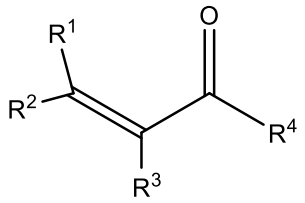
Claims:

We claim:

1. A process to prepare a supported alumoxane, comprising:

(a) forming a solution by, in an aliphatic hydrocarbon fluid, which is a C_3 to C_{12} alkane, combining at least one hydrocarbyl aluminum with at least one non-hydrolytic oxygen-containing compound and a support material, wherein the molar ratio of aluminum to non-hydrolytic oxygen in the solution is greater than or equal to 1.5, wherein the aliphatic hydrocarbon fluid has a boiling point of less than 70 degrees Celsius, and wherein the combining is conducted at a temperature of less than 70 degrees Celsius and at the reflux temperature of the aliphatic hydrocarbon fluid; and wherein

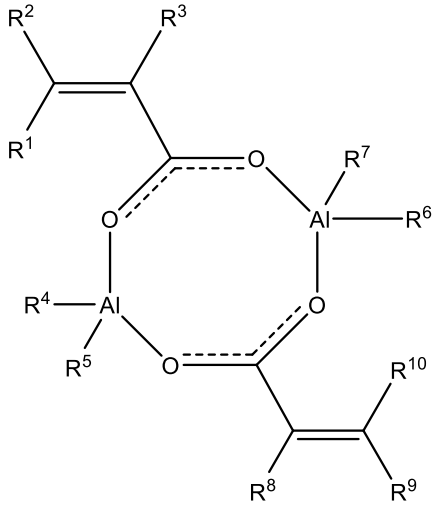
(A) the at least one non-hydrolytic oxygen-containing compound comprises one or more compounds represented by the Formula (**I**):



(**I**)

wherein R^1 and R^2 independently are hydrogen or a hydrocarbyl group; R^3 is a hydrocarbyl group; optionally R^1, R^2, or R^3 may be joined together to form a ring; and R^4 is –OH, $-OC(O)CR^3{=}CR^1R^2$, $OCR^3{}_3$, -F, or –Cl; or

(B) the at least one non-hydrolytic oxygen-containing compound comprises one or more compounds represented by the Formula (**II**):



(**II**)

where R^1 R^2, R^9, and R^{10} independently are hydrogen or a hydrocarbyl group; R^3 and R^8 is a hydrocarbyl group; optionally R^1, R^2, or R^3 may be joined together to form a ring; optionally

R^8, R^9, or R^{10} may be joined together to form a ring; and each of R^4, R^5, R^6, and R^7 is independently a C_2-C_{20} hydrocarbyl group, a methyl group, hydrogen, or a heteroatom containing group;

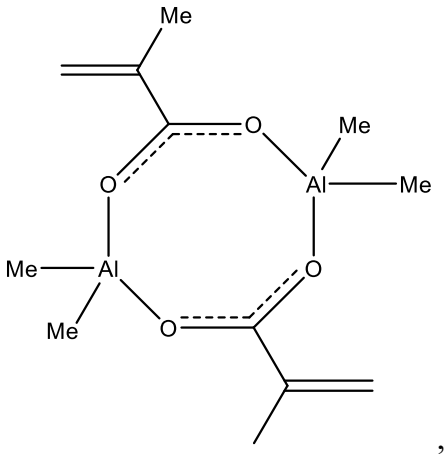
(b) distilling the solution at a pressure of greater than 50.7 kPa (0.5 atm) to form a supported alumoxane precursor , wherein the precursor comprises from 0 wt% to 50 wt%, preferably from 1 wt% to 20 wt%, of the aliphatic hydrocarbon fluid based on the total weight of the precursor; and

(c) heating the precursor to a temperature greater than the boiling point of the aliphatic hydrocarbon fluid and less than 160 degrees Celsius to form a supported alumoxane, wherein heating the precursor produces volatile compounds; and

(d) removing at least a portion of the volatile compounds.

