obtained from Cambridge Isotopes (Cambridge, MA) and dried over 3 Angstrom molecular sieves before use.

[00145] SMAO used below was prepared according to the description "Preparation of SMAO for ES™757 Silica" above.

[00146] Fluorided silica, F-Si, used below was prepared according to the description " Fluorided Supported Catalysts" above.

Products were characterized as follows:

^{1}H NMR

[00147] Unless otherwise indicated, ^{1}H NMR data of non-polymeric compounds was collected at room temperature in a 5 mm probe using either a Bruker or Varian NMR spectrometer operating with a ^{1}H frequency of 400 or 500 MHz. Data was recorded using a 30° flip angle RF pulse, 8 scans, with a delay of 5 seconds between pulses. Samples were prepared using approximately 5-10 mg of compound dissolved in approximately 1 mL of an appropriate deuterated solvent, as listed in the experimental examples. Samples are referenced to residual protium of the solvents at 7.15, 7.24, 5.32, 5.98, and 2.10 for D5-benzene, chloroform, D-dichloromethane, D-1,1,2,2-tetrachloroethane, and $C_6D_5CD_2H$, respectively. Unless stated otherwise, NMR spectroscopic data of polymers was recorded in a 5 mm probe on a Varian NMR spectrometer at 120^{o}C using a d_2-1,1,2,2-tetrachloroethane solution prepared from approximately 20 mg of polymer and 1 mL of solvent. Unless stated otherwise, data was recorded using a 30° flip angle RF pulse, 120 scans, with a delay of 5 seconds between pulses.

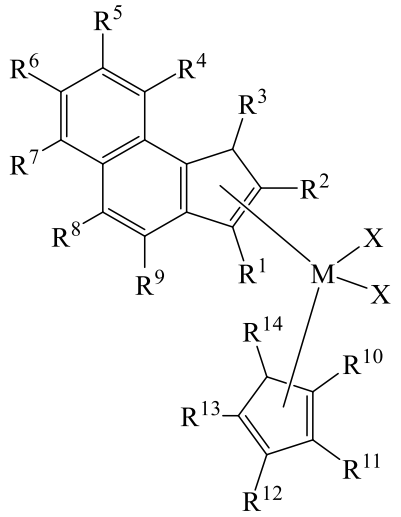
High Throughput - Polymerizations:

[00148] Solvents, polymerization grade toluene and isohexane were supplied by ExxonMobil Chemical Company and thoroughly dried and degassed prior to use. Polymerization grade ethylene (custom tanks of ethylene with 300 ppm H_2 supplied by Air Liquide) was used and further purified by passing it through a series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, CA) followed by a 500 cc column packed with dried 3Å mole sieves purchased from Aldrich Chemical Company, and a 500 cc column packed with dried 5Å mole sieves purchased from Aldrich Chemical Company. TnOAl (tri-*n*-octylaluminum, neat) was used as a 2 mmol/L solution in toluene.

Reactor Description and Preparation: Polymerizations were conducted in an inert atmosphere (N_2) using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor = 22.5 mL), septum inlets, regulated supply of nitrogen,

CLAIMS:

1. A catalyst system comprising an activator, a fluorided silica support, and catalyst compound represented by Formula (I):



(I)

where M is Zr,

each of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, and R^{14} is independently hydrogen, or a linear or branched C_1-C_{50} substituted or unsubstituted hydrocarbyl, halocarbyl or silylcarbyl, wherein at least one of R^1 and R^3 is a linear or branched C_1-C_{10} substituted or unsubstituted hydrocarbyl, and

each X is independently a halide or C_1-C_{50} substituted or unsubstituted hydrocarbyl, hydride, amide, alkoxide, sulfide, phosphide, halide, diene, amine, phosphine, ether, or a combination thereof, or two Xs are joined together to form a metallocycle ring, or two Xs are joined to form a chelating ligand, a diene ligand, or an alkylidene.

