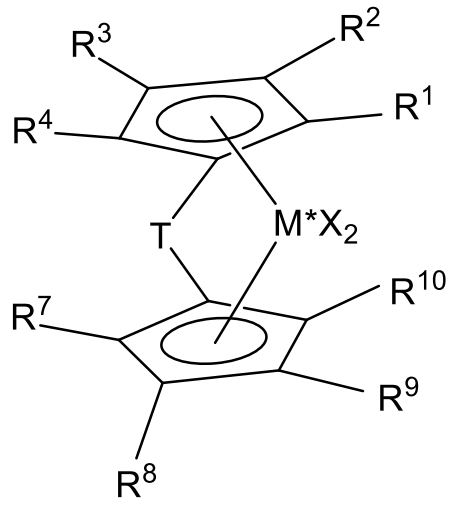
CLAIMS

1. A supported catalyst system comprising: a bridged group 4 metallocene compound; an unbridged metallocene compound; a support material; and an activator; wherein the bridged group 4 metallocene compound is represented by the formula (A):



(A) ,

wherein:

M* is a group 4 metal,

each R^1, R^2, and R^4 is independently hydrogen, an alkoxide, or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group,

R^3 is independently hydrogen, an alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, or a $-R^{20}-SiR'_3$ or $-R^{20}-CR'_3$ group, wherein R^{20} is a C_1 to C_4 hydrocarbyl group and each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl group provided that at least one R' is not hydrogen,

each R^7, R^8, and R^{10} is independently hydrogen, a halide, an alkoxide, or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group,

R^9 is $-R^{20}-SiR'_3$ group,

T is a bridging group, and

each X is, independently, a univalent anionic ligand, or two Xs are joined and bound to the metal atom to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand, provided that the bridged metallocene is not symmetrically substituted,

and wherein the unbridged metallocene compound is represented by the formula (B):

$$Cp_mMX_q \quad (B),$$

wherein each Cp is, independently, a substituted or unsubstituted cyclopentadienyl group,

M is zirconium or hafnium,

X is a leaving group,

m=2 or 3,

q=0, 1, 2, or 3,

m+q is equal to the oxidation state of M, and

each Cp and X is bound to M.

2. The supported catalyst system according to claim 1, wherein M* is hafnium or zirconium, each R^1, R^2, R^3, and R^4 is a C_1 to C_{20} alkyl group and R^9 is a $-R^{20}$-SiR'_3group, wherein R^{20} is CH_2, and each R' is independently a C_1 to C_{20} alkyl group or a C_1 to C_{20} aryl group.

3. The supported catalyst system according to claim 1, wherein M in formula B is zirconium and R^9 is $-R^{20}$-SiR'_3 wherein R^{20} is CH_2, and each R' is independently a C_1 to C_{20} alkyl group or a C_1 to C_{20} aryl group.

4. The supported catalyst system according to claim 1, wherein the bridged metallocene compound is one or more of: $SiMe_2(Me_4Cp)(3\text{-}nPrCp)HfMe_2$; $SiPh_2(Me_4Cp)(3\text{-}nPrCp)HfMe_2$; $Me_2Ge(Me_4Cp)(3\text{-}nPrCp)HfMe_2$; $Ph_2Ge(Me_4Cp)(3\text{-}nPrCp)HfMe_2$; $PhMeSi(Me_4Cp)(3\text{-}nPrCp)HfMe_2$; $Et_2Si(Me_4Cp)(3\text{-}nPrCp)HfMe_2$; $SiMe_2(EtMe_3Cp)(3\text{-}nPrCp)HfMe_2$; $SiMe_2(Me_4Cp)(3\text{-}nBuCp)HfMe_2$; $SiPh_2(Me_4Cp)(3\text{-}nBuCp)HfMe_2$; $Me_2Ge(Me_4Cp)(3\text{-}nBuCp)HfMe_2$; $Ph_2Ge(Me_4Cp)(3\text{-}nBuCp)HfMe_2$; $PhMeSi(Me_4Cp)(3\text{-}nBuCp)HfMe_2$; $Et_2Si(Me_4Cp)(3\text{-}nBuCp)HfMe_2$; $SiMe_2(EtMe_3Cp)(3\text{-}nBuCp)HfMe_2$; $SiMe_2(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; $SiPh_2(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; $Me_2Ge(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; $Ph_2Ge(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; $PhMeSi(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; $Et_2Si(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; $SiMe_2(EtMe_3Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; $SiMe_2(Me_4Cp)(3\text{-}CH_2\text{-}SiPhMe_2\text{-}Cp)HfMe_2$; $SiPh_2(Me_4Cp)(3\text{-}CH_2\text{-}SiPhMe_2\text{-}Cp)HfMe_2$; $Me_2Ge(Me_4Cp)(3\text{-}CH_2\text{-}SiPhMe_2)HfMe_2$; $Ph_2Ge(Me_4Cp)(3\text{-}CH_2\text{-}SiPhMe_2)HfMe_2$; $PhMeSi(Me_4Cp)(3\text{-}CH_2\text{-}SiPhMe_2\text{-}Cp)HfMe_2$; $Et_2Si(Me_4Cp)(3\text{-}CH_2\text{-}SiPhMe_2\text{-}Cp)HfMe_2$; $SiMe_2(EtMe_3Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; $SiMe_2(Me_4Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; $SiPh_2(Me_4Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; $Me_2Ge(Me_4Cp)(3\text{-}CH_2\text{-}SiPh_3)HfMe_2$; $Ph_2Ge(Me_4Cp)(3\text{-}CH_2\text{-}SiPh_3)HfMe_2$; $PhMeSi(Me_4Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; $Et_2Si(Me_4Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; $SiMe_2(EtMe_3Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; $SiMe_2(2\text{-}Me,3\text{-}n\text{-}Pr\text{-}Ind)_2HfMe_2$; $SiPh_2(2\text{-}Me,3\text{-}n\text{-}Pr\text{-}Ind)_2HfMe_2$; $GeMe_2(2\text{-}Me,3\text{-}n\text{-}Pr\text{-}Ind)_2HfMe_2$; $GePh_2(2\text{-}Me,3\text{-}n\text{-}Pr\text{-}Ind)_2HfMe_2$;

$SiPhMe(2\text{-}Me,3\text{-}n\text{-}Pr\text{-}Ind)_2HfMe_2$; $Et_2Si(2\text{-}Me,3\text{-}n\text{-}Pr\text{-}Ind)_2HfMe_2$; $SiMe_2(2\text{-}Me,3\text{-}n\text{-}Bu\text{-}Ind)_2HfMe_2$; $SiPh_2(2\text{-}Me,3\text{-}n\text{-}Bu\text{-}Ind)_2HfMe_2$; $GeMe_2(2\text{-}Me,3\text{-}n\text{-}Bu\text{-}Ind)_2HfMe_2$; $GePh_2(2\text{-}Me,3\text{-}n\text{-}Bu\text{-}Ind)_2HfMe_2$; $SiPhMe(2\text{-}Me,3\text{-}n\text{-}Bu\text{-}Ind)_2HfMe_2$; $Et_2Si(2\text{-}Me,3\text{-}n\text{-}Bu\text{-}Ind)_2HfMe_2$; $SiMe_2(2\text{-}Me,3\text{-}CH_2\text{-}SiMe_3\text{-}Ind)_2HfMe_2$; $SiPh_2(2\text{-}Me,3\text{-}CH_2\text{-}SiMe_3\text{-}Ind)_2HfMe_2$; $GeMe_2(2\text{-}Me,3\text{-}CH_2\text{-}SiMe_3\text{-}Ind)_2HfMe_2$; $GePh_2(2\text{-}Me,3\text{-}CH_2\text{-}SiMe_3\text{-}Ind)_2HfMe_2$; $SiPhMe(2\text{-}Me,3\text{-}CH_2\text{-}SiMe_3\text{-}Ind)_2HfMe_2$; $Et_2Si(2\text{-}Me,3\text{-}CH_2\text{-}SiMe_3\text{-}Ind)_2HfMe_2$; $SiMe_2(2\text{-}Me,3\text{-}CH_2\text{-}SiPhMe_2\text{-}Ind)_2HfMe_2$; $SiPh_2(2\text{-}Me,3\text{-}CH_2\text{-}SiPhMe_2\text{-}Ind)_2HfMe_2$; $GeMe_2(2\text{-}Me,3\text{-}CH_2\text{-}SiPhMe_2\text{-}Ind)_2HfMe_2$; $GePh_2(2\text{-}Me,3\text{-}CH_2\text{-}SiPhMe_2\text{-}Ind)_2HfMe_2$; $SiPhMe(2\text{-}Me,3\text{-}CH_2\text{-}SiPhMe_2\text{-}Ind)_2HfMe_2$; $Et_2Si(2\text{-}Me,3\text{-}CH_2\text{-}SiPhMe_2\text{-}Ind)_2HfMe_2$; $SiMe_2(2\text{-}Me,3\text{-}CH_2\text{-}SiPh_3\text{-}Ind)_2HfMe_2$; $SiPh_2(2\text{-}Me,3\text{-}CH_2\text{-}SiPh_3\text{-}Ind)_2HfMe_2$; $GeMe_2(2\text{-}Me,3\text{-}CH_2\text{-}SiPh_3\text{-}Ind)_2HfMe_2$; $GePh_2(2\text{-}Me,3\text{-}CH_2\text{-}SiPh_3\text{-}Ind)_2HfMe_2$; $SiPhMe(2\text{-}Me,3\text{-}CH_2\text{-}SiPh_3\text{-}Ind)_2HfMe_2$; $Et_2Si(2\text{-}Me,3\text{-}CH_2\text{-}SiPh_3\text{-}Ind)_2HfMe_2$, and the alkyl or halide versions thereof, wherein the Me_2 is substituted with Et_2, Cl_2, Br_2, I_2, or Ph_2.

5. The supported catalyst system according to claim 1, wherein the unbridged metallocene compound is represented by the formula $Cp^ACp^BZrX'_n$, wherein each Cp^A and Cp^B is independently selected from the group consisting of cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, either or both Cp^A and Cp^B optionally contains heteroatoms, and either or both Cp^A and Cp^B is optionally substituted; each X′ is independently a leaving group, and n is 0, 1, or 2.

6. The supported catalyst system according to claim 1, wherein the unbridged metallocene compound is selected from the group consisting of:
bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)zirconium dimethyl, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)zirconium dimethyl, bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)zirconium dimethyl, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(pentamethylcyclopentadienyl)zirconium dimethyl, bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dichloride, bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dimethyl, bis(1-methyl-3-phenylcyclopentadienyl)zirconium dichloride, bis(1-methyl-3-phenylcyclopentadienyl)zirconium dimethyl, bis(1-methyl-3-n-butylcyclopentadienyl)hafnium dichloride, bis(1-methyl-3-n-butylcyclopentadienyl)zirconium

dimethyl, bis(indenyl)zirconium dichloride, bis(indenyl)zirconium dimethyl, bis(tetrahydro-1-indenyl)zirconium dichloride, bis(tetrahydro-1-indenyl)zirconium dimethyl, (n-propyl cyclopentadienyl)(pentamethyl cyclopentadienyl)zirconium dichloride, (n-propyl cyclopentadienyl)(pentamethyl cyclopentadienyl)zirconium dimethyl, rac/meso-(1-ethylindenyl)zirconium dichloride, rac/meso-(1-ethylindenyl)zirconium dimethyl, rac/meso-(1-methylindenyl)zirconium dichloride, rac/meso-(1-methylindenyl)zirconium dimethyl, rac/meso-(1-propylindenyl)zirconium dichloride, rac/meso-(1-propylindenyl)zirconium dimethyl, rac/meso-(1-butylindenyl)zirconium dichloride, rac/meso-(1-butylindenyl)zirconium dimethyl, meso-(1ethylindenyl) zirconium dichloride, meso-(1ethylindenyl) zirconium dimethyl, (1-methylindenyl)(pentamethyl cyclopentadienyl) zirconium dichloride, and (1-methylindenyl)(pentamethyl cyclopentadienyl) zirconium dimethyl.

7. The supported catalyst system according to claim 1, wherein the support material has a surface area in the range of from 10 m^2/g to 700 m^2/g and an average particle diameter in the range of from 10 μm to 500 μm.

8. The supported catalyst system according to claim 1, wherein the support material is selected from the group consisting of silica, alumina, silica-alumina, and combinations thereof.

9. The supported catalyst system according to claim 1, wherein the support material is fluorided.

10. The supported catalyst system of claim 9, wherein the support material has a fluorine concentration in the range of 0.6 wt% to 3.5 wt%, based upon the weight of the support material.

11. The supported catalyst system according to claim 1, wherein the activator comprises alumoxane, a non-coordinating anion, or a combination thereof.

12. The supported catalyst system according to claim 1, wherein the unbridged metallocene compound represented by formula B is present in the catalyst system as at least two isomers.

13. The supported catalyst system according to claim 1, wherein the activator comprises one or more of: N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorophenyl)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, $[Me_3NH^+][B(C_6F_5)_4^-]$, 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl) pyrrolidinium; $[Me_3NH^+][B(C_6F_5)_4^-]$, 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl) pyrrolidinium, sodium tetrakis(pentafluorophenyl)borate, potassium tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridinium, solidium tetrakis(perfluorophenyl)aluminate, potassium tetrakis(pentafluorophenyl), and N,N-dimethylanilinium tetrakis(perfluorophenyl)aluminate.

14. A process for polymerization of olefin monomers comprising contacting one or more monomers with the supported catalyst system of claim 1 to produce a polymer.

15. The process according to claim 14, wherein a reactivity of the bridged group 4 metallocene compound to hydrogen is different that a reactivity of the unbridged metallocene compound to hydrogen.

16. The process according to claim 14, wherein the olefin monomers comprise ethylene and one or more comonomers selected from the group consisting of propylene, 1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, and combinations thereof.

17. The process according to claim 14, wherein the polymerization is carried out in a slurry polymerization process or a gas phase polymerization process.

18. The process of claim 14, wherein the olefin monomers comprise ethylene and one or more comonomers, and wherein the polymer produced by the process has: 1) an RCI,m of greater than 30, and an Mw/Mn of greater than 3 and less than 5, and optionally a T_{75}-T_{25} of 15°C to 20°C; or 2) an RCI,m of greater than 50, and an Mw/Mn of greater than 5, and optionally a T_{75}-T_{25} of 25°C to 45°C.

19. The process of claim 14, wherein:

1) when the bridged group 4 metallocene compound (A) is run under the same polymerization conditions as a supported catalyst composition comprising (A) and (B), except that the unbridged metallocene compound (B) is absent, a polymer having an RCI,m of 20 or more is produced, and

2) when the unbridged metallocene compound (B) is run under the same polymerization conditions as step 1), except that the bridged group 4 metallocene compound (A) is absent, a polymer having an RCI,m of less than zero is produced.

20. A process to produce linear low density polyethylene comprising contacting one or more monomers with the supported catalyst system of claim 1, wherein:

1) when the bridged group 4 metallocene catalyst compound (A), the unbridged metallocene catalyst compound (B), and the activator are supported on the same support material and run under the polymerization conditions, an ethylene polymer is produced having: a) an RCI,m of greater than 30 and an Mw/Mn of greater than 3 and less than 5; or b) an RCI,m of greater than 50 and an Mw/Mn of greater than 5;

2) when the supported bridged group 4 metallocene catalyst compound (A) is run under the same polymerization conditions of step 1) except that the unbridged metallocene catalyst compound (B) is absent, an ethylene polymer is produced having an RCI,m of greater than 20; and

3) when the supported unbridged metallocene catalyst compound (B) is run under the same polymerization conditions of step 1) except that the bridged group 4 metallocene catalyst compound (A) is absent, an ethylene polymer is produced having a negative RCI,m.

21. The supported catalyst system according to claim 1, wherein R^9 is $-R^{20}-SiR'_3$, and wherein R^{20} is CH_2 and each R' is independently a C_1 to C_{20} alkyl group or a C_1 to C_{20} aryl group.

22. The supported catalyst system according to claim 1, wherein the bridged A group 4 metallocene compound is one or more of: $SiMe_2(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; $SiPh_2(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$; alkyl versions thereof, wherein the Me_2 is substituted with Et_2 or Ph_2, and halide versions thereof, wherein the Me_2 is substituted with Cl_2, Br_2, or I_2.

23. The supported catalyst system according to claim 1, wherein the bridged group 4 metallocene compound comprises $SiMe_2(Me_4Cp)(3\text{-}nPrCp)HfMe_2$, $SiMe_2(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$, $SiPh_2(Me_4Cp)(3\text{-}CH_2\text{-}SiMe_3\text{-}Cp)HfMe_2$, $SiMe_2(2\text{-}Me, 3\text{-}n\text{-}Pr\text{-}Ind)_2HfMe_2$, or a combination thereof.