2. The process of claim 1, wherein the non-hydrolytic oxygen-containing compound comprises a plurality of compounds represented by the Formula (**II**), and further wherein R^4, R^5, R^6, and R^7 is at least 85% methyl, up to 15% C_2-C_{20} hydrocarbyl group or a heteroatom containing group, and up to 10 mol% hydrogen based on the total amount of moles of R^4, R^5, R^6, and R^7 in the plurality of compounds.

3. The process of any of claims 1 or 2, wherein the at least one non-hydrolytic oxygen containing compound is selected from the group consisting of methacrylic acid, a compound represented by the Formula (**III**):



, (**III**)

or combinations thereof.

4. The process of claim 3, wherein the at least one non-hydrolytic oxygen containing compound comprises methacrylic acid.

5. The process of any of the preceding claims, wherein the aliphatic hydrocarbon fluid has a boiling point of at least 40 degrees Celsius less that the boiling point of the hydrocarbyl aluminum.

6. The process of any of the preceding claims, wherein the aliphatic hydrocarbon fluid is selected from the group consisting of propane, butane, 2-methylpropane, pentane, cyclopentane, 2-methylbutane, 2-methylpentane, hexane, cyclohexane, methylcyclopentane, 2,4-dimethylpentane, heptane, 2,2,4-trimethylpentane, methylcyclohexane, octane, nonane, decane, dodecane and combination(s) thereof.

7. The process of any of the preceding claims, wherein the at least one hydrocarbyl aluminum comprises one or more compounds represented by the formula $R_1R_2R_3Al$, wherein each of R_1, R_2, and R_3 is independently a C_1 to C_{20} alkyl group, hydrogen, or a heteroatom containing group.

8. The process of claim 7, wherein the at least one hydrocarbyl aluminum comprises a plurality of compounds represented by the formula $R_1R_2R_3Al$, wherein R_1, R_2, and R_3 is at least 85% methyl, up to 15 mol% C_1-C_{20} hydrocarbyl group or a heteroatom containing group, and from 0 to 10 mol% hydrogen based on the total amount of moles of R_1, R_2, and R_3 in the plurality of compounds.

9. The process of any of the preceding claims, wherein the at least one hydrocarbyl aluminum comprises trimethyl aluminum.

10. The process of any of the preceding claims, wherein the support material and/or the solution is free of absorbed water.

11. The process of any of the preceding claims, wherein the support material is silica, alumina, alumina-silica or a derivative thereof, wherein the support material has an average particle size between 1 and 200 microns, an average pore volume of between 0.05 and 5 mL/g, and a surface area between 50 and 800 m^2/g.

12. The process of any of the preceding claims, wherein the support material has been treated with one or more of a Bronsted acid, a Lewis acid, a salt, and a Lewis base.

13. The process of any of the preceding claims, wherein the support material comprises a silylating agent and/or a hydrocarbyl aluminum compound, optionally wherein the support material and/or the hydrocarbyl aluminum compound comprises an electron withdrawing anion, wherein the electron withdrawing anion is selected from sulfate, bisulfate, flurodie, chloride, bromide, iodide flurosulfate, fluoroborate, phosphate fluorophosphate, trofluoroacetate, triflate, fluorozirconate, flurotitanate, phophos-tungstate, or mixtures thereor, or combination thereof.

14. The process of any of claims 1 or 5-9, wherein the molar ratio of the at least one hydrocarbyl aluminum to the at least one non-hydrolytic oxygen containing compound is greater than or equal to [A*B + 0.5(C*D)]/B, wherein;

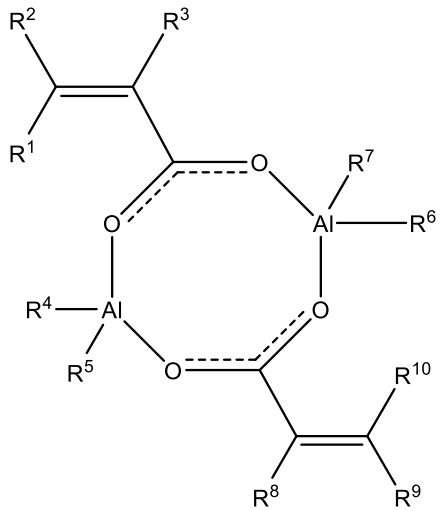
A is 2 or 3;

B is the moles of the non-hydrolytic oxygen containing compound;

C is the moles of hydrocarbyl aluminum chemisorbed to the surface of the support material in the absence of the non-hydrolytic oxygen containing compound per gram of the support material;

D is the grams of the support material; and

wherein A is 2 if the non-hydrolytic oxygen containing compound comprises a compound represented by the Formula (**II**):

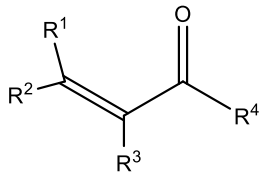


(**II**),

where R^1 R^2, R^9, and R^{10} independently are hydrogen or a hydrocarbyl group; R^3 and R^8 is a hydrocarbyl group; optionally R^1, R^2, or R^3 may be joined together to form a ring; optionally R^8, R^9, or R^{10} may be joined together to form a ring; and each of R^4, R^5, R^6, and R^7 is independently a C_2-C_{20} hydrocarbyl group, a methyl group, hydrogen, or a heteroatom

containing group,

wherein A is 3 if the non-hydrolytic oxygen-containing compound comprises a compound represented by the Formula (**I**):



(**I**)

wherein R^1 and R^2 independently are hydrogen or a hydrocarbyl group; R^3 is a hydrocarbyl group; optionally R^1, R^2, or R^3 may be joined together to form a ring; and R^4 is –OH, -OC(O)CR^3=CR^1R^2, OCR^3_3, -F, or –Cl,

and wherein B/D is greater than or equal to 1.5 mmol/g.

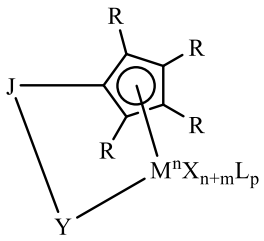
15. The process of any of the preceding claims, further comprising (e) introducing at least one catalyst compound, and optionally a continuity additive, to the supported alumoxane to form a catalyst system.

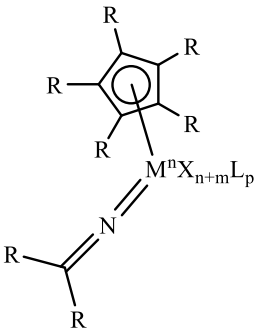
16. The process of claim 15, wherein the catalyst compound is an unbridged metallocene catalyst compound represented by the formula: $Cp^ACp^BM'X'_n$, wherein each of Cp^A and Cp^B is independently selected from the group consisting of cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, one or both of Cp^A and Cp^B may contain heteroatoms, and one or both of Cp^A and Cp^B may be substituted by one or more R'' groups, wherein M' is an element selected from the group consisting of Groups 3 through 12 and lanthanide Group, wherein X' is an anionic ligand, wherein n is 0 or an integer from 1 to 4, wherein R'' is selected from the group consisting of alkyl, substituted alkyl, heteroalkyl, alkenyl, substituted alkenyl, heteroalkenyl, alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, lower alkoxy, aryloxy, alkylthio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylene, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino, phosphine, amino, amine, ether, and thioether.

