

CLAIMS

The invention claimed is:

1. A compound represented by Formula (I):



wherein:

Ar is an aryl group;

E is nitrogen or phosphorous;

R¹ is a C₁-C₃₀, optionally substituted, linear alkyl group;

10 R² is a C₁-C₃₀, optionally substituted, linear alkyl group;

R³ is a C₁₀-C₃₀, optionally substituted, linear alkyl group;

M is an element selected from group 13 of the Periodic Table of the Elements;

d is 1, 2 or 3; k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6; n - k = d; and

15 each Q is independently hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical.

2. The compound of claim 1, wherein R¹ is a C₁ to C₁₀ linear alkyl group.

3. The compound of any of claim 1 or claim 2, wherein R¹ is methyl, ethyl, propyl, butyl, pentyl, or hexyl.

20 4. The compound of any one of claims 1-3, wherein R² is a C₁-C₂₀, optionally substituted, linear alkyl group.

5. The compound of any one of claims 1-4, wherein R³ is a C₁₀-C₂₀, optionally substituted, linear alkyl group.

6. The compound of any one of claims 1-5, wherein R¹ is methyl.

25 7. The compound of any one of claims 1-6, wherein R² is methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, or n-icosyl.

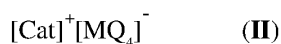
8. The compound of any one of claims 1-7, wherein R³ is n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, n-nonadecyl, or 30 n-icosyl.

9. The compound of any one of claims 1-8, wherein E is nitrogen.

10. The compound of any one of claims 1-9, wherein M is boron and k is 3.

11. The compound of any one of claims 1-10, wherein M is boron and E is nitrogen.

12. The compound of any one of claims 1-11, wherein Q is an optionally substituted aryl group.
13. The compound of any one of claims 1-12, wherein Q is a halogen substituted aryl group.
14. The compound of any one of claims 1-13, wherein Q is a perfluoroaryl group.
- 5 15. The compound of any one of claims 1-14, wherein Q is a perfluorophenyl group.
16. The compound of any one of claims 1-14, wherein Q is a perfluoronaphthyl group.
17. The compound of any one of claims 1-16, wherein R¹, R², and R³ together comprise 20 or more carbon atoms.
18. The compound of any one of claims 1-16, wherein Ar is a phenyl group.
- 10 19. A compound represented by Formula (II):

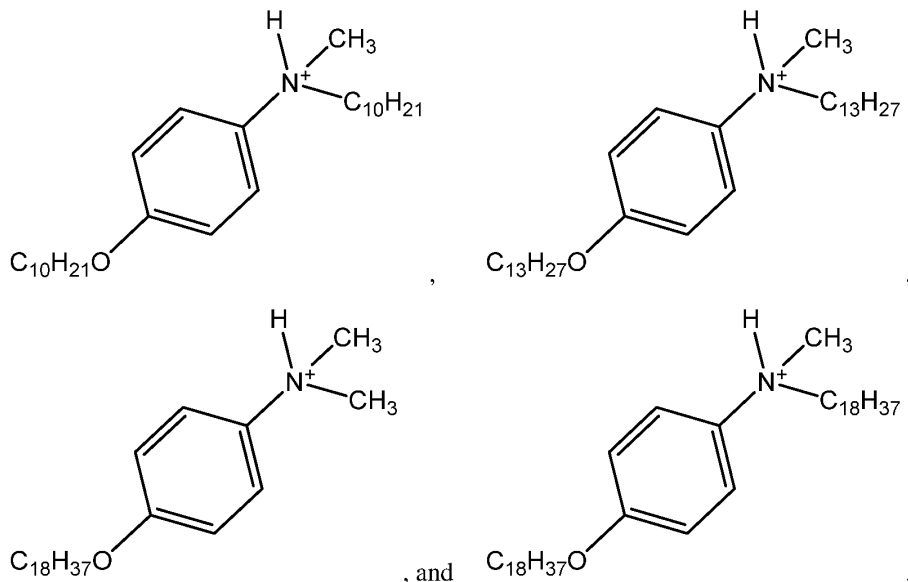


wherein:

M is an element selected from group 13 of the Periodic Table of the Elements;

