected from phenyl groups that are substituted with 0, 1, 2, 3, 4, or 5 substituents selected from the group consisting of F, Cl, Br, I, CF_3, NO_2, alkoxy, dialkylamino, hydrocarbyl, and substituted hydrocarbyl groups with from one to ten carbons.

9. The process of claim 1, wherein Q^1 is selected from:



,

where the ~ symbols indicate the connections to R^2 and the aromatic ring, and alkyl is an alkyl group.

10. The process of claim 1, wherein each L is independently selected from the group consisting of halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, triflate, alkylsulfonate, arylsulfonate, and alkynyl; and each L' is

independently selected from the group consisting of ethers, thio-ethers, amines, nitriles, imines, pyridines, and phosphines.

11. The process of claim 1, wherein Q^3 is CHCHCH, ~~CHCH~~ CH_2CH, CHN(alkyl), CH-S, ~~CHC(alkyl)CH~~ CHC(alkyl)=CH, ~~C(alkyl)CHC(alkyl)~~ C(alkyl)CH=C(alkyl), CH-O, or NO.

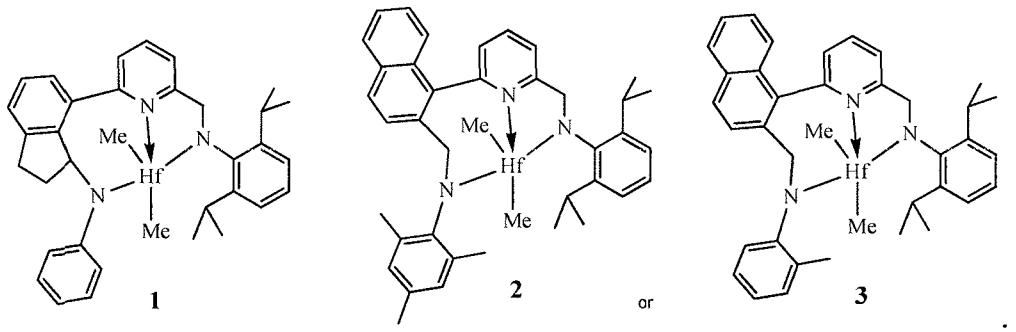
12. The process of claim 1, wherein the complex is represented by formula (A).

13. The process of claim 1, wherein the complex is represented by formula (B).

14. The process of claim 1, wherein the complex is represented by formula (C).

15. The process of claim 1, wherein the complex is represented by formula (D).

16. The process of claim 1, wherein the complex is one or more of the compounds represented by the formula:



17. The process of claim 1, wherein the activator comprises an alumoxane.

18. The process of claim 1, wherein the activator comprises a non-coordinating anion.

19. The process of claim 1, wherein the activator comprises one or more of: trimethylammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, trimethylammonium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium

tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, ~~triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate,~~ triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, ~~$[Ph_3C^+][B(C_6F_5)_4^-]$,~~ $[Me_3NH^+][B(C_6F_5)_4^-]$, 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium, ~~tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine,~~ triphenylcarbenium tetraphenylborate, and triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate.

20. The process of claim 1 wherein the monomer comprises ethylene.

21. The process of claim 1 wherein the monomer comprises propylene.

22. The process of claim 1 wherein the pyridyldiamido transition metal complex is supported.

23. The process of claim 1 wherein the chain transfer agent is dialkyl zinc, trialkyl aluminum, or a mixture thereof.

24. The process of claim 1 wherein the chain transfer agent is one or more of diethylzinc, tri(n-octyl)aluminum, or di(n-propyl)zinc.

25. The process of claim 1 further comprising obtaining an ethylene copolymer having an Mw(LS)/Mn(Dri) of from 1 to 2.5.

26. The process of claim 1 further comprising obtaining an ethylene copolymer having:

1) an Mw(LS)/Mn(Dri) of from 1 to 2.5;

2) an Mw of from 3,000 to 300,000 g/mol;

3) a g'vis of 0.90 or more;

4) an ethylene content of 35 to 85 mol% or more;

5) an C3 to C20 alpha olefin content of 15 to 65 mol%;

6) a ratio of thickening efficiency to shear stability index of 1:3 to 1:20;

7) a melting point (Tm) of 65 °C or less; and

8) a viscosity index of 150 or greater.

27. The process of claim 1 where the polymerization occurs in ~~on~~ one or more tubular reactors.

28. The process of claim 1 where the polymerization occurs in ~~on~~ one or more continuous stirred tank reactors.

29. The process of claim 1 where the polymerization occurs in ~~on~~ one or more semi-continuous batch reactors.

30. The process of claim 1 where the ethylene, the one or more C3 to C20 comonomers, the activator, and the pyridyldiamido transition metal complex are contacted prior to addition of the chain transfer agent.

31. The process of claim 26, where the ethylene copolymer is blended with lubricating oil and the ~~Kinematic~~ kinematic viscosity at 100°C of the lubricating oil is increased by at least 50%.

32. A lubricating composition comprising the ethylene copolymer produced by the process of claim 26.

33. A fuel composition comprising the ethylene copolymer produced by the process of claim 26.

34. An ethylene copolymer having:

1) an Mw(LS)/Mn(Dri) of from 1 to 2.5;

2) an Mw (LS) of from 3,000 to 300,000 g/mol;

3) a g'vis of 0.90 or more;

4) an ethylene content of 35 mol% to 85 mol%;

5) a C3 to C20 comonomer(s) content of from 15 to 65 mol%;

6) a ratio of thickening efficiency to shear stability index (30 cycles) of 1:3 to 1:20;

7) a melting point (Tm) of 65°C or less; and

8) a viscosity index of 150 or greater.

35. The copolymer of claim 34 wherein the ethylene copolymer has a ratio of thickening efficiency to lubricating oil viscosity (KV100) of 2:1 or more, when 1 wt% of the ethylene copolymer is added to a basestock having a KV100 of 10cSt.

36. The copolymer of claim 34, wherein the comonomer(s) are selected from the group consisting of C3 to C20 comonomers~~, preferably C3 to C20 alpha olefins, preferably one or more of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, and isomers thereof~~.

37. The copolymer of claim 34 wherein the comonomer is propylene.

38. The copolymer of claim 34 wherein

1) the Mw(LS)/Mn(Dri) is 1 to 2.0;

2) the Mw (LS) is 50,000 to 300,000 g/mol;

3) the g'vis is 0.95 or more;

4) the ethylene content of is 60 to 75 mol%;

5) the ratio of thickening efficiency to shear stability index (30 cycles) is 1:4 to 1:18;

6) the viscosity index is 170 or more.

39. The copolymer of claim 34 wherein the copolymer does not increase the color of a lubricant by more than 1 unit, as measured by ASTM 1500, when added to the lubricant at 2 wt%.

40. The copolymer of claim 34, wherein the copolymer has a thickening efficiency of 2.1 or more and the shear stability index at 30 cycles is less than 50.