

ARYL-HETEROCYCLE-PYRROLE CATALYSTS FOR OLEFIN POLYMERIZATION

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/493,440 filed March 31, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally directed to processes for polymerizing olefin monomers in the presence of aryl-heterocyclic-pyrrole catalyst, and the synthesis and study of aryl-heterocyclic-pyrrole catalysts.

BACKGROUND

[0003] Olefin-based polymers such as polyethylene, ethylene-based polymers, polypropylene, and propylene-based polymers are produced via various catalyst systems. Selection of such catalyst systems used in the polymerization process of the olefin-based polymers is an important factor contributing to the characteristics and properties of such olefin-based polymers.

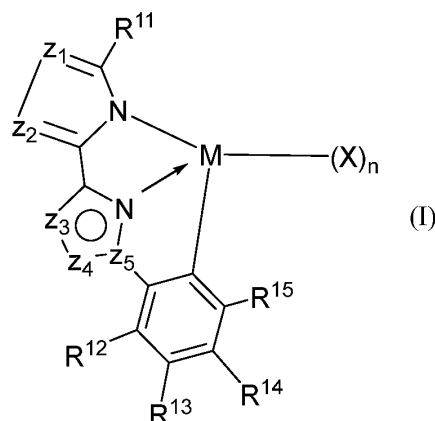
[0004] Ethylene-based polymers and propylene-based are manufactured for a wide variety of articles. The polyethylene and polypropylene polymerization process can be varied in a number of respects to produce a wide variety of resultant polyethylene resins having different physical properties that render the various resins suitable for use in different applications. The ethylene monomers and, optionally, one or more co-monomers are present in liquid diluents (such as solvents), such as an alkane or isoalkane, for example isobutene. Hydrogen may also be added to the reactor. The catalyst systems for producing ethylene-based polyolefin resins may typically comprise a chromium-based catalyst system, a Ziegler-Natta catalyst system, and/or a molecular (either metallocene or non-metallocene (molecular)) catalyst system. The reactants in the diluent and the catalyst system are circulated at an elevated polymerization temperature around the reactor, thereby producing ethylene-based homopolymer or copolymer. Either periodically or continuously, part of the reaction mixture, including the polyethylene product dissolved in the diluent, together with unreacted ethylene and one or more optional co-monomers, is removed from the reactor. The reaction mixture, when removed from the reactor, may be processed to remove the polyethylene product from the diluent and the unreacted reactants, with the diluent and unreacted reactants typically being recycled back into the reactor. Alternatively, the reaction mixture may be sent to a second reactor, serially connected to the first reactor, where a second polyethylene fraction may be produced. Despite the research efforts in developing catalyst

systems suitable for olefin polymerization, such as polyethylene or polypropylene polymerization, there is still a need to increase the efficiencies of catalyst systems that are capable of producing polymer with high molecular weights and a narrow molecular weight distribution.

SUMMARY

[0005] There is an ongoing need to create catalyst systems or metal–ligand complexes with a high selectivity toward ethylene during ethylene and α -olefin copolymerization reactions. Additionally, the metal–ligand complex should have high catalyst efficiency and a versatile ability to produce polymers with a high molecular weight at high reactor temperatures (such as greater than 120 °C, greater than 150 °C, or approximately 190 °C).

[0006] Embodiments of this disclosure include a metal–ligand complex according to formula (I):



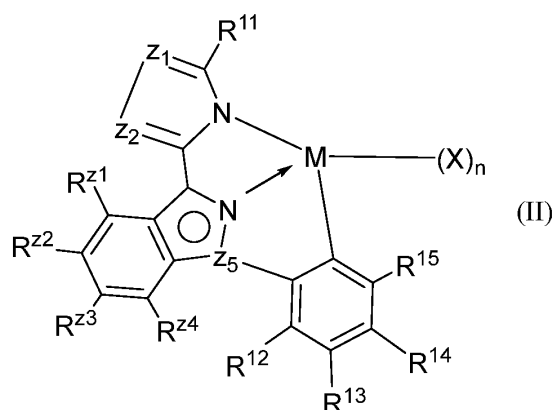
[0007] In formula (I), M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4. Each X is a monodentate or bidentate ligand independently chosen from (C_1-C_{50}) hydrocarbyl, halogen, $-(CH_2)_wSi(R^X)_3$, $-N(R^N)_2$, and $-NCOR^C$, where w is 1 to 10 and R^X is (C_1-C_{20}) alkyl. When X is monodentate, subscript n of $(X)_n$ is 2, and when X is bidentate, subscript n of $(X)_n$ is 1 or 2.

[0008] In formula (I), z_1 is independently selected from N or $C(R^1)$, and R^1 and R^{11} are not covalently connected to form an aromatic ring or a non-aromatic ring; z_2 is independently selected from N or $C(R^2)$, and R^1 and R^2 may be covalently connected to form an aromatic ring or a non-aromatic ring; z_3 is independently selected from O, S, N, R^N or $C(R^3)$, and R^3 and R^4 may be covalently connected to form an aromatic ring or a non-aromatic ring; and z_4 is independently selected from O, S, N, NR^N or $C(R^4)$, and R^4 and R^3 may be covalently connected to form an aromatic ring or a non-aromatic ring.

[0009] In formula (I), R^1 , R^2 , R^3 , R^4 , R^{11} , R^{12} , R^{13} , R^{14} , and R^{15} are independently selected from the group consisting of (C_1-C_{50}) hydrocarbyl, (C_1-C_{50}) heterohydrocarbyl, (C_6-C_{50}) aryl, (C_4-C_{50}) heteroaryl, $-\text{Si}(\text{R}^C)_3$, $-\text{Ge}(\text{R}^C)_3$, $-\text{P}(\text{R}^P)_2$, $-\text{N}(\text{R}^N)_2$, $-\text{OR}^C$, $-\text{SR}^C$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^C\text{S}(\text{O})-$, $-\text{P}(\text{O})(\text{R}^P)_2$, $\text{R}^C\text{S}(\text{O})_2-$, $(\text{R}^C)_2\text{C}=\text{N}-$, $\text{R}^C\text{C}(\text{O})\text{O}-$, $\text{R}^C\text{OC}(\text{O})-$, $\text{R}^C\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^C)_2\text{NC}(\text{O})-$, halogen, and $-\text{H}$, wherein R^{12} and R^{13} are optionally connected to form a ring, R^{13} and R^{14} are optionally connected to form a ring, and R^{14} and R^{15} are optionally connected to form a ring.

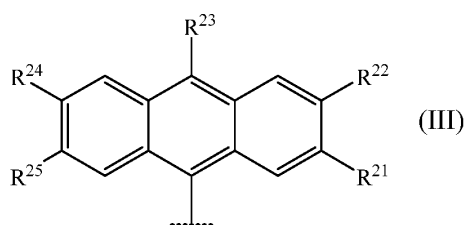
[0010] In formula (I), each R^N , R^C , and R^P is independently selected from the group consisting of (C_1-C_{20}) hydrocarbyl, (C_1-C_{20}) heterohydrocarbyl, and $-\text{H}$.

[0011] In one or more embodiments, the metal-ligand complex of formula (I) includes z_3 is CR^3 , z_4 is CR^4 , and R^3 and R^4 are connected to form an aromatic ring, and the metal-ligand structure has a structure according to formula (II):



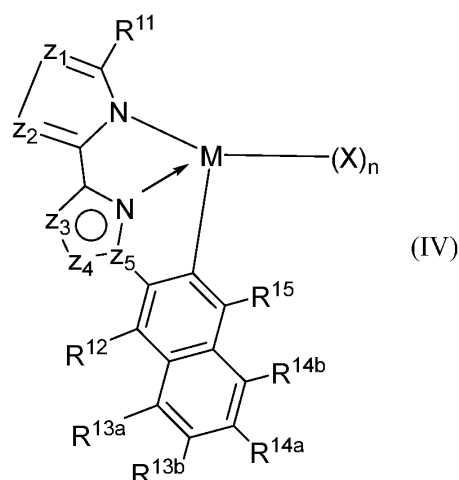
[0012] In formula (I), z_1 , z_2 , z_5 , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , X , n , and M are defined as in formula (I), and R^{z1} , R^{z2} , R^{z3} , R^{z4} selected from the group consisting of hydrogen, (C_1-C_{20}) alkyl, (C_6-C_{50}) aryl, (C_1-C_{10}) heterohydrocarbyl, $-\text{NR}^N$, $-\text{OR}^C$, $-\text{SR}^C$, halogen, CF_3-NO_2 , or $-\text{CN}$, where R^C is (C_1-C_{20}) alkyl, (C_6-C_{20}) aryl. In some embodiments, in formula (II), z_5 is N .

[0013] In some embodiments, the metal-ligand complex of formula (I) includes R^{11} is a radical of formula (III):



[0014] In formula (III), R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is independently chosen from (C_1-C_{10}) alkyl, (C_6-C_{10}) aryl, or $-H$.