- Q is a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, or halosubstituted-hydrocarbyl radical; and
- 15

[Cat]⁺ is a cation represented by a structure selected from the group consisting of



20. The compound of claim 19, wherein Q is an optionally substituted aryl group.

21. The compound of any one of claims 19-20, wherein Q is a halogen substituted aryl group.
22. The compound of any one of claims 19-21, wherein Q is a perfluoroaryl group.
23. The compound of any one of claims 19-22, wherein Q is a perfluorophenyl group.
- 5 24. The compound of any one of claims 19-22, wherein Q is a perfluoronaphthyl group.
25. The compound of any one of claims 19-24, wherein M is boron.
26. A compound represented by Formula (III):

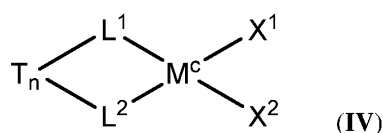


wherein:

- 10 E is nitrogen or phosphorous;
 each of R^{11} , R^{12} , and R^{13} is independently a C_1 - C_{30} linear alkyl group or an aryl group, wherein the aryl group is substituted with at least one C_{10} - C_{30} alkoxy group, wherein R^{11} , R^{12} , and R^{13} together comprise 26 or more carbon atoms; and
 each of R^{14} , R^{15} , R^{16} , and R^{17} is independently an aryl group, wherein at least one of R^{14} ,
 15 R^{15} , R^{16} , and R^{17} is substituted with from one to seven fluorine atoms.
27. The compound of claim 26, wherein each of R^{11} and R^{12} is independently a C_1 - C_{30} linear alkyl, and R^{13} is an aryl group substituted with a C_{10} - C_{30} alkoxy group.
28. The compound of any one of claims 26-27, wherein R^{11} , R^{12} , and R^{13} together comprise 30 or more carbon atoms.
- 20 29. The compound of any one of claims 26-28, wherein R^{11} , R^{12} , and R^{13} together comprise 40 or more carbon atoms.
30. The compound of any one of claims 26-29, wherein E is nitrogen.
31. The compound of any one of claims 1-30, wherein the compound has a solubility of at least 10 mM at 25°C in methylcyclohexane.
- 25 32. The compound of any one of claims 1-30, wherein the compound has a solubility of at least 10 mM at 25°C in isohexane.
33. The compound of any one of claims 1-30, wherein the compound has a solubility of at least 10 mM at 25°C in methylcyclohexane and a solubility of at least 10 mM at 25°C in isohexane.
- 30 34. A catalyst system comprising a catalyst and an activator comprising the compound of any one of claims 1-33.
35. The catalyst system of claim 34, further comprising a support material.

36. The catalyst system of claim 35, wherein the support material is selected from Al_2O_3 , ZrO_2 , SiO_2 , $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{SiO}_2/\text{TiO}_2$, silica clay, silicon oxide/clay, and mixtures thereof.

37. The catalyst system of any one of claims 34-36, wherein the catalyst is represented by Formula (IV):



wherein in Formula (IV):

M^c is an element selected from group 4 of the Periodic Table of the Elements;

n is 0 or 1;

T is an optional bridging group selected from S, O, PR' , NR' , SiR''_2 , CH_2 , CHR'' , or CR''_2 , wherein R' is a C_1 - C_{30} , optionally substituted, hydrocarbyl group and R'' is hydrogen or a C_1 - C_{30} , optionally substituted, hydrocarbyl group;

L^1 and L^2 are independently cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, tetrahydroindenyl, substituted tetrahydroindenyl, fluorenyl, or substituted fluorenyl groups; and

X^1 and X^2 are, independently, hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silyl, silylcarbyl, substituted silylcarbyl, germylcarbyl, substituted germylcarbyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, substituted alkoxy, aryloxy, substituted aryloxy, boryl, amino, phosphino, ether, thioether, phosphine, amine, carboxylate, alkylthio, arylthio, 1,3-dionate, oxalate, carbonate, nitrate, or sulphate, or both X^1 and X^2 are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand.

38. The catalyst system of claim 37, wherein T is an optional bridging group selected from dialkylsilyl, diarylsilyl, dialkylmethyl, diarylmethyl, ethylenyl, or hydrocarbylethylenyl wherein one, two, three or four of the hydrogen atoms in ethylenyl are substituted by hydrocarbyl.

39. The catalyst system of claim 37, wherein the catalyst is C_2 symmetrical.

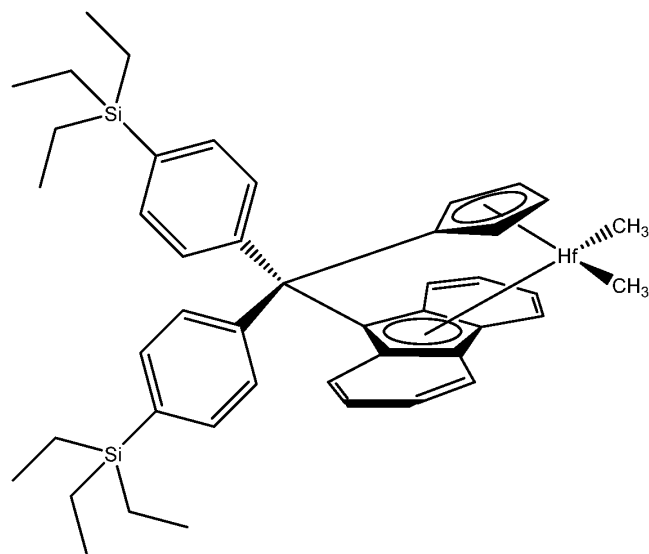
40. The catalyst system of claim 37, wherein the catalyst is one or more of:

dimethylsilyl bis(indenyl) $\text{M}^c(\text{R})_2$;

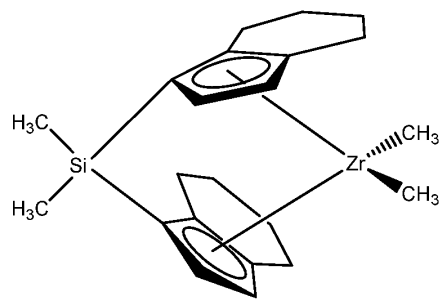
dimethylsilyl bis(tetrahydroindenyl) $\text{M}^c(\text{R})_2$;

bis(1-methyl, 3-n-butyl cyclopentadienyl) $\text{M}^c(\text{R})_2$;

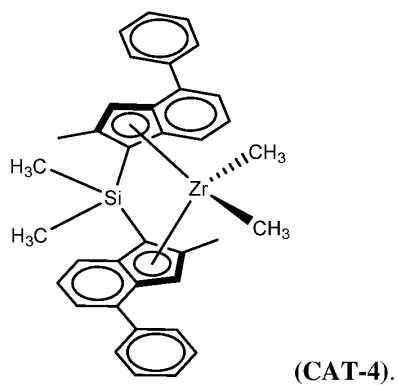
- bis(indenyl) $M^c(R)_2$;
 dimethylsilyl bis(tetrahydroindenyl) $M^c(R)_2$;
 bis(n-propylcyclopentadienyl) $M^c(R)_2$;
 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido) $M^c(R)_2$;
 5 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido) $M^c(R)_2$;
 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido) $M^c(R)_2$;
 dimethylsilyl (tetramethylcyclopentadienyl)(t-butylamido) $M^c(R)_2$;
 1,1'-bis(4-triethylsilylphenyl)(methylene)(cyclopentadienyl)(fluorenyl) $M^c(R)_2$;
 $\mu-(CH_3)_2Si(cyclopentadienyl)(1-adamantylamido)M^c(R)_2$;
 10 $\mu-(CH_3)_2Si(3-tertbutylcyclopentadienyl)(1-adamantylamido)M^c(R)_2$;
 $\mu-(CH_3)_2(tetramethylcyclopentadienyl)(1-adamantylamido)M^c(R)_2$;
 $\mu-(CH_3)_2Si(tetramethylcyclopentadienyl)(1-adamantylamido)M^c(R)_2$;
 $\mu-(CH_3)_2C(tetramethylcyclopentadienyl)(1-adamantylamido)M^c(R)_2$;
 $\mu-(CH_3)_2Si(tetramethylcyclopentadienyl)(1-tertbutylamido)M^c(R)_2$;
 15 $\mu-(CH_3)_2Si(fluorenyl)(1-tertbutylamido)M^c(R)_2$;
 $\mu-(CH_3)_2Si(tetramethylcyclopentadienyl)(1-cyclododecylamido)M^c(R)_2$;
 $\mu-(C_6H_5)_2C(tetramethylcyclopentadienyl)(1-cyclododecylamido)M^c(R)_2$;
 $\mu-(CH_3)_2Si(\eta^5-2,6,6-trimethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)(tertbutylamido)M^c(R)_2$;
 where M^c is selected from Ti, Zr, and Hf; and R is selected from halogen or C_1 to C_5 alkyl.
 20 41. The catalyst system of any of claims 37-40, wherein the catalyst is rac-dimethylsilyl-bis(indenyl)hafnium dimethyl.
 42. The catalyst system of claim 37, wherein the catalyst is represented by Formula (CAT-2):



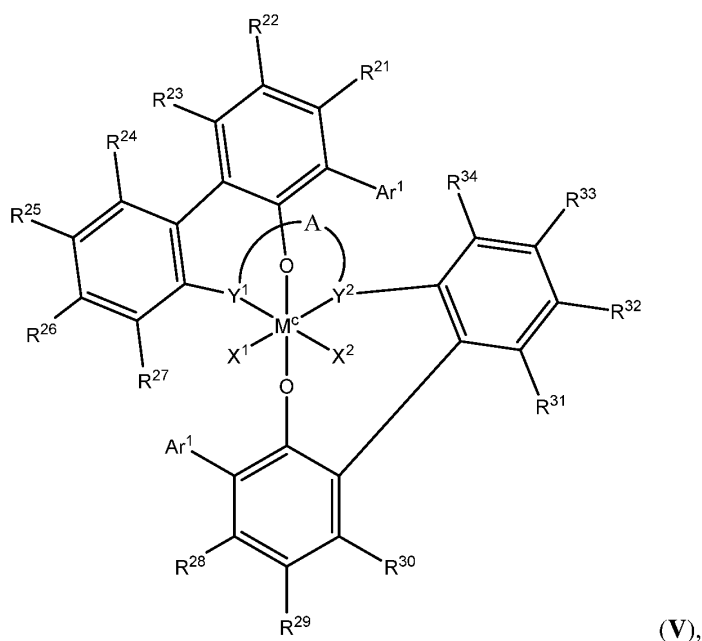
43. The catalyst system of claim 37, wherein the catalyst is represented by Formula (CAT-3):



5 44. The catalyst system of claim 37, wherein the catalyst is represented by Formula (CAT-4):



45. The catalyst system of claim 37, wherein the catalyst is represented by Formula (V):



wherein in Formula (V):

M^c is an element selected from group 4 of the Periodic Table of the Elements;

- 5 R^{21} , R^{22} , R^{23} , R^{24} , R^{25} , R^{26} , R^{27} , R^{28} , R^{29} , R^{30} , R^{31} , R^{32} , R^{33} and R^{34} are independently hydride, halide, optionally substituted hydrocarbyl, heteroatom-containing optionally substituted hydrocarbyl, alkoxy, aryloxy, silyl, boryl, dialkyl amino, alkylthio, arylthio and seleno; optionally two or more R groups can combine together into ring structures with such ring structures having from 3 to 100 non-hydrogen atoms in the ring;

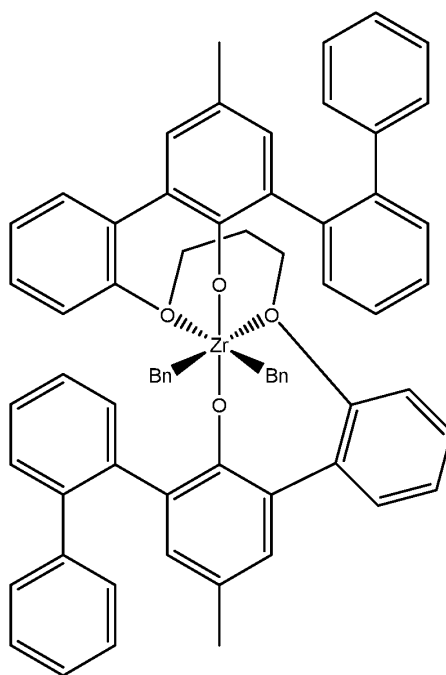
A is a C_1 - C_{50} alkyl group;

- 10 Y^1 and Y^2 are independently selected from O, S, NR^a and PR^a wherein R^a is optionally substituted hydrocarbyl;

Ar^1 is phenyl, naphthyl, biphenyl, anthracenyl, or phenanthrenyl; and

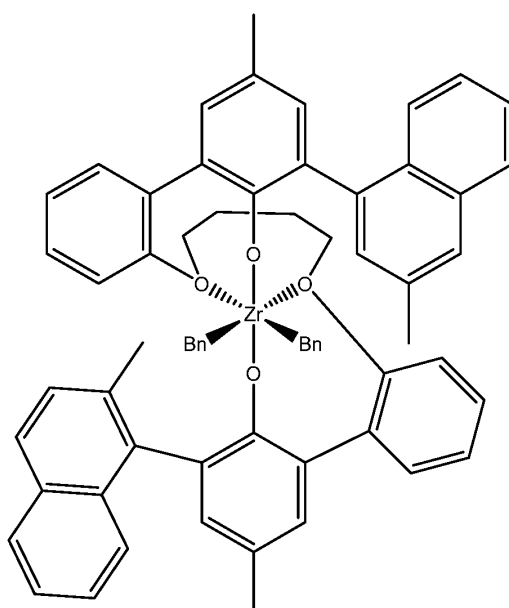
- X^1 and X^2 are, independently, hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silyl, silylcarbyl, substituted silylcarbyl, germylcarbyl, substituted germylcarbyl, aryl, substituted aryl, alkylaryl, heteroaryl, substituted heteroaryl, alkoxy, substituted alkoxy, aryloxy, substituted aryloxy, boryl, amino, phosphino, ether, thioether, phosphine, amine, carboxylate, alkylthio, arylthio, 1,3-dionate, oxalate, carbonate, nitrate, or sulphate, or both X^1 and X^2 are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be
- 20 an olefin, diolefin or aryne ligand.

46. The catalyst system of claim 45, wherein M^c is Zr.
47. The catalyst system of any one of claims 45-46, wherein Y^1 and Y^2 are O.
48. The catalyst system of any one of claims 45-47, wherein X^1 and X^2 are benzyl.
49. The catalyst system of any one of claims 45-48, wherein A is propyl or butyl.
- 5 50. The catalyst system of any one of claims 45-49, wherein the catalyst is represented by Formula (CAT-5):



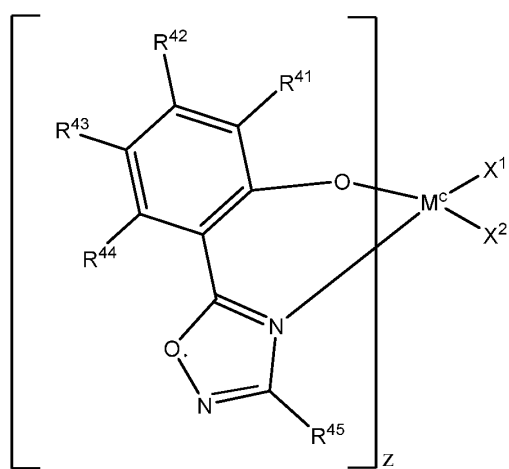
(CAT-5)

51. The catalyst system of any one of claims 45-49, wherein the catalyst is represented by Formula (CAT-6):

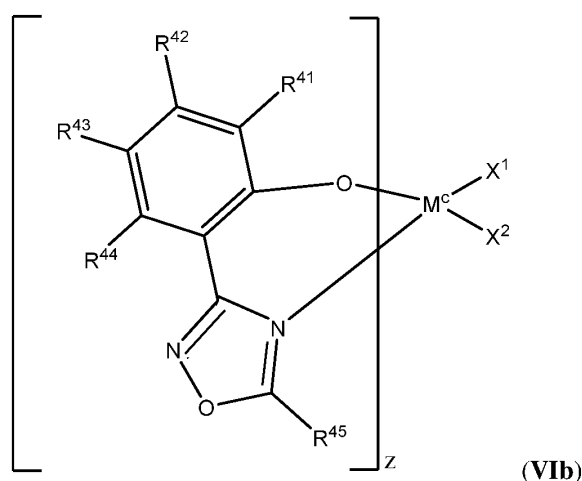


(CAT-6)

52. The catalyst system of any one of claims 34-36, wherein the catalyst is represented by Formulas (VIa) or (VIb):



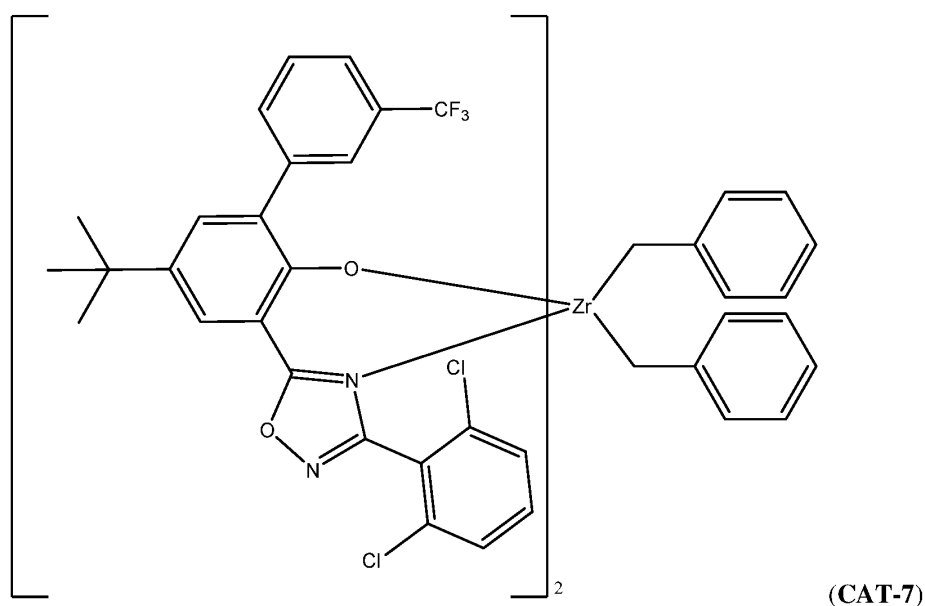
(VIa)



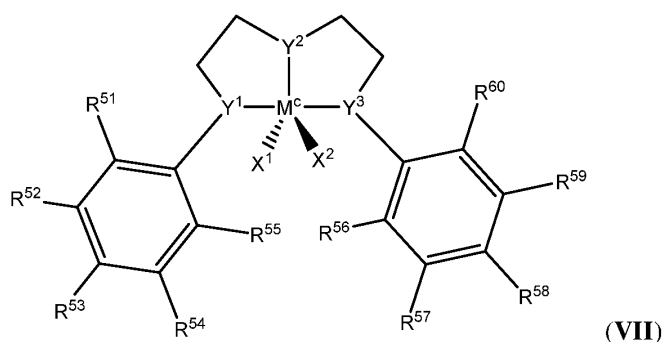
wherein in Formulas (VIa) or (VIb):

M^c is an element selected from group 4 of the Periodic Table of the Elements

- 5 R^{41} , R^{42} , R^{43} , R^{44} , R^{45} are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, halo, silyl, boryl, phosphino, amino, thioalkyl, thioaryl, nitro, and combinations thereof;
- 10 X^1 and X^2 are, independently, hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silyl, silylcarbyl, substituted silylcarbyl, germylcarbyl, substituted germylcarbyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, substituted alkoxy, aryloxy, substituted aryloxy, boryl, amino, phosphino, ether, thioether, phosphine, amine, carboxylate, alkylthio, arylthio, 1,3-dionate, oxalate, carbonate, nitrate, or sulphate, or both X^1 and X^2 are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand; and
- z is 1, 2, 3, or 4.
53. The catalyst system of claim 52, wherein M^c is Zr.
- 20 54. The catalyst system of any of claims 52-53, wherein X^1 and X^2 are benzyl.
55. The catalyst system of any one of claims 52-54, wherein the catalyst is represented by Formula (CAT-7):



56. The catalyst system of any of claims 34-36, wherein the catalyst is represented by Formula (VII):



wherein in Formula (VII):

M^c is an element selected from group 4 of the Periodic Table of the Elements

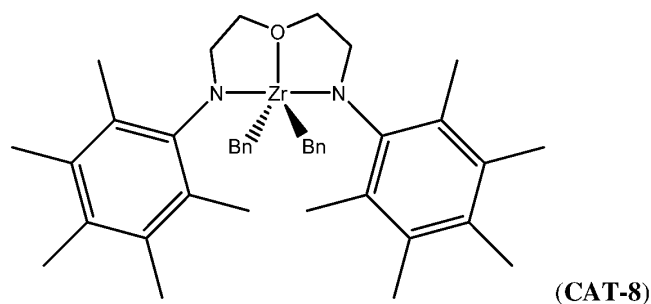
R^{51} , R^{52} , R^{53} , R^{54} , R^{55} , R^{56} , R^{57} , R^{58} , R^{59} , R^{60} are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, substituted heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, halo, silyl, boryl, phosphino, amino, thioalkyl, thioaryl, nitro, and combinations thereof;

Y^1 and Y^2 are independently O, N, NH, or S; and

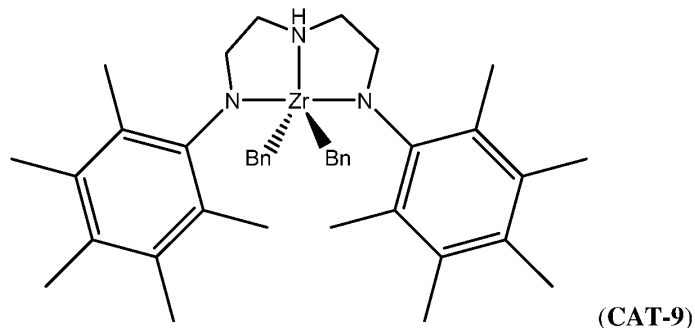
X^1 and X^2 are, independently, hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silyl, silylcarbyl, substituted silylcarbyl, germylcarbyl,

- substituted germylcarbonyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, substituted alkoxy, aryloxy, substituted aryloxy, boryl, amino, phosphino, ether, thioether, phosphine, amine, carboxylate, alkylthio, arylthio, 1,3-dionate, oxalate, carbonate, nitrate, or sulphate, or both X^1 and X^2 are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand.

57. The catalyst system of claim 56, wherein the catalyst is represented by Formula (CAT-8):



58. The catalyst system of claim 56, wherein the catalyst is represented by Formula (CAT-9):



59. A method comprising contacting at least one olefin with the catalyst system of any one of claims 34-58, and obtaining a polyolefin.
60. The method of claim 59, wherein the at least one olefin comprises propylene.
61. The method of claim 60, wherein the polyolefin has an Mw of about 25,000 to about 300,000 g/mol and a melt temperature of about 100°C to about 130°C.
62. The method of claim 59, wherein the at least one olefin comprises ethylene.
63. The method of claim 62, wherein the polyolefin has an Mw of about 250,000 to about 2,500,000 g/mol and a melt temperature of about 120°C to about 140°C.

64. A method comprising contacting two or more different olefins with the catalyst system of any one of claims 34-58; and obtaining a polyolefin.
65. The method of claim 64, wherein the two or more olefins are ethylene and octene.
66. The method of claim 65, wherein the polyolefin has an Mw of from about 50,000 to
5 about 1,500,000 g/mol and a melt temperature of from about 25°C to about 100°C.
67. The method of any one of claims 59-66, wherein contacting is performed in the gas phase or slurry phase.
68. A solution comprising the compound of any one of claims 1-33 and an aliphatic solvent; wherein aromatic solvents are absent.
- 10 69. A solution comprising the catalyst system of any one of claims 34-57 and an aliphatic solvent; wherein aromatic solvents are absent.