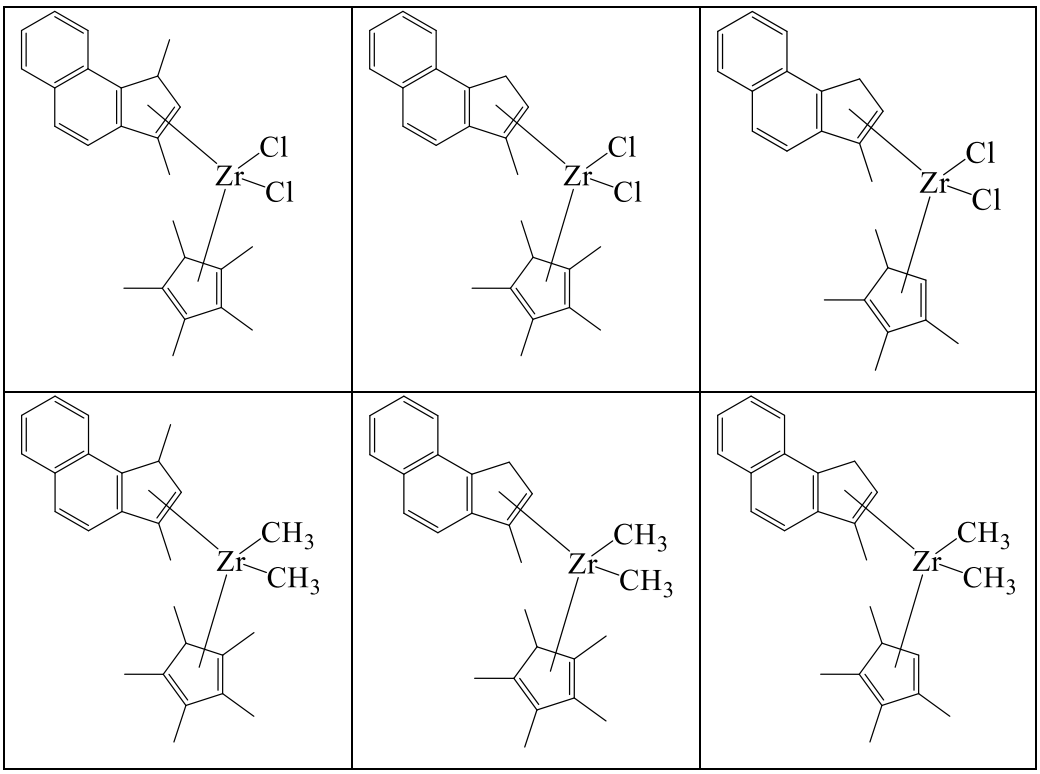
2. The catalyst system of claim 1, wherein each of R^1 and R^3 is independently linear or branched C_1-C_5 unsubstituted hydrocarbyl.

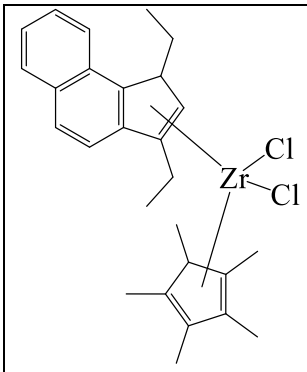
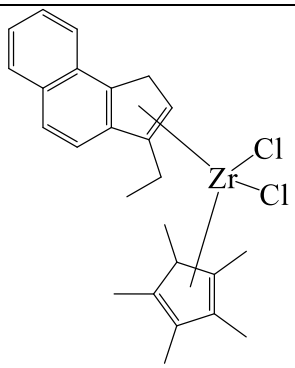
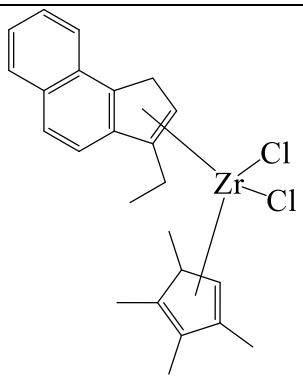
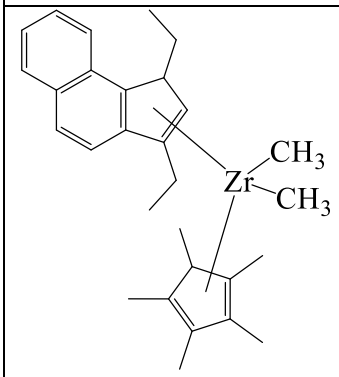
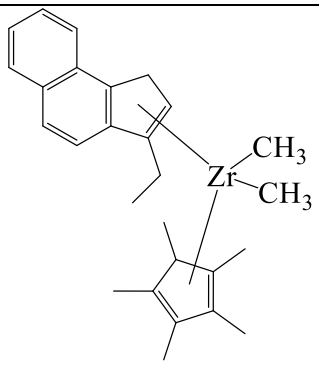
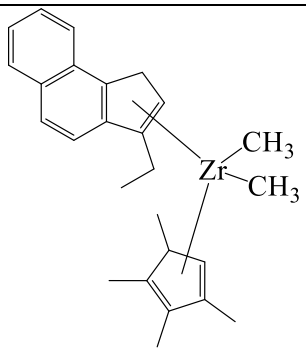
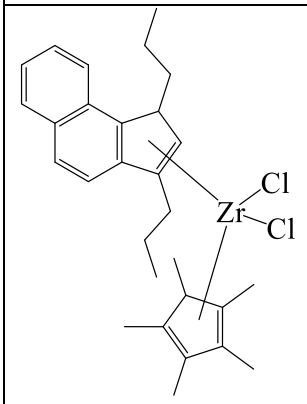
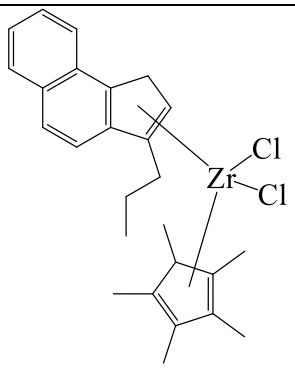
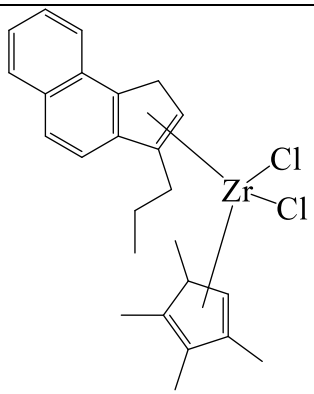
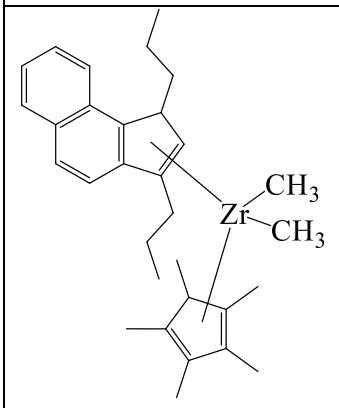
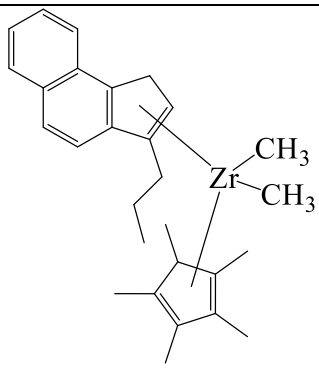
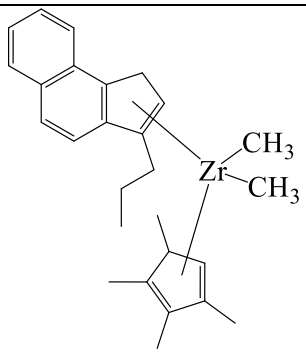
3. The catalyst system of any of claims 1 to 2, wherein each X is independently a halide or C_1-C_{10} substituted or unsubstituted hydrocarbyl.

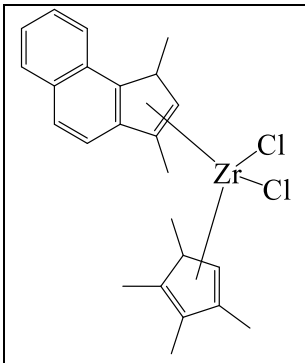
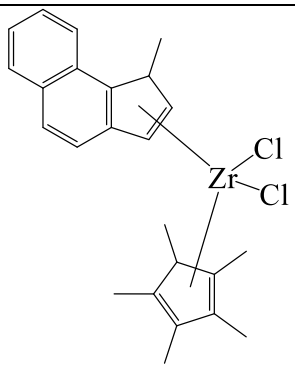
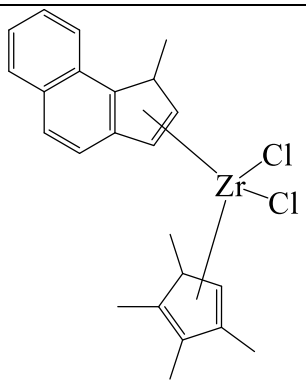
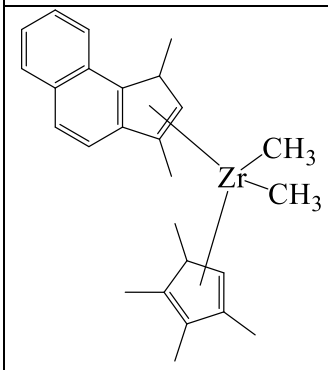
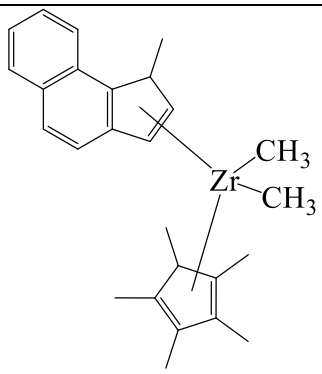
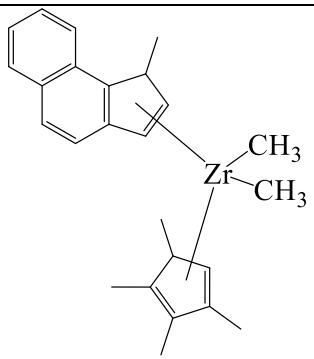
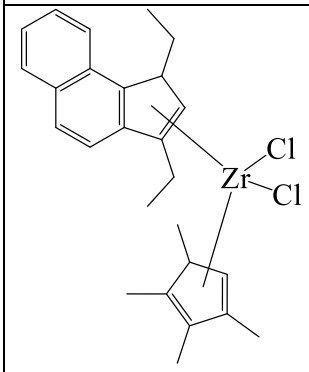
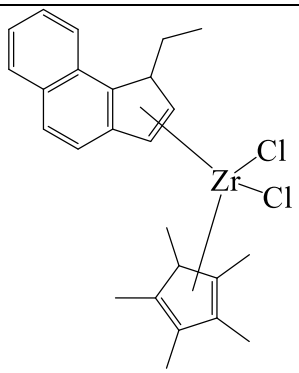
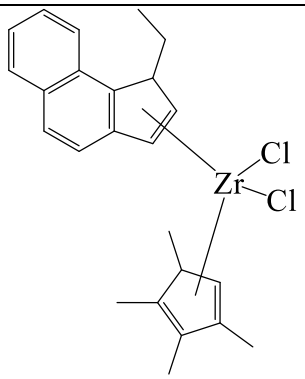
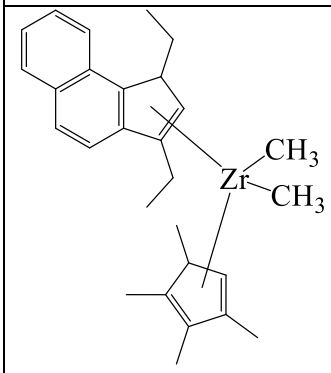
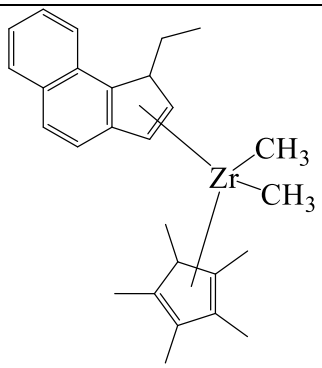
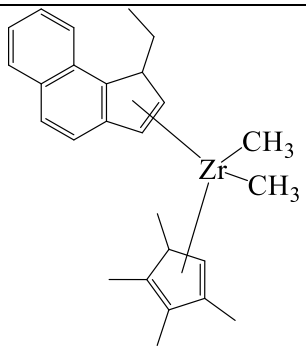
4. The catalyst system of any of claims 1 to 3, wherein R^{10} is hydrogen or C_1-C_{10} substituted or unsubstituted hydrocarbyl, and wherein each of R^{11}, R^{12}, R^{13}, and R^{14} is independently C_1-C_{10} substituted or unsubstituted hydrocarbyl.

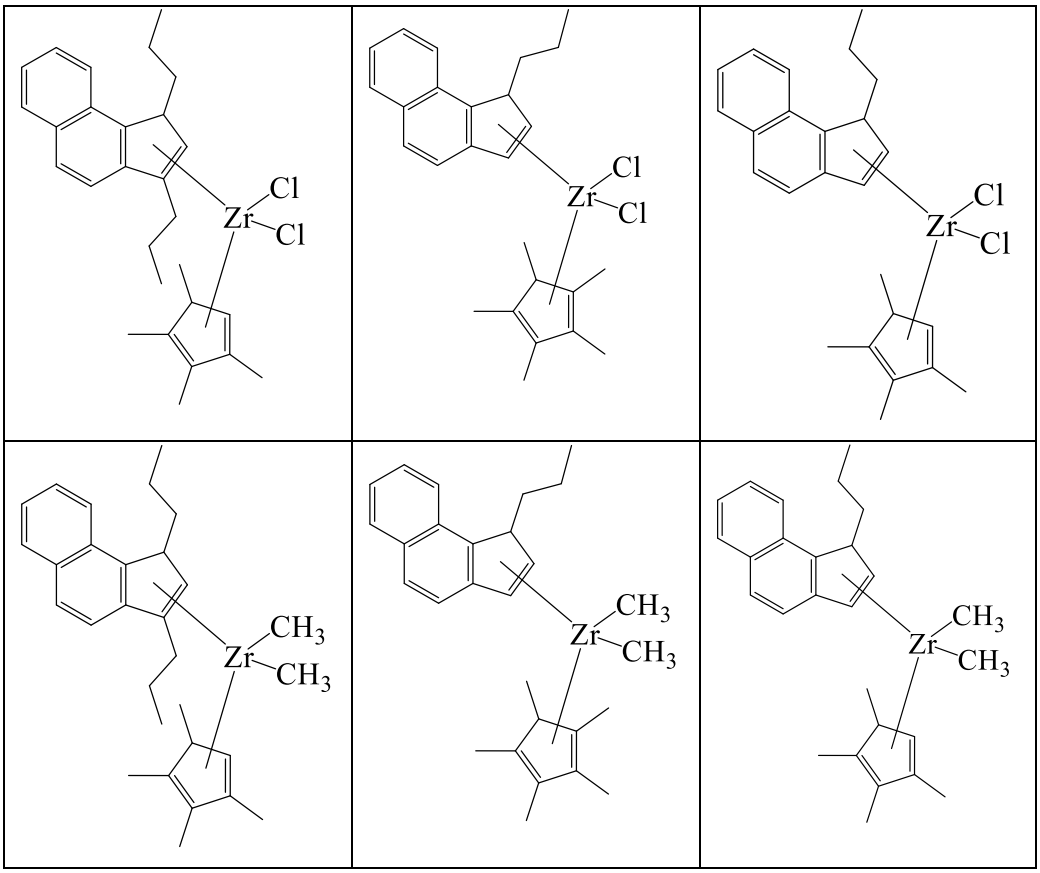
5. The catalyst system of claim 1, wherein each of R^1 and R^3 is independently linear or branched C_1-C_5 unsubstituted hydrocarbyl; wherein each X is independently a halide or C_1-C_{10} substituted or unsubstituted hydrocarbyl; wherein R^{10} is hydrogen or C_1-C_{10} substituted or unsubstituted hydrocarbyl; and wherein each of R^{11}, R^{12}, R^{13}, and R^{14} is independently C_1-C_{10} substituted or unsubstituted hydrocarbyl.

6. The catalyst system of claim 1, wherein the catalyst compound represented by Formula (I) comprises one or more of:





7. The catalyst system of any of claims 1 to 6 further comprising a bridged or unbridged metallocene catalyst compound other than a catalyst compound represented by the Formula (I) represented by the formula:

$Cp^ACp^BM'X'_n$, or $Cp^A(A)Cp^BM'X'_n$,

wherein each Cp^A and Cp^B is independently selected from the group consisting of cyclopentadienyl ligands, one or both Cp^A and Cp^B may contain heteroatoms, and one or both Cp^A and Cp^B may be substituted by one or more R'' groups, wherein M' is selected from the group consisting of Groups 3 through 12 atoms and lanthanide Group atoms, wherein X' is an anionic leaving group, wherein n is 0 or an integer from 1 to 4, wherein R'' is selected from the group consisting of alkyl, lower alkyl, substituted alkyl, heteroalkyl, alkenyl, lower alkenyl, substituted alkenyl, heteroalkenyl, alkynyl, lower alkynyl, substituted alkynyl, heteroalkynyl, alkoxy, lower alkoxy, aryloxy, alkylthio, lower alkyl thio, arylthio, aryl, substituted aryl, heteroaryl, aralkyl, aralkylene, alkaryl, alkarylene, haloalkyl, haloalkenyl, haloalkynyl, heteroalkyl, heterocycle, heteroaryl, a heteroatom-containing group, hydrocarbyl, lower hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl, silyl, boryl, phosphino,

phosphine, amino, amine, ether, and thioether; wherein (A) is selected from the group consisting of divalent alkyl, divalent lower alkyl, divalent substituted alkyl, divalent heteroalkyl, divalent alkenyl, divalent lower alkenyl, divalent substituted alkenyl, divalent heteroalkenyl, divalent alkynyl, divalent lower alkynyl, divalent substituted alkynyl, divalent heteroalkynyl, divalent alkoxy, divalent lower alkoxy, divalent aryloxy, divalent alkylthio, divalent lower alkyl thio, 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 lower hydrocarbyl, divalent substituted hydrocarbyl, divalent heterohydrocarbyl, divalent silyl, divalent boryl, divalent phosphino, divalent phosphine, divalent amino, divalent amine, divalent ether, and divalent thioether.

8. The catalyst system of any of claims 1 to 6 further comprising one or more of:
bis(n-propylcyclopentadienyl)hafnium dichloride,
bis(n-propylcyclopentadienyl)hafnium dimethyl,
bis(n-propylcyclopentadienyl)zirconium dichloride,
bis(n-propylcyclopentadienyl)zirconium dimethyl,
bis(n-propylcyclopentadienyl)titanium dichloride,
bis(n-propylcyclopentadienyl)titanium dimethyl,
(n-propylcyclopentadienyl, pentamethylcyclopentadienyl)zirconium dichloride,
(n-propylcyclopentadienyl, pentamethylcyclopentadienyl)zirconium dimethyl,
(n-propylcyclopentadienyl, pentamethylcyclopentadienyl)hafnium dichloride,
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(n-propylcyclopentadienyl, tetramethylcyclopentadienyl)zirconium dimethyl,
(n-propylcyclopentadienyl, tetramethylcyclopentadienyl)hafnium dichloride,
(n-propylcyclopentadienyl, tetramethylcyclopentadienyl)hafnium dimethyl,
(n-propylcyclopentadienyl, tetramethylcyclopentadienyl)titanium dichloride,
(n-propylcyclopentadienyl, tetramethylcyclopentadienyl)titanium dimethyl,

bis(cyclopentadienyl)zirconium dichloride,
bis(cyclopentadienyl)titanium dichloride,
bis(cyclopentadienyl)hafnium dichloride,
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bis(cyclopentadienyl)hafnium dimethyl,
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bis(pentamethylcyclopentadienyl)titanium dimethyl,
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bis(1-methyl-3-n-butylcyclopentadienyl)hafnium dimethyl,
bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dichloride,
bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dimethyl,
bis(1-methyl-3-n-butylcyclopentadienyl)titanium dichloride, and
bis(1-methyl-3-n-butylcyclopentadienyl)titanium dimethyl.

9.. The catalyst system of any of claims 1 to 8 further comprising bis(n-propylcyclopentadienyl)hafnium dimethyl.

10. The catalyst system of claim 7, wherein each of Cp^A and Cp^B is independently selected from the group consisting of: cyclopentadienyl, n-propylcyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, and n-butylcyclopentadienyl.

11. The catalyst system of claim 1, wherein the support comprises silica.

12. The catalyst system of any of claims 1 to 11 where the support material is slurried in a non-polar solvent and the resulting slurry is first contacted with the activator for a period of time between 0.5 hours and 24 hours, then is contacted with a solution of at least one catalyst compound.

13. The catalyst system of any of claims 1 to 12, wherein the activator comprises one or more of:
N,N-dimethylanilinium tetra(perfluorophenyl)borate,
N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethylanilinium 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 tetra(perfluorophenyl)borate,
trimethylammonium tetrakis(perfluoronaphthyl)borate,
triethylammonium tetrakis(perfluoronaphthyl)borate,
tripropylammonium tetrakis(perfluoronaphthyl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, and
tropillium tetrakis(perfluoronaphthyl)borate.

14. The catalyst system of any of claims 1 to 13, wherein the activator comprises an alumoxane.

15. The catalyst system of any of claims 1 to 10, 12, 13, or 14, wherein the support material is selected from the group consisting of Al_2O_3, ZrO_2, SiO_2, or SiO_2/Al_2O_3.

16. A process for producing a polyolefin composition comprising contacting at least one olefin with the catalyst system of any of claims 1 to 15 and obtaining a polyolefin.

17. The process of claim 16, wherein the polyolefin composition is a multi-modal polyolefin composition comprising a low molecular weight fraction, wherein the low molecular weight fraction is produced by the catalyst compound represented by Formula (I).

18. The process of claim 16 or 17, wherein the activator comprises alumoxane, non-coordinating anion or a mixture thereof.

19. The process of any of claims 16 to 18, wherein the process occurs at a temperature of from 0°C to 300°C, at a pressure in the range of from 0.35 MPa to 10 MPa, and at a time up to 300 minutes.

20. The process of any of claims 16 to 19, wherein the at least one olefin comprises ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, or mixtures thereof.

21. The process of any of claims 16 to 20, wherein the process is a gas phase process or a slurry phase process.

22. A process for producing a polyolefin composition comprising contacting at least one olefin comprising ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, or mixtures thereof, with the catalyst system of claim 1, where the support material is slurried in a non-polar solvent and the resulting slurry is first contacted with the activator for a period of time between 0.5 hours and 24 hours, then is contacted with a solution of at least one catalyst compound.