[0015] In one or more embodiments, R^{13} and R^{14} are covalently connected to form an aromatic ring, the metal-ligand has a structure according to formula (IV):



[0016] In formula (IV), R^{11} , R^{12} , R^{15} , Z_1 , Z_2 , Z_3 , Z_4 , Z_5 , M , X and n are as defined in formula (I). In formula (IV), R^{13a} , R^{13b} , R^{14a} and R^{14b} are selected from the group consisting of hydrogen, chloro, fluoro, benzyl, (C_1-C_{10}) alkyl, cyclic (C_1-C_{10}) heteroalkyl, $-OR^C$, $-NR^N_2$, wherein R^C and R^N are (C_1-C_{12}) alkyl.

DETAILED DESCRIPTION

[0017] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure.

[0018] Common abbreviations are listed below:

[0019] **R, Z, M, X and n**: as defined above; **Me**: methyl; **Et**: ethyl; **Ph**: phenyl; **Bn**: benzyl; **i-Pr**: *iso*-propyl; **t-Bu**: *tert*-butyl; **t-Oct**: *tert*-octyl (2,4,4-trimethylpentan-2-yl); **Tf**: trifluoromethane sulfonate; **CV**: column volume (used in column chromatography); **EtOAc**: ethyl acetate; **TEA**: triethylaluminum; **MAO**: methylaluminoxane; **MMAO**: modified methylaluminoxane; **LiCH₂TMS**: (trimethylsilyl)methyl lithium; **TMS**: trimethylsilyl; **Pd(AmPhos)Cl₂**: Bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II); **Pd(AmPhos)**: Chloro(crotyl)(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)palladium(II); **Pd(dppf)Cl₂**: [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride; **ScCl₃**: scandium(III) chloride; **PhMe**: toluene; **THF**: tetrahydrofuran; **CH₂Cl₂**: dichloromethane; **DMF**:

N,N-dimethylformamide; **EtOAc**: ethyl acetate; **Et₂O**: diethyl ether; **MeOH**: methanol; **NH₄Cl**: ammonium chloride; **MgSO₄**: magnesium sulfate; **Na₂SO₄**: sodium sulfate; **NaOH**: sodium hydroxide; **brine**: saturated aqueous sodium chloride; **SiO₂**: silica; **CDCl₃**: chloroform-D; **GC**: gas chromatography; **LC**: liquid chromatography; **NMR**: nuclear magnetic resonance; **MS**: mass spectrometry; **mmol**: millimoles; **mL**: milliliters; **M**: molar; **min or mins**: minutes; **h or hrs**: hours; **d**: days; **TLC**: thin layered chromatography; **rpm**: revolution per minute; **rt**: room temperature.

[0020] The term “independently selected” is used herein to indicate that the R groups, such as, R¹, R², R³, R⁴, and R⁵, can be identical or different (e.g., R¹, R², R³, R⁴, and R⁵ may all be substituted alkyls or R¹ and R² may be a substituted alkyl and R³ may be an aryl, etc.) A chemical name associated with an R group is intended to convey the chemical structure that is recognized in the art as corresponding to that of the chemical name. Thus, chemical names are intended to supplement and illustrate, not preclude, the structural definitions known to those of skill in the art.

[0021] When used to describe certain carbon atom-containing chemical groups, a parenthetical expression having the form “(C_x–C_y)” means that the unsubstituted form of the chemical group has from x carbon atoms to y carbon atoms, inclusive of x and y. For example, a (C₁–C₅₀)alkyl is an alkyl group having from 1 to 50 carbon atoms in its unsubstituted form. In some embodiments and general structures, certain chemical groups may be substituted by one or more substituents such as R^S. An R^S substituted chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S. For example, a “(C₁–C₅₀)alkyl substituted with exactly one group R^S, where R^S is phenyl (–C₆H₅)” may contain from 7 to 56 carbon atoms. Thus, in general when a chemical group defined using the “(C_x–C_y)” parenthetical is substituted by one or more carbon atom-containing substituents R^S, the minimum and maximum total number of carbon atoms of the chemical group is determined by adding to both x and y the combined sum of the number of carbon atoms from all of the carbon atom-containing substituents R^S.

[0022] The term “substitution” means that at least one hydrogen atom (–H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g., R^S). The term “persubstitution” means that every hydrogen atom (H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g., R^S). The term “polysubstitution” means that at least two, but fewer than all, hydrogen atoms bonded to carbon atoms or heteroatoms of a corresponding

unsubstituted compound or functional group are replaced by a substituent. The term “-H” means a hydrogen or hydrogen radical that is covalently bonded to another atom. “Hydrogen” and “-H” are interchangeable, and unless clearly specified have identical meanings.

[0023] The term “(C₁-C₅₀)hydrocarbyl” means a hydrocarbon radical of from 1 to 50 carbon atoms and the term “(C₁-C₅₀)hydrocarbylene” means a hydrocarbon diradical of from 1 to 50 carbon atoms, in which each hydrocarbon radical and each hydrocarbon diradical is aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (having three carbons or more, and including mono- and poly-cyclic, fused and non-fused polycyclic, and bicyclic) or acyclic, and substituted by one or more R^S or unsubstituted.

[0024] In this disclosure, a (C₁-C₅₀)hydrocarbyl may be an unsubstituted or substituted (C₁-C₅₀)alkyl, (C₃-C₅₀)cycloalkyl, (C₃-C₂₀)cycloalkyl-(C₁-C₂₀)alkylene, (C₆-C₄₀)aryl, or (C₆-C₂₀)aryl-(C₁-C₂₀)alkylene (such as benzyl (-CH₂-C₆H₅)).

[0025] The terms “(C₁-C₅₀)alkyl” and “(C₁-C₁₈)alkyl” mean a saturated straight or branched hydrocarbon radical of from 1 to 50 carbon atoms and a saturated straight or branched hydrocarbon radical of from 1 to 18 carbon atoms, respectively, that is unsubstituted or substituted by one or more R^S. Examples of unsubstituted (C₁-C₅₀)alkyl are unsubstituted (C₁-C₂₀)alkyl; unsubstituted (C₁-C₁₀)alkyl; unsubstituted (C₁-C₅)alkyl; methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2-butyl; 2-methylpropyl; 1,1-dimethylethyl; 1-pentyl; 1-hexyl; 1-heptyl; 1-nonyl; and 1-decyl. Examples of substituted (C₁-C₄₀)alkyl are substituted (C₁-C₂₀)alkyl, substituted (C₁-C₁₀)alkyl, trifluoromethyl, and [C₄₅]alkyl. The term “[C₄₅]alkyl” means there is a maximum of 45 carbon atoms in the radical, including substituents, and is, for example, a (C₂₇-C₄₀)alkyl substituted by one R^S, which is a (C₁-C₅)alkyl, respectively. Each (C₁-C₅)alkyl may be methyl, trifluoromethyl, ethyl, 1-propyl, 1-methylethyl, or 1,1-dimethylethyl.

[0026] The term “(C-C₅₀)aryl” means an unsubstituted or substituted (by one or more R^S) monocyclic, bicyclic, or tricyclic aromatic hydrocarbon radical of from 6 to 40 carbon atoms, of which at least from 6 to 14 of the carbon atoms are aromatic ring carbon atoms. A monocyclic aromatic hydrocarbon radical includes one aromatic ring; a bicyclic aromatic hydrocarbon radical has two rings; and a tricyclic aromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic aromatic hydrocarbon radical is present, at least one of the rings of the radical is aromatic. The other ring or rings of the aromatic radical may be independently fused or non-fused and aromatic or non-aromatic. Examples of unsubstituted (C₆-C₅₀)aryl include: unsubstituted (C₆-C₂₀)aryl, unsubstituted (C₆-C₁₈)aryl; 2-(C₁-C₅)alkyl-phenyl; phenyl; fluorenyl;

tetrahydrofluorenyl; indacenyl; hexahydroindacenyl; indenyl; dihydroindenyl; naphthyl; tetrahydronaphthyl; and phenanthrene. Examples of substituted (C₆–C₄₀)aryl include: substituted (C₁–C₂₀)aryl; substituted (C₆–C₁₈)aryl; 2,4-bis([C₂₀]alkyl)-phenyl; polyfluorophenyl; pentafluorophenyl; and fluoren-9-one-1-yl.

[0027] The term “(C₃–C₅₀)cycloalkyl” means a saturated cyclic hydrocarbon radical of from 3 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S. Other cycloalkyl groups (e.g., (C_x–C_y)cycloalkyl) are defined in an analogous manner as having from x to y carbon atoms and being either unsubstituted or substituted with one or more R^S. Examples of unsubstituted (C₃–C₄₀)cycloalkyl are unsubstituted (C₃–C₂₀)cycloalkyl, unsubstituted (C₃–C₁₀)cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted (C₃–C₄₀)cycloalkyl are substituted (C₃–C₂₀)cycloalkyl, substituted (C₃–C₁₀)cycloalkyl, cyclopentanone-2-yl, and 1-fluorocyclohexyl.