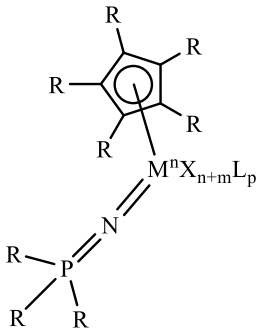
17. The process of claim 15, wherein the metallocene catalyst compound is a bridged metallocene catalyst compound represented by the formula: $Cp^A(A)Cp^BM'X'_n$, wherein each of Cp^A and Cp^B is independently selected from the group consisting of cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, one or both of Cp^A and Cp^B may contain

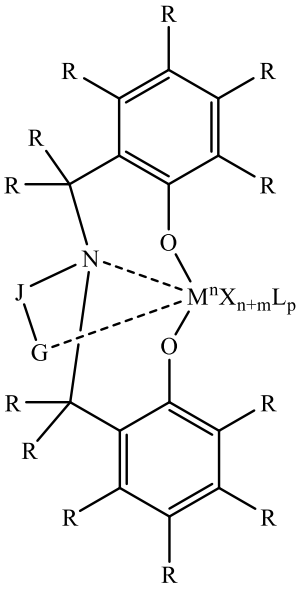
heteroatoms, and one or both of Cp^A and Cp^B may be substituted by one or more R'' groups, wherein M' is an element selected from the group consisting of Groups 3 through 12 and lanthanide Group, wherein X' is an anionic ligand, wherein n is 0 or an integer from 1 to 4, wherein (A) is selected from the group consisting of divalent alkyl, divalent substituted alkyl, divalent heteroalkyl, divalent alkenyl, divalent substituted alkenyl, divalent heteroalkenyl, divalent alkynyl, divalent substituted alkynyl, divalent heteroalkynyl, divalent alkoxy, divalent aryloxy, divalent alkylthio, divalent arylthio, divalent aryl, divalent substituted aryl, divalent heteroaryl, divalent aralkyl, divalent aralkylene, divalent alkaryl, divalent alkarylene, divalent haloalkyl, divalent haloalkenyl, divalent haloalkynyl, divalent heteroalkyl, divalent heterocycle, divalent heteroaryl, a divalent heteroatom-containing group, divalent hydrocarbyl, divalent substituted hydrocarbyl, divalent heterohydrocarbyl, divalent silyl, divalent boryl, divalent phosphino, divalent phosphine, divalent amino, divalent amine, divalent ether, divalent thioether; wherein R'' is selected from the group consisting of alkyl, lower alkyl, substituted alkyl, heteroalkyl, alkenyl, substituted alkenyl, heteroalkenyl, alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, aryloxy, alkylthio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylene, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino, phosphine, amino, amine, ether, and thioether.

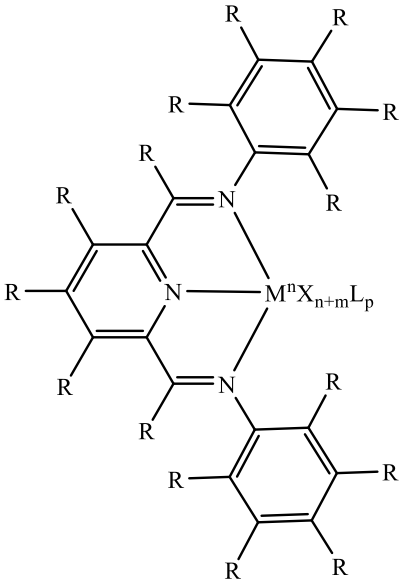
18. The process of claim 15, wherein the catalyst compound is represented by the formulae:

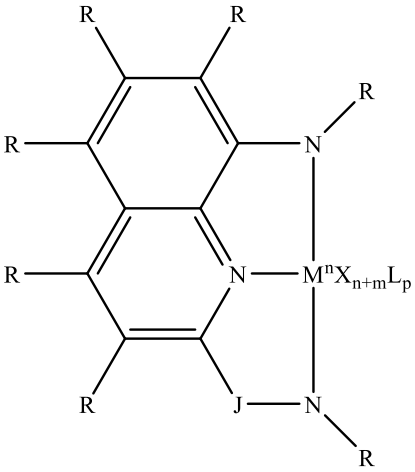

R
R
R
J
R
R
M^nX_{n+m}L_p
Y

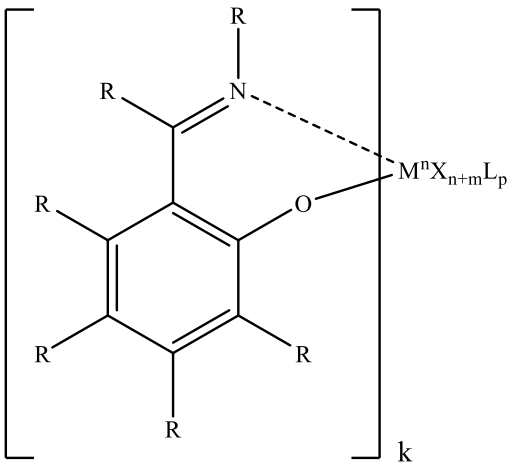

R
R
R
R
R
M^nX_{n+m}L_p
N
R
R

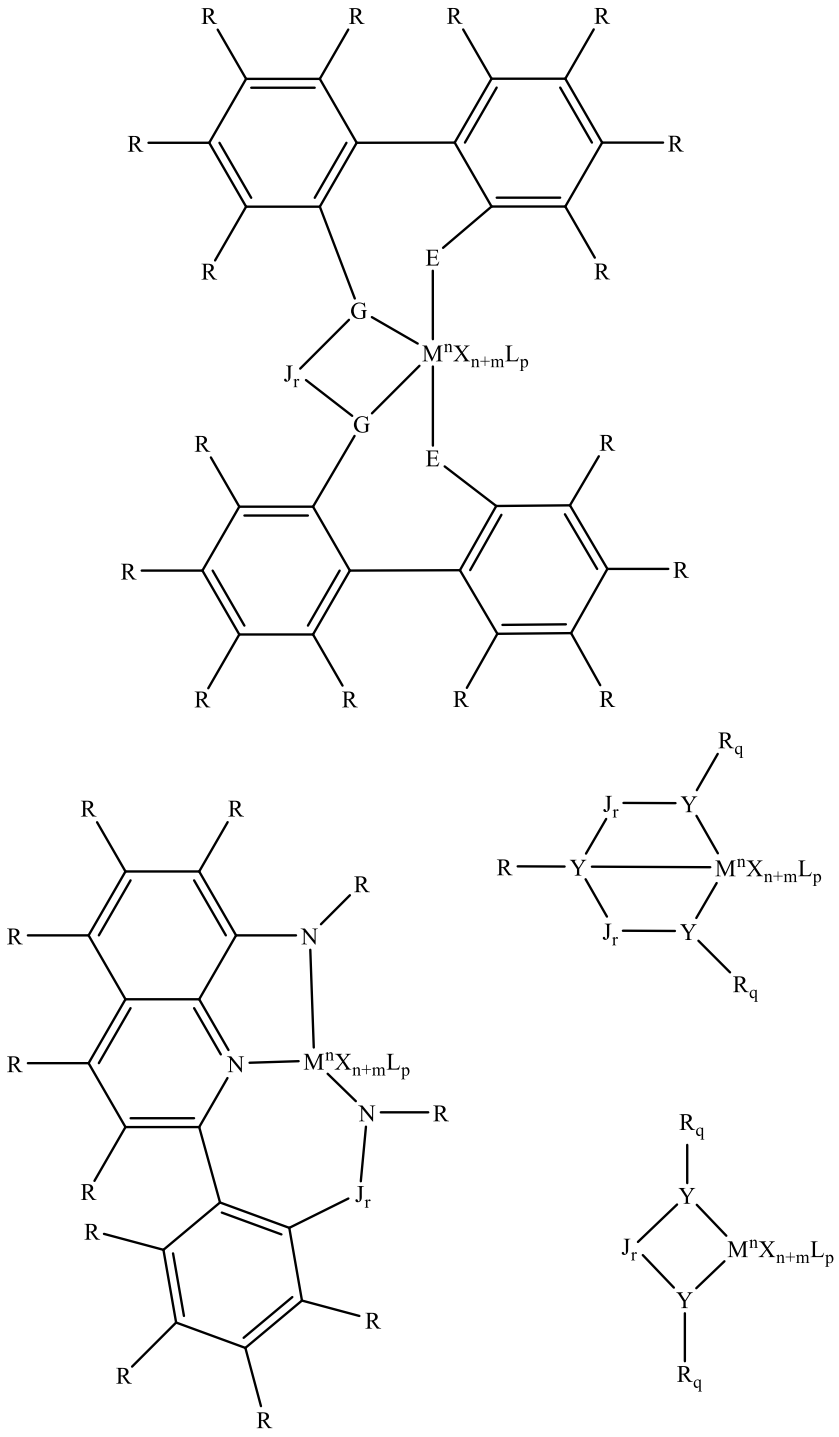

R
R
R
R
R
M^nX_{n+m}L_p
N
R
P
R
R
R


R
R
R
R
R
R
O
N
J
M^nX_{n+m}L_p
G
O
R
R
R
R
R
R
R


R
R
R
R
R
R
N
R
R
N
M^nX_{n+m}L_p
R
N
R
R
R
R
R
R


R
R
R
R
N
R
R
N
M^nX_{n+m}L_p
R
J
N
R

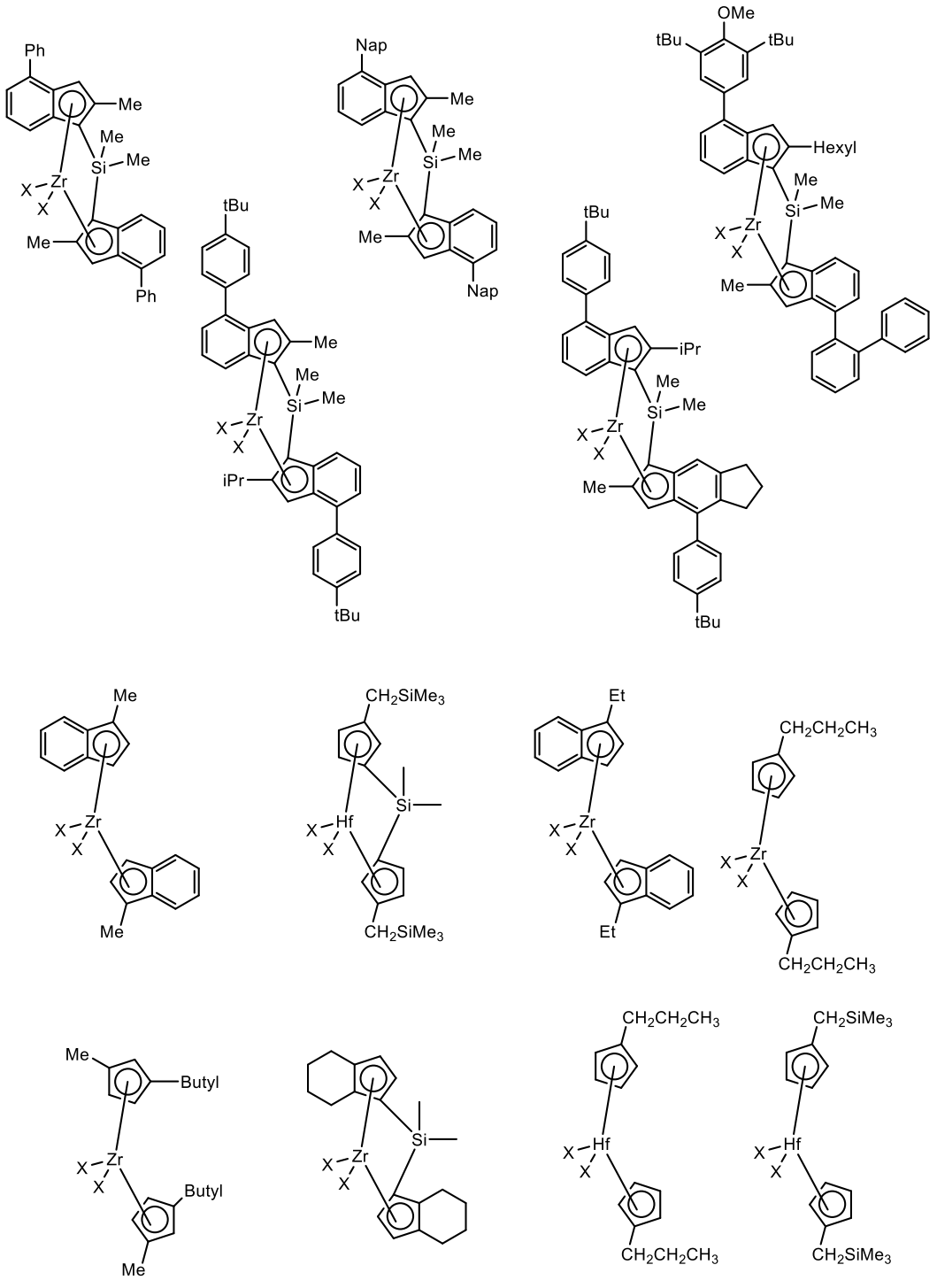

R
R
N
R
R
O
R
R
R
k



where R is independently H, hydrocarbyl, substituted hydrocarbyl, a halide, a substituted heteroatom group or SiR_3; R may be combined together to form a ring; when there is an aromatic ring present, any one or more of the ring C-R may be substituted to form a heterocyclic ring; G is a neutral Lewis Base derived from substituted OR, SR, NR_2, or PR_2 groups; E is O, S, NR, or PR; Y is either G or E; J is independently a formal diradical O, S, NR, PR, CR_2, SiR_2; L is a formally neutral ligand or Lewis acid; X is a halide, hydride, hydrocarbyl or a labile anionic group capable of conversion into a metal hydrocarbyl group;

M is a group 3-12 metal; n is the formal oxidation state of the metal between 0 and 6; m is the sum of the formal anionic charges on the non-X ligands, between -1 and -6; p = 0 to 4; r = 1 to 20; k = 1 to 4.

19. The process of claim 15, wherein the catalyst compound comprises one or more of the following metallocenes or their isomers:



wherein X is a halide, hydride, hydrocarbyl or a labile anionic group capable of conversion into a metal hydrocarbyl group.

20. The process of any of claims 15 19, further comprising (f) contacting the catalyst system with one or more monomers to produce a polymer product.

21. The process of claim 20, wherein the contacting of step (f) is carried out in a gas phase fluidized bed, solution phase, and/or a slurry phase.

22. The process of claim 20 or 21, wherein the contacting of step (f) is conducted at a temperature of from 0°C to 300°C and a pressure in the range of from 0.35 MPa to 10 MPa.

23. The process of any of claims 20-22, wherein the contacting of step (f) is carried out in the presence of a scavenger and/or a chain transfer agent.

24. The process of any of claims 20-23, wherein the contacting of step (f) is carried out presence of a continuity additive and/or a static control agent.

25. The process of any of claims 20-24, wherein the monomer(s) include at least one of ethylene and propylene, optionally with at least one C_3-C_{20} olefin comonomer.

26. The process of any of claims 20-24, wherein the monomer(s) are selected from the group consisting of ethylene, propylene, butene, hexene, octene, and a diene.

27. The process of any of claims 20-26, wherein the polymer product has one or more of the following properties:

(i) a density of from 0.880 g/cm^3 to 0.965 g/cm^3;

(ii) an M_w/M_n of from 2 to 50;

(iii) an M_w of from 5,000 to 10,000,000 g/mol;

(iv) an MI (I_2) of less than 400 g/10 min; and

(v) an HLMI/MI ratio of from 12 to 100.