[0028] Examples of (C₁–C₅₀)hydrocarbylene include unsubstituted or substituted (C₆–C₅₀)arylene, (C₃–C₅₀)cycloalkylene, and (C₁–C₅₀)alkylene (e.g., (C₁–C₂₀)alkylene). The diradicals may be on the same carbon atom (e.g., –CH₂–) or on adjacent carbon atoms (i.e., 1,2-diradicals), or are spaced apart by one, two, or more than two intervening carbon atoms (e.g., 1,3-diradicals, 1,4-diradicals, etc.). Some diradicals include 1,2-, 1,3-, 1,4-, or an α,ω-diradical, and others a 1,2-diradical. The α,ω-diradical is a diradical that has maximum carbon backbone spacing between the radical carbons. Some examples of (C₂–C₂₀)alkylene α,ω-diradicals include ethan-1,2-diyl (i.e. –CH₂CH₂–), propan-1,3-diyl (i.e. –CH₂CH₂CH₂–), 2-methylpropan-1,3-diyl (i.e. –CH₂CH(CH₃)CH₂–). Some examples of (C₆–C₅₀)arylene α,ω-diradicals include phenyl-1,4-diyl, naphthalen-2,6-diyl, or naphthalen-3,7-diyl.

[0029] The term “(C₁–C₅₀)alkylene” means a saturated straight chain or branched chain diradical (i.e., the radicals are not on ring atoms) of from 1 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S. Examples of unsubstituted (C₁–C₅₀)alkylene are unsubstituted (C₁–C₂₀)alkylene, including unsubstituted –CH₂CH₂–, –(CH₂)₃–, –(CH₂)₄–, –(CH₂)₅–, –(CH₂)₆–, –(CH₂)₇–, –(CH₂)₈–, –CH₂C*HCH₃, and –(CH₂)₄C*(H)(CH₃), in which “C*” denotes a carbon atom from which a hydrogen atom is removed to form a secondary or tertiary alkyl radical. Examples of substituted (C₁–C₅₀)alkylene are substituted (C₁–C₂₀)alkylene, –CF₂–, –C(O)–, and –(CH₂)₁₄C(CH₃)₂(CH₂)₅– (i.e., a 6,6-dimethyl substituted normal-1,20-eicosylene). Since as mentioned previously two R^S may be taken together to form a (C₁–C₁₈)alkylene, examples of substituted (C₁–C₅₀)alkylene also include 1,2-bis(methylene)cyclopentane, 1,2-

bis(methylene)cyclohexane, 2,3-bis(methylene)-7,7-dimethyl-bicyclo[2.2.1]heptane, and 2,3-bis(methylene)bicyclo[2.2.2]octane.

[0030] The term “(C₃–C₅₀)cycloalkylene” means a cyclic diradical (i.e., the radicals are on ring atoms) of from 3 to 50 carbon atoms that either is unsubstituted or is substituted by one or more R^S.

[0031] The term “heteroatom,” refers to an atom other than hydrogen or carbon. Examples of groups containing one or more than one heteroatom include O, S, S(O), S(O)₂, Si(R^C)₂, P(R^P), N(R^N), –N=C(R^C)₂, –Ge(R^C)₂–, –Si(R^C)–, boron (B), aluminum (Al), gallium (Ga), or indium (In), where each R^C and each R^P is unsubstituted (C₁–C₁₈)hydrocarbyl or –H, and where each R^N is unsubstituted (C₁–C₁₈)hydrocarbyl. The term “heterohydrocarbon” refers to a molecule or molecular framework in which one or more carbon atoms of a hydrocarbon are replaced with a heteroatom. The term “(C₁–C₅₀)heterohydrocarbyl” means a heterohydrocarbon radical of from 1 to 50 carbon atoms, and the term “(C₁–C₅₀)heterohydrocarbylene” means a heterohydrocarbon diradical of from 1 to 50 carbon atoms. The heterohydrocarbon of the (C₁–C₅₀)heterohydrocarbyl or the (C₁–C₅₀)heterohydrocarbylene has one or more heteroatoms. The radical of the heterohydrocarbyl may be on a carbon atom or a heteroatom. The two radicals of the heterohydrocarbylene may be on a single carbon atom or on a single heteroatom. Additionally, one of the two radicals of the diradical may be on a carbon atom and the other radical may be on a different carbon atom; one of the two radicals may be on a carbon atom and the other on a heteroatom; or one of the two radicals may be on a heteroatom and the other radical on a different heteroatom. Each (C₁–C₅₀)heterohydrocarbyl and (C₁–C₅₀)heterohydrocarbylene may be unsubstituted or substituted (by one or more R^S), aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (including mono- and poly-cyclic, fused and non-fused polycyclic), or acyclic.

[0032] The (C₁–C₅₀)heterohydrocarbyl may be unsubstituted or substituted. Non-limiting examples of the (C₁–C₅₀)heterohydrocarbyl include (C₁–C₅₀)heteroalkyl, (C₁–C₅₀)hydrocarbyl-O–, (C₁–C₅₀)hydrocarbyl-S–, (C₁–C₅₀)hydrocarbyl-S(O)–, (C₁–C₅₀)hydrocarbyl-S(O)₂–, (C₁–C₅₀)hydrocarbyl-Si(R^C)₂–, (C₁–C₅₀)hydrocarbyl-N(R^N)–, (C₁–C₅₀)hydrocarbyl-P(R^P)–, (C₂–C₅₀)heterocycloalkyl, (C₂–C₁₉)heterocycloalkyl-(C₁–C₂₀)alkylene, (C₃–C₂₀)cycloalkyl-(C₁–C₁₉)heteroalkylene, (C₂–C₁₉)heterocycloalkyl-(C₁–C₂₀)heteroalkylene, (C₁–C₅₀)heteroaryl, (C₁–C₁₉)heteroaryl-(C₁–C₂₀)alkylene, (C₆–C₂₀)aryl-(C₁–C₁₉)heteroalkylene, or (C₁–C₁₉)heteroaryl-(C₁–C₂₀)heteroalkylene.

[0033] The term “(C₁–C₅₀)heteroaryl” means an unsubstituted or substituted (by one or more R^S) mono-, bi-, or tricyclic heteroaromatic hydrocarbon radical of from 1 to 50 total carbon atoms and from 1 to 10 heteroatoms. A monocyclic heteroaromatic hydrocarbon radical includes one heteroaromatic ring; a bicyclic heteroaromatic hydrocarbon radical has two rings; and a tricyclic heteroaromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic heteroaromatic hydrocarbon radical is present, at least one of the rings in the radical is heteroaromatic. The other ring or rings of the heteroaromatic radical may be independently fused or non-fused and aromatic or non-aromatic. Other heteroaryl groups (e.g., (C_x–C_y)heteroaryl generally, such as (C₁–C₁₂)heteroaryl) are defined in an analogous manner as having from x to y carbon atoms (such as 1 to 12 carbon atoms) and being unsubstituted or substituted by one or more than one R^S. The monocyclic heteroaromatic hydrocarbon radical is a 5-membered ring or a 6-membered ring. The 5-membered ring monocyclic heteroaromatic hydrocarbon radical has 5 minus h carbon atoms, where h is the number of heteroatoms and may be 1, 2, 3, or 4; and each heteroatom may be O, S, N, or P. Examples of 5-membered ring heteroaromatic hydrocarbon radicals include pyrrol-1-yl; pyrrol-2-yl; furan-3-yl; thiophen-2-yl; pyrazol-1-yl; isoxazol-2-yl; isothiazol-5-yl; imidazol-2-yl; oxazol-4-yl; thiazol-2-yl; 1,2,4-triazol-1-yl; 1,3,4-oxadiazol-2-yl; 1,3,4-thiadiazol-2-yl; tetrazol-1-yl; tetrazol-2-yl; and tetrazol-5-yl. The 6-membered ring monocyclic heteroaromatic hydrocarbon radical has 6 minus h carbon atoms, where h is the number of heteroatoms and may be 1 or 2 and the heteroatoms may be N or P. Examples of 6-membered ring heteroaromatic hydrocarbon radicals include pyridine-2-yl; pyrimidin-2-yl; and pyrazin-2-yl. The bicyclic heteroaromatic hydrocarbon radical can be a fused 5,6- or 6,6-ring system. Examples of the fused 5,6-ring system bicyclic heteroaromatic hydrocarbon radical are indol-1-yl; and benzimidazole-1-yl. Examples of the fused 6,6-ring system bicyclic heteroaromatic hydrocarbon radical are quinolin-2-yl; and isoquinolin-1-yl. The tricyclic heteroaromatic hydrocarbon radical can be a fused 5,6,5-; 5,6,6-; 6,5,6-; or 6,6,6-ring system. An example of the fused 5,6,5-ring system is 1,7-dihydropyrrolo[3,2-f]indol-1-yl. An example of the fused 5,6,6-ring system is 1H-benzo[f]indol-1-yl. An example of the fused 6,5,6-ring system is 9H-carbazol-9-yl. An example of the fused 6,5,6- ring system is 9H-carbazol-9-yl. An example of the fused 6,6,6-ring system is acrydin-9-yl.

[0034] The term “(C₁–C₅₀)heteroalkyl” means a saturated straight or branched chain radical containing one to fifty carbon atoms and one or more heteroatom. The term “(C₁–C₅₀)heteroalkylene” means a saturated straight or branched chain diradical containing from

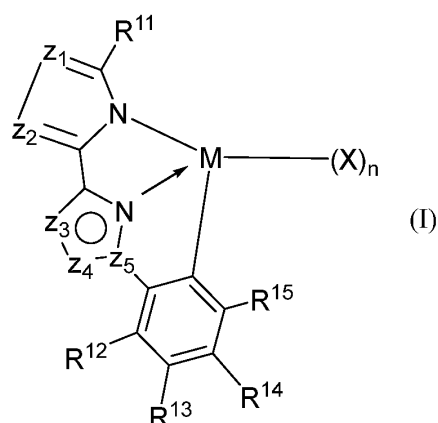
1 to 50 carbon atoms and one or more than one heteroatoms. The heteroatoms of the heteroalkyls or the heteroalkylenes may include Si(R^C)₃, Ge(R^C)₃, Si(R^C)₂, Ge(R^C)₂, P(R^P)₂, P(R^P), N(R^N)₂, N(R^N), N, O, OR^C, S, SR^C, S(O), and S(O)₂, wherein each of the heteroalkyl and heteroalkylene groups are unsubstituted or are substituted by one or more R^S.

[0035] Examples of unsubstituted (C₂–C₄₀)heterocycloalkyl include unsubstituted (C₂–C₂₀)heterocycloalkyl, unsubstituted (C₂–C₁₀)heterocycloalkyl, aziridin-1-yl, oxetan-2-yl, tetrahydrofuran-3-yl, pyrrolidin-1-yl, tetrahydrothiophen-S,S-dioxide-2-yl, morpholin-4-yl, 1,4-dioxan-2-yl, hexahydroazepin-4-yl, 3-oxa-cyclooctyl, 5-thio-cyclononyl, and 2-aza-cyclodecyl.

[0036] The term “halogen atom” or “halogen” means the radical of a fluorine atom (F), chlorine atom (Cl), bromine atom (Br), or iodine atom (I). The term “halide” means anionic form of the halogen atom: fluoride (F[−]), chloride (Cl[−]), bromide (Br[−]), or iodide (I[−]).

[0037] The term “saturated” means lacking carbon–carbon double bonds, carbon–carbon triple bonds, and (in heteroatom-containing groups) carbon–nitrogen, carbon–phosphorous, and carbon–silicon double bonds. Where a saturated chemical group is substituted by one or more substituents R^S, one or more double and/or triple bonds optionally may be present in substituents R^S. The term “unsaturated” means containing one or more carbon–carbon double bonds or carbon–carbon triple bonds, or (in heteroatom-containing groups) one or more carbon–nitrogen double bonds, carbon–phosphorous double bonds, or carbon–silicon double bonds, not including double bonds that may be present in substituents R^S, if any, or in aromatic rings or heteroaromatic rings, if any.

[0038] Embodiments of this disclosure include one or more catalyst systems. The catalyst systems include one or more metal–ligand complexes according to formula (I):



[0039] In formula (I), M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4. Each X is a monodentate or bidentate ligand independently chosen from (C₁–C₅₀)hydrocarbyl, halogen, $-(CH_2)_wSi(R^X)_3$, $-N(R^N)_2$, and $-NCOR^C$, where w is 1 to 10 and R^X is (C₁–C₂₀)alkyl. When X is monodentate, subscript n of (X)_n is 2, and when X is bidentate, subscript n of (X)_n is 1 or 2.

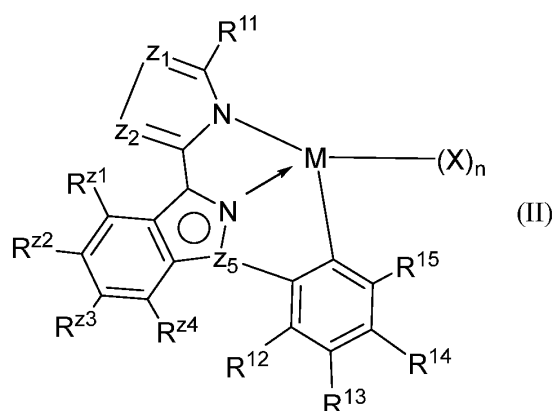
[0040] In formula (I), z₁ is independently selected from N or C(R¹), and R¹ and R¹¹ are not covalently connected to form an aromatic ring or a non-aromatic ring; z₂ is independently selected from N or C(R²), and R¹ and R² may be covalently connected to form an aromatic ring or a non-aromatic ring; z₃ is independently selected from O, S, N, R^N or C(R³), and R³ and R⁴ may be covalently connected to form an aromatic ring or a non-aromatic ring; and z₄ is independently selected from O, S, N, NR^N or C(R⁴), and R⁴ and R³ may be covalently connected to form an aromatic ring or a non-aromatic ring.

[0041] In formula (I), R¹, R², R³, R⁴, R¹¹, R¹², R¹³, R¹⁴, and R¹⁵ are independently selected from the group consisting of (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $-P(O)(R^P)_2$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, halogen, and $-H$, wherein R¹² and R¹³ are optionally connected to form a ring, R¹³ and R¹⁴ are optionally connected to form a ring, and R¹⁴ and R¹⁵ are optionally connected to form a ring.

[0042] In formula (I), each R^N, R^C, and R^P is independently selected from the group consisting of (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, and $-H$.

[0043] In one or more embodiments, when z₃ is CR³, z₄ is CR⁴, and R³ and R⁴ are connected to form an aromatic ring, and the metal–ligand structure has a structure according to formula (II):

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[0044] In formula (II), z_1 , z_2 , z_5 , R^{11} , R^{12} , R^{13} , R^{14} , R^{15} , X , n , and M are defined as in formula (I), and R^{z1} , R^{z2} , R^{z3} , R^{z4} selected from the group consisting of hydrogen, (C_1-C_{20}) alkyl, (C_6-C_{50}) aryl, (C_1-C_{10}) heterohydrocarbyl, $-NR^N$, $-OR^C$, $-SR^C$, halogen, CF_3-NO_2 , or $-CN$, where R^C is (C_1-C_{20}) alkyl, (C_6-C_{20}) aryl. In some embodiments, in formula (II), z_5 is N.

[0045] In one or more embodiments, in formula (I), z_5 is N. In some embodiments, z_1 is N; in other embodiments, z_2 is N. In some embodiments, in formula (I) or formula (II), only one of z_1 and z_2 is N.

[0046] In various embodiments, in formula (I) or formula (II), when z_2 is N and z_1 is CR^1 , R^1 and R^{11} are not covalently connected to form an aromatic or non-aromatic ring.

[0047] In one or more embodiments, in formula (I) or formula (II), X is benzyl, (C_1-C_{20}) alkyl, $-CH_2Si[(C_1-C_{30})alkyl]_3$, $-N[(C_1-C_{20})alkyl]_3$ or halogen.

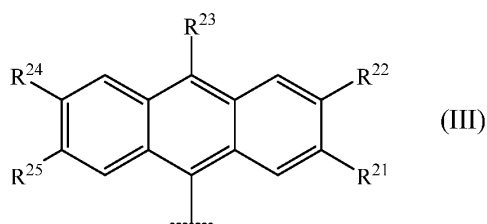
[0048] In one or more embodiments, in formula (I) or formula (II), X is benzyl, methyl, $-CH_2Si[(C_1-C_{20})alkyl]_3$, $-N[(C_1-C_{10})alkyl]_3$ or chloro.

[0049] In some embodiments, in formula (I) or formula (II), R^{11} is 2,4,6-triisopropylphenyl, mesityl, substituted and unsubstituted anthracenyl, 3,5-ditertbutylphenyl, naphthyl.

[0050] In some embodiment of the metal-ligand catalyst according to formula (I) or formula (II), R^{11} is chosen from 3,5-di-*tert*-butylphenyl; 2,4,6-trimethylphenyl; 2,4,6-triisopropylphenyl; 3,5-diisopropylphenyl; carbazoyl; carbazol-9-yl, 1,2,3,4-tetrahydrocarbazoyl; 1,2,3,4,5,6,7,8-octahydrocarbazoyl; 3,6-bis-(3,5-di-*tert*-butylphenyl)carbazol-9-yl; 3,6-bis-(2,4,6-trimethylphenyl)carbazol-9-yl; 3,6-bis-(2,4,6-triisopropylphenyl)carbazol-9-yl; 2,7-di(tertiarybutyl)-carbazol-9-yl; 2,7-di(tertiary-octyl)-carbazol-9-yl; 2,7-diphenylcarbazol-9-yl; 2,7-bis(2,4,6-trimethylphenyl)-carbazol-9-yl anthracenyl; 1,2,3,4-tetrahydroanthracenyl; 1,2,3,4,5,6,7,8-octahydroanthracenyl; phenanthrenyl;

1,2,3,4,5,6,7,8-octahydrophenanthrenyl; 1,2,3,4-tetrahydronaphthyl; 2,6-dimethylphenyl; 2,6-diisopropylphenyl; 3,5-diphenylphenyl; 1-naphthyl; 2-methyl-1-naphthyl; 2-naphthyl; 1,2,3,4-tetrahydronaphth-5-yl; 1,2,3,4-tetrahydronaphth-6-yl; anthracen-9-yl; 1,2,3,4-tetrahydroanthracen-9-yl; 1,2,3,4,5,6,7,8-octahydroanthracen-9-yl; 1,2,3,4,5,6,7,8-octahydrophenanthren-9-yl; indolyl; indolinyl; quinolinyl; 1,2,3,4-tetrahydroquinolinyl; isoquinolinyl; or 1,2,3,4-tetrahydroisoquinolinyl.

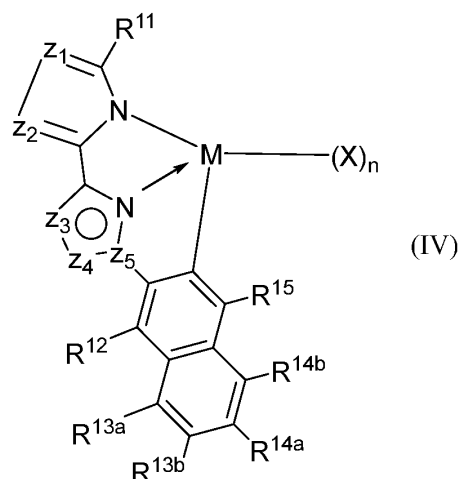
[0051] In various embodiments, in formula (I) or formula (II), R^{11} is a radical of formula (III):



[0052] In formula (III), R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is independently chosen from (C_1-C_{10}) alkyl, (C_6-C_{10}) aryl, or $-H$.

[0053] In various embodiments, in formula (III), R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is independently chosen from *tert*-butyl, 3,5-di-*tert*-butylphenyl, or $-H$.

[0054] In embodiments of the present disclosure, R^{13} and R^{14} are covalently connected to form an aromatic ring, the metal-ligand has a structure according to formula (IV):



[0055] In one or more embodiments, in formulas (I), (II), and (IV), R^{12} , R^{13} (including R^{13a} and R^{13b}), R^{14} (including R^{14a} and R^{14b}), and R^{15} are selected from the group consisting of hydrogen, chloro, fluoro, benzyl, (C_1-C_{10}) alkyl, cyclic (C_1-C_{10}) heteroalkyl, $-OR^C$, $-NR^N_2$, wherein R^C and R^N are (C_1-C_{12}) alkyl.

[0056] In one or more embodiments, R^{13} and R^{15} are chloro or fluoro, or (C_1-C_{10}) alkyl.

[0057] In some embodiments, R^{13} and R^{14} are $-OR^C$, wherein R^C is (C_1-C_8) alkyl.

[0058] In various embodiments, R^{14} is selected from the group consisting of (C_1-C_{10}) alkyl, cyclic (C_1-C_{10}) heteroalkyl, $-OR^C$, $-NR^N$, wherein R^C and R^N are (C_1-C_8) alkyl.

[0059] In some embodiments, any or all of the chemical groups (e.g., X and R^{1-59}) of the metal-ligand complex of formula (I) may be unsubstituted. In other embodiments, none, any, or all of the chemical groups X and R^{1-59} of the metal-ligand complex of formula (I) may be substituted with one or more than one R^S . When two or more than two R^S are bonded to a same chemical group of the metal-ligand complex of formula (I), the individual R^S of the chemical group may be bonded to the same carbon atom or heteroatom or to different carbon atoms or heteroatoms. In some embodiments, none, any, or all of the chemical groups X and R^{1-59} may be persubstituted with R^S . In the chemical groups that are persubstituted with R^S , the individual R^S may all be the same or may be independently chosen. In one or more embodiments, R^S is chosen from (C_1-C_{20}) hydrocarbyl, (C_1-C_{20}) alkyl, (C_1-C_{20}) heterohydrocarbyl, or (C_1-C_{20}) heteroalkyl.

[0060] In the metal-ligand complex according to formula (I), X bonds with M through a covalent bond or an ionic bond. In some embodiments, X may be a monoanionic ligand having a net formal oxidation state of -1 . Each monoanionic ligand may independently be hydride, (C_1-C_{40}) hydrocarbyl carbanion, (C_1-C_{40}) heterohydrocarbyl carbanion, halide, nitrate, carbonate, phosphate, sulfate, $HC(O)O^-$, $HC(O)N(H)^-$, (C_1-C_{40}) hydrocarbylC(O) O^- , (C_1-C_{40}) hydrocarbylC(O)N $((C_1-C_{20})$ hydrocarbyl) $^-$, (C_1-C_{40}) hydrocarbylC(O)N(H) $^-$, $R^KR^LB^-$, $R^KR^LN^-$, R^KO^- , R^KS^- , $R^KR^LP^-$, or $R^MR^KR^LSi^-$, where each R^K , R^L , and R^M independently is hydrogen, (C_1-C_{40}) hydrocarbyl, or (C_1-C_{40}) heterohydrocarbyl, or R^K and R^L are taken together to form a (C_2-C_{40}) hydrocarbylene or (C_1-C_{20}) heterohydrocarbylene and R^M is as defined above.

[0061] In some embodiments, X is a halogen, unsubstituted (C_1-C_{20}) hydrocarbyl, unsubstituted (C_1-C_{20}) hydrocarbylC(O) O^- , or $R^KR^LN^-$, wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{20}) hydrocarbyl. In some embodiments, each monodentate ligand X is a chlorine atom, (C_1-C_{10}) hydrocarbyl (e.g., (C_1-C_6) alkyl or benzyl), unsubstituted (C_1-C_{10}) hydrocarbylC(O) O^- , or $R^KR^LN^-$, wherein each of R^K and R^L independently is an unsubstituted (C_1-C_{10}) hydrocarbyl.

[0062] In further embodiments, X is selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; or chloro. X is methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; phenyl; benzyl; and chloro. In one

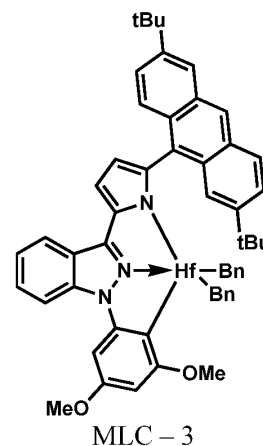
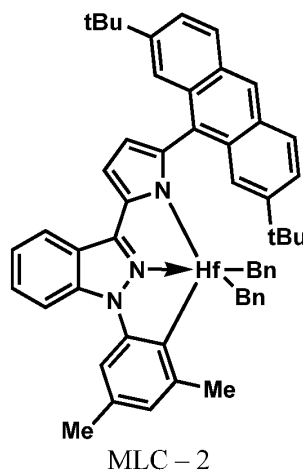
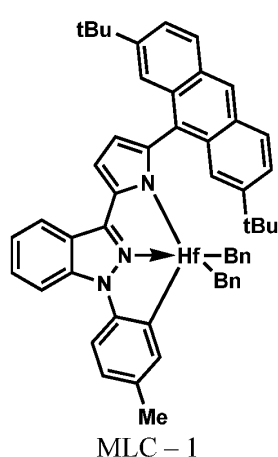
embodiment, n is 2 and at least two X independently are monoanionic monodentate ligands. In a specific embodiment, n is 2 and the two X groups join to form a bidentate ligand. In further embodiments, the bidentate ligand is 2,2-dimethyl-2-silapropane-1,3-diyl or 1,3-butadiene.

[0063] In one or more embodiments, each X is independently $-(CH_2)SiR^X_3$, in which each R^X is independently a (C_1-C_{30}) alkyl or a (C_1-C_{30}) heteroalkyl and at least one R^X is (C_1-C_{30}) alkyl. In some embodiments, when one of R^X is a (C_1-C_{30}) heteroalkyl, the heteroatom is silica or oxygen atom. In some embodiments, R^X is methyl, ethyl, propyl, 2-propyl, butyl, 1,1-dimethylethyl (or *tert*-butyl), pentyl, hexyl, heptyl, *n*-octyl, *tert*-octyl, or nonyl.

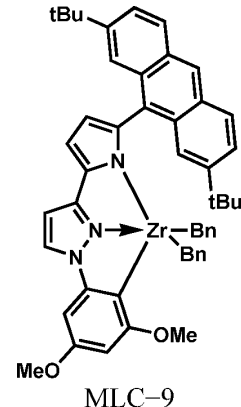
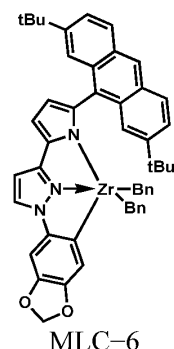
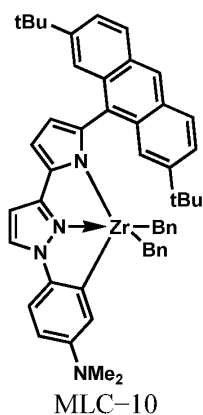
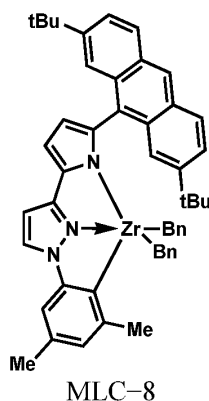
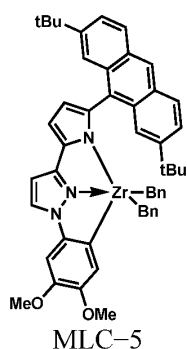
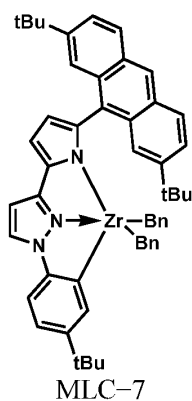
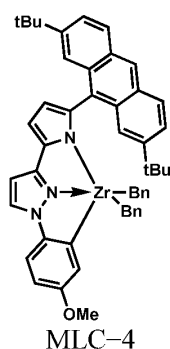
[0064] In one or more embodiments X is $-(CH_2)Si(CH_3)_3$, $-(CH_2)Si(CH_3)_2(CH_2CH_3)$; $-(CH_2)Si(CH_3)(CH_2CH_3)_2$, $-(CH_2)Si(CH_2CH_3)_3$, $-(CH_2)Si(CH_3)_2(n\text{-butyl})$, $-(CH_2)Si(CH_3)_2(n\text{-hexyl})$, $-(CH_2)Si(CH_3)(n\text{-Oct})R^X$, $-(CH_2)Si(n\text{-Oct})R^X_2$, $-(CH_2)Si(CH_3)_2(2\text{-ethylhexyl})$, $-(CH_2)Si(CH_3)_2(\text{dodecyl})$, $-CH_2Si(CH_3)_2CH_2Si(CH_3)_3$ (herein referred to as $-CH_2Si(CH_3)_2CH_2TMS$). Optionally, in some embodiments, the metal–ligand complex according to formula (I), exactly two R^X are covalently linked or exactly three R^X are covalently linked.

[0065] In some embodiments, X is $-CH_2Si(R^C)_{3-Q}(OR^C)_Q$, $-Si(R^C)_{3-Q}(OR^C)_Q$, $-OSi(R^C)_{3-Q}(OR^C)_Q$, in which subscript Q is 0, 1, 2 or 3 and each R^C is independently a substituted or unsubstituted (C_1-C_{30}) hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl.

[0066] In illustrative embodiments, the catalyst systems may include a metal–ligand complex according to formula (I) having the structure of any of the Metal–ligand complex 1 to 10



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Additive Component

[0067] In some embodiments, the catalyst system does not include additives. An additive is a chemical agent present during the polymerization reaction that does not deter olefin propagation. In one or more embodiments, the catalyst system further comprises an additive. In some embodiments, the additives function as a co-catalyst. In other embodiments, the additives function as a scavenger or scavenging agent. A co-catalyst is a reagent that reacts in cooperation with a catalyst to catalyze the reaction or improve the catalytic activity of the catalyst.

[0068] A scavenging agent sequesters impurities in the reactor prior to addition of the precatalyst, and as such, does not constitute an activator. Lower loading of alumoxanes do not act as co-catalysts, rather they serve as scavenging agent.

[0069] Suitable additives may include, but are not limited to, alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). Combinations of one or more of the foregoing additives and techniques are also contemplated. The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Examples of polymeric or oligomeric alumoxanes include methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

[0070] In some embodiments, the additive is a Lewis acid Group 13 metal compounds containing (C₁–C₂₀)hydrocarbyl substituents as described herein. In some embodiments, the additives include tri((C₁–C₂₀)hydrocarbyl)-substituted-aluminum or tri((C₁–C₂₀)hydrocarbyl)-boron compounds. In other embodiments, the additives are chosen from tri(hydrocarbyl)-substituted-aluminum, tri((C₁–C₂₀)hydrocarbyl)-boron compounds, tri((C₁–C₁₀)alkyl)aluminum, tri((C₆–C₁₈)aryl)boron compounds, and halogenated (including perhalogenated) derivatives thereof.

[0071] In one or more embodiments, the polymerization process further includes a borate-based additive. In some embodiments, the borate-based additive is selected from tris(fluoro-substituted phenyl)boranes, tris(pentafluorophenyl)borane. In some embodiments, the co-catalyst is a tri((C₁–C₂₀)hydrocarbyl)ammonium tetra((C₁–C₂₀)hydrocarbyl)borate (e.g. bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borate). As used herein, the term “ammonium” means a nitrogen cation that is a ((C₁–C₂₀)hydrocarbyl)₄N⁺, a ((C₁–C₂₀)hydrocarbyl)₃N(H)⁺, a ((C₁–C₂₀)hydrocarbyl)₂N(H)₂⁺, (C₁–C₂₀)hydrocarbylN(H)₃⁺, or N(H)₄⁺, wherein each (C₁–C₂₀)hydrocarbyl, when two or more are present, may be the same or different.

[0072] In one or more embodiments, the additive may be chosen from polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable additives include, but are not limited to modified methyl aluminoxane (MMAO), bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1–)ammonium, triethyl aluminum, butylatedhydroxy-toluene

diethyl aluminum, bis-(butylatedhydroxy-toluene) ethyl aluminum, tris-(butylatedhydroxy-toluene) aluminum and combinations thereof.

[0073] In some embodiments, one or more co-catalysts may be used in combination with each other. A specific example of a co-catalyst combination is a mixture of a tri((C₁–C₈)hydrocarbyl)aluminum, tri((C₁–C₄)hydrocarbyl)borane, tri((C₆–C₁₈)aryl)borane or an ammonium borate with an oligomeric or polymeric alumoxane compound. The ratio of total number of moles of one or more metal-ligand complexes of formula (I) to total number of moles of one or more of the co-catalysts is from 1:10,000 to 100:1. In some embodiments, the ratio is at least 1:5000, in some other embodiments, at least 1:1000; and 10:1 or less, and in some other embodiments, 1:1 or less. When an alumoxane alone is used as the co-catalyst, preferably the ratio Al of the alumoxane and metal of the metal ligand complex of formula (I) (Al/M) is at least 20. When tris(pentafluorophenyl)borane alone is used as the co-catalyst, in some other embodiments, the number of moles of the tris(pentafluorophenyl)borane that are employed to the total number of moles of one or more metal–ligand complexes of formula (I) from 0.5: 1 to 10:1, from 1:1 to 6:1, or from 1:1 to 5:1.

Polymerization Process

[0074] Embodiments of this disclosure includes polymerization processes. The polymerization processes include polymerizing ethylene and one or more olefins in the presence of a catalyst system under olefin polymerization conditions to form an ethylene-based polymer, the catalyst system comprising a metal–ligand complex according to formula (I) or formula (II) or formula (IV).

[0075] One or more embodiments of this disclosure include processes for polymerizing polymers, the process comprising: contacting ethylene and optionally one or more (C₃–C₁₂) α -olefins in the presence of a catalyst system in a reactor. The catalyst system may include procatalyst according to the metal–ligand complex of formula (I) and an activator. The polymerization processes may include, but are not limited to, solution polymerization process, gas phase polymerization process, slurry phase polymerization process, and combinations thereof using one or more reactors such as loop reactors, isothermal reactors, fluidized bed gas phase reactors, continuous stirred tank reactors, batch reactors in parallel, series, and/or any combinations thereof.

[0076] The polymerization process of this disclosure may produce ethylene based polymers, for example homopolymers and/or interpolymers (including copolymers) of ethylene and

optionally one or more comonomers such as α -olefins may, for example, be produced via solution-phase polymerization process using one or more loop reactors, isothermal reactors, and combinations thereof.

[0077] In some embodiments, the solution phase polymerization process occurs in one or more well-stirred reactors such as one or more loop reactors or one or more spherical isothermal reactors at a temperature in the range of from 120 to 300 °C; for example, from 150 to 190 °C, and at pressures in the range of from 300 to 1500 psi; for example, from 400 to 750 psi. The residence time in solution phase polymerization process is typically in the range of from 2 to 30 minutes; for example, from 10 to 20 minutes. Ethylene, one or more solvents, one or more catalyst systems, such as catalyst system that includes a procatalyst according to the metal–ligand complex of formula (I), optionally one or more cocatalysts, and optionally one or more comonomers are fed continuously to the one or more reactors. Exemplary solvents include, but are not limited to, isoparaffins. For example, such solvents are commercially available under the name ISOPAR E from ExxonMobil Chemical Co., Houston, Texas. The resultant mixture of the ethylene based polymer and solvent is then removed from the reactor and the ethylene based polymer is isolated. Solvent is typically recovered via a solvent recovery unit, i.e. heat exchangers and vapor liquid separator drum, and is then recycled back into the polymerization system.

Cocatalyst Component

[0078] The catalyst system comprising a metal–ligand complex of formula (I) may be rendered catalytically active by any technique known in the art for activating metal-based catalysts of olefin polymerization reactions. For example, the procatalyst according to a metal–ligand complex of formula (I) may be rendered catalytically active by contacting the complex to, or combining the complex with, an activating co-catalyst. Additionally, the metal–ligand complex according for formula (I) includes both a procatalyst form, which is neutral, and a catalytic form, which may be positively charged due to the loss of a monoanionic ligand, such a benzyl or phenyl. Suitable activating co-catalysts for use herein include alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). A suitable activating technique is bulk electrolysis. Combinations of one or more of the foregoing activating co-catalysts and techniques are also contemplated. The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Examples of polymeric or

oligomeric alumoxanes include methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

[0079] In some embodiments, suitable cocatalysts for use include polymeric or oligomeric aluminosiloxanes, especially methyl aluminosiloxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable cocatalysts include, but are not limited to modified methyl aluminosiloxane (MMAO), bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(l-) amine (RIBS-2), triethyl aluminum (TEA), and combinations thereof.

[0080] Lewis acid activating co-catalysts include Group 13 metal compounds containing (C₁–C₂₀)hydrocarbyl substituents as described herein. In some embodiments, Group 13 metal compounds are tri((C₁–C₂₀)hydrocarbyl)-substituted-aluminum or tri((C₁–C₂₀)hydrocarbyl)-boron compounds. In other embodiments, Group 13 metal compounds are tri(hydrocarbyl)-substituted-aluminum, tri((C₁–C₂₀)hydrocarbyl)-boron compounds, tri((C₁–C₁₀)alkyl)aluminum, tri((C₆–C₁₈)aryl)boron compounds, and halogenated (including perhalogenated) derivatives thereof. In further embodiments, Group 13 metal compounds are tris(fluoro-substituted phenyl)boranes, tris(pentafluorophenyl)borane. In some embodiments, the activating co-catalyst is a tris((C₁–C₂₀)hydrocarbyl borate (e.g. trityl tetrafluoroborate) or a tri((C₁–C₂₀)hydrocarbyl)ammonium tetra((C₁–C₂₀)hydrocarbyl)borane (e.g. bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borane). As used herein, the term “ammonium” means a nitrogen cation that is a ((C₁–C₂₀)hydrocarbyl)₄N⁺, a ((C₁–C₂₀)hydrocarbyl)₃N(H)⁺, a ((C₁–C₂₀)hydrocarbyl)₂N(H)₂⁺, (C₁–C₂₀)hydrocarbylN(H)₃⁺, or N(H)₄⁺, wherein each (C₁–C₂₀)hydrocarbyl, when two or more are present, may be the same or different.

[0081] Combinations of neutral Lewis acid activating co-catalysts include mixtures comprising a combination of a tri((C₁–C₄)alkyl)aluminum and a halogenated tri((C₆–C₁₈)aryl)boron compound, especially a tris(pentafluorophenyl)borane. Other embodiments are combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane. Ratios of numbers of moles of (metal–ligand complex): (tris(pentafluoro-phenyl)borane): (alumoxane) [e.g., (Group 4 metal–ligand complex) : (tris(pentafluoro-phenyl)borane): (alumoxane)] are from 1:1:1 to 1:10:30, in other embodiments, from 1:1:1.5 to 1:5:10.

[0082] The catalyst system that includes the metal–ligand complex of formula (I) may be activated to form an active catalyst composition by combination with one or more cocatalysts, for example, a cation forming cocatalyst, a strong Lewis acid, or combinations thereof. Suitable activating co-catalysts include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable co-catalysts include, but are not limited to modified methyl aluminoxane (MMAO), bis(hydrogenated tallow alkyl)methyl, tetrakis(pentafluorophenyl)borate(1–) amine, and combinations thereof.

[0083] In some embodiments, more than one of the foregoing activating co-catalysts may be used in combination with each other. A specific example of a co-catalyst combination is a mixture of a tri((C₁–C₄)hydrocarbyl)aluminum, tri((C₁–C₄)hydrocarbyl)borane, or an ammonium borate with an oligomeric or polymeric alumoxane compound. The ratio of total number of moles of one or more metal–ligand complexes of formula (I) to total number of moles of one or more of the activating co-catalysts is from 1:10,000 to 100:1. In some embodiments, the ratio is at least 1:5000, in some other embodiments, at least 1:1000; and 10:1 or less, and in some other embodiments, 1:1 or less. When an alumoxane alone is used as the activating co-catalyst, preferably the number of moles of the alumoxane that are employed is at least 100 times the number of moles of the metal–ligand complex of formula (I). When tris(pentafluorophenyl)borane alone is used as the activating co-catalyst, in some other embodiments, the number of moles of the tris(pentafluorophenyl)borane that are employed to the total number of moles of one or more metal–ligand complexes of formula (I) from 0.5:1 to 10:1, from 1:1 to 6:1, or from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately mole quantities equal to the total mole quantities of one or more metal–ligand complexes of formula (I).

Polyolefins

[0084] The catalytic systems described in the preceding paragraphs are utilized in the polymerization of olefins, primarily ethylene and propylene. In some embodiments, there is only a single type of olefin or α -olefin in the polymerization scheme, creating a homopolymer. However, additional α -olefins may be incorporated into the polymerization procedure. The additional α -olefin co-monomers typically have no more than 20 carbon atoms. For example, the α -olefin co-monomers may have 3 to 10 carbon atoms or 3 to 8 carbon atoms. Exemplary α -olefin co-monomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. For example, the one or more α -olefin co-

monomers may be selected from the group consisting of propylene, 1-butene, 1-hexene, and 1-octene; or in the alternative, from the group consisting of 1-hexene and 1-octene.

[0085] The ethylene based polymers, for example homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α -olefins, may comprise from at least 50 percent by weight monomer units derived from ethylene. All individual values and subranges encompassed by “from at least 50 weight percent” are disclosed herein as separate embodiments; for example, the ethylene based polymers, homopolymers and/or interpolymers (including copolymers) of ethylene and optionally one or more co-monomers such as α -olefins may comprise at least 60 weight percent monomer units derived from ethylene; at least 70 weight percent monomer units derived from ethylene; at least 80 weight percent monomer units derived from ethylene; or from 50 to 100 weight percent monomer units derived from ethylene; or from 80 to 100 weight percent units derived from ethylene.

[0086] In some embodiments, the ethylene based polymers may comprise at least 90 mole percent units derived from ethylene. All individual values and subranges from at least 90 mole percent are included herein and disclosed herein as separate embodiments. For example, the ethylene based polymers may comprise at least 93 mole percent units derived from ethylene; at least 96 mole percent units; at least 97 mole percent units derived from ethylene; or in the alternative, from 90 to 100 mole percent units derived from ethylene; from 90 to 99.5 mole percent units derived from ethylene; or from 97 to 99.5 mole percent units derived from ethylene.

[0087] In some embodiments of the ethylene based polymer, the amount of additional α -olefin is less than 50%; other embodiments include at least 0.5 mole percent (mol%) to 25 mol%; and in further embodiments the amount of additional α -olefin includes at least 5 mol% to 10 mol%. In some embodiments, the additional α -olefin is 1-octene.

[0088] Any conventional polymerization processes may be employed to produce the ethylene based polymers. Such conventional polymerization processes include, but are not limited to, solution polymerization processes, gas phase polymerization processes, slurry phase polymerization processes, and combinations thereof using one or more conventional reactors such as loop reactors, isothermal reactors, fluidized bed gas phase reactors, stirred tank reactors, batch reactors in parallel, series, or any combinations thereof, for example.

[0089] In one embodiment, the ethylene based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system, as

described herein, and optionally one or more co-catalysts. In another embodiment, the ethylene based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system in this disclosure, and as described herein, and optionally one or more other catalysts. The catalyst system, as described herein, can be used in the first reactor, or second reactor, optionally in combination with one or more other catalysts. In one embodiment, the ethylene based polymer may be produced via solution polymerization in a dual reactor system, for example a dual loop reactor system, wherein ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system, as described herein, in both reactors.

[0090] In another embodiment, the ethylene based polymer may be produced via solution polymerization in a single reactor system, for example a single loop reactor system, in which ethylene and optionally one or more α -olefins are polymerized in the presence of the catalyst system, as described within this disclosure, and optionally one or more cocatalysts, as described in the preceding paragraphs.

[0091] The ethylene based polymers may further comprise one or more additives. Such additives include, but are not limited to, antistatic agents, color enhancers, dyes, lubricants, pigments, primary antioxidants, secondary antioxidants, processing aids, UV stabilizers, and combinations thereof. The ethylene based polymers may contain any amounts of additives. The ethylene based polymers may comprise from about 0 to about 10 percent by the combined weight of such additives, based on the weight of the ethylene based polymers and the one or more additives. The ethylene based polymers may further comprise fillers, which may include, but are not limited to, organic or inorganic fillers. The ethylene based polymers may contain from about 0 to about 20 weight percent fillers such as, for example, calcium carbonate, talc, or $\text{Mg}(\text{OH})_2$, based on the combined weight of the ethylene based polymers and all additives or fillers. The ethylene based polymers may further be blended with one or more polymers to form a blend.

[0092] In some embodiments, a polymerization process for producing an ethylene-based polymer may include polymerizing ethylene and at least one additional α -olefin in the presence of a catalyst system, wherein the catalyst system incorporates at least one metal–ligand complex of formula (I). The polymer resulting from such a catalyst system that incorporates the metal–ligand complex of formula (I) may have a density according to ASTM D792 (incorporated herein

by reference in its entirety) from 0.850 g/cm³ to 0.950 g/cm³, from 0.880 g/cm³ to 0.920 g/cm³, from 0.880 g/cm³ to 0.910 g/cm³, or from 0.880 g/cm³ to 0.900 g/cm³, for example.

[0093] In another embodiment, the polymer resulting from the catalyst system that includes the metal–ligand complex of formula (I) has a melt flow ratio (I_{10}/I_2) from 5 to 15, in which melt index I_2 is measured according to ASTM D1238 (incorporated herein by reference in its entirety) at 190 °C and 2.16 kg load, and melt index I_{10} is measured according to ASTM D1238 at 190 °C and 10 kg load. In other embodiments the melt flow ratio (I_{10}/I_2) is from 5 to 10, and in others, the melt flow ratio is from 5 to 9.

[0094] In some embodiments, the polymer resulting from the catalyst system that includes the metal–ligand complex of formula (I) has a molecular-weight distribution (MWD) from 1 to 25, where MWD is defined as M_w/M_n with M_w being a weight-average molecular weight and M_n being a number-average molecular weight. In other embodiments, the polymers resulting from the catalyst system have a MWD from 1 to 6. Another embodiment includes a MWD from 1 to 3; and other embodiments include MWD from 1.5 to 2.5.

[0095] Embodiments of the catalyst systems described in this disclosure yield unique polymer properties as a result of the high molecular weights of the polymers formed and the amount of the co-monomers incorporated into the polymers.

[0096] All solvents and reagents are obtained from commercial sources and used as received unless otherwise noted. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether are purified *via* passage through activated alumina and, in some cases, Q-5 reactant. Solvents used for experiments performed in a nitrogen-filled glovebox are further dried by storage over activated 4Å molecular sieves. Glassware for moisture-sensitive reactions is dried in an oven overnight prior to use. NMR spectra are recorded on Varian 400-MR and VNMRS-500 spectrometers. LC-MS analyses are performed using a Waters e2695 Separations Module coupled with a Waters 2424 ELS detector, a Waters 2998 PDA detector, and a Waters 3100 ESI mass detector. LC-MS separations are performed on an XBridge C18 3.5 µm 2.1x50 mm column using a 5:95 to 100:0 acetonitrile to water gradient with 0.1% formic acid as the ionizing agent. HRMS analyses are performed using an Agilent 1290 Infinity LC with a Zorbax Eclipse Plus C18 1.8µm 2.1x50 mm column coupled with an Agilent 6230 TOF Mass Spectrometer with electrospray ionization. ¹H NMR data are reported as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet and m = multiplet), integration, and assignment). Chemical shifts for ¹H NMR data are reported in ppm downfield from internal

tetramethylsilane (TMS, δ scale) using residual protons in the deuterated solvent as references. ^{13}C NMR data are determined with ^1H decoupling, and the chemical shifts are reported downfield from tetramethylsilane (TMS, δ scale) in ppm versus the using residual carbons in the deuterated solvent as references.

[0097] HT-GPC Analysis with IR Detection of Octene Incorporation

[0098] High-temperature GPC analysis was performed using a Dow Robot Assisted Delivery (RAD) system equipped with a PolymerChar infrared detector (IR5) and Agilent PLgel Mixed A columns. Decane (10 μL) was added to each sample for use as an internal flow marker. Samples were first diluted in 1,2,4-trichlorobenzene (TCB) stabilized with 300 ppm of butylated hydroxytoluene (BHT) to a concentration of 10 mg/mL and dissolved by stirring at 160 $^{\circ}\text{C}$ for 120 minutes. Prior to injection samples were further diluted with TCB stabilized with BHT to a concentration of 2 mg/mL. Samples (250 μL) were eluted through one PL-gel 20 μm (50 x 7.5 mm) guard column followed by two PL-gel 20 μm (300 x 7.5 mm) Mixed-A columns maintained at 160 $^{\circ}\text{C}$ with TCB stabilized with BHT at a flowrate of 1.0 mL/min. The total run time was 24 minutes. To calibrate for molecular weight Agilent EasiCal polystyrene standards (PS-1 and PS-2) were diluted with 1.5 mL of TCB stabilized with BHT and dissolved by stirring at 160 $^{\circ}\text{C}$ for 15 minutes. The PS standards were injected into the system without further dilution to create a 3rd-order MW calibration curve with apparent units adjusted to homo-polyethylene (PE) using known Mark-Houwink coefficients for PS and PE. Octene incorporation was determined by use of a linear calibration developed by analyzing copolymers of known compositions.

[0099] Batch Reactor Polymerization Procedure

[00100] The batch reactor polymerizations were conducted in a 2-L ParrTM batch reactor. The reactor is heated by an electrical heating mantle, and is cooled by an internal serpentine cooling coil containing cooling water. Both the reactor and the heating/cooling system are controlled and monitored by a CamileTM TG process computer. The bottom of the reactor is fitted with a dump valve, which empties the reactor contents into a stainless-steel dump pot, which is prefilled with a catalyst kill solution (typically 5 mL of an Irgafos / Irganox / toluene mixture). The dump pot is vented to a 30-gal. blow-down tank, with both the pot and the tank purged with nitrogen. All solvents used for polymerization or catalyst makeup are run through solvent purification columns to remove any impurities that may affect polymerization. The 1-octene and Isopar E were passed through two columns, the first containing activated A2 alumina, the second containing activated Q5 reactant. The ethylene was passed through two columns, the first containing A204 alumina

and 4Å mol sieves, the second containing Q5 reactant. The N₂, used for transfers, was passed through a single column containing A204 alumina, 4Å mol sieves and Q5.

[00101] The reactor is loaded first from the shot tank that contains Isopar E solvent and/or 1-octene, depending on desired reactor loading. The shot tank is filled to the load set points by use of a lab scale to which the shot tank is mounted. After liquid feed addition, the reactor is heated up to the polymerization temperature set point. If ethylene is used, it is added to the reactor when at reaction temperature to maintain reaction pressure set point. Ethylene addition amounts are monitored by a micro-motion flow meter.

[00102] The catalyst and activators were mixed with the appropriate amount of purified toluene to achieve a solution of the desired molarity. The catalyst and activators were handled in an inert glove box, drawn into a syringe and pressure transferred into the catalyst shot tank. This was followed by three rinses of toluene, 5-mL each. Immediately after catalyst addition the run timer began. If ethylene was used, it was then added by the Camile to maintain reaction the pressure set point in the reactor. These polymerizations were run for 10 min., then the agitator was stopped and the bottom dump valve was opened to empty reactor contents into the dump pot. The dump pot contents were poured into trays placed in a lab hood where the solvent was evaporated off overnight. The trays containing the remaining polymer were then transferred to a vacuum oven, where they were heated up to 140 °C under vacuum to remove any remaining solvent. After the trays cooled to ambient temperature, the polymers were weighed for yield/efficiencies, and submitted for polymer testing.

EXAMPLES

[00103] Examples 1 to 20 are synthetic procedures for ligand intermediates, ligands, and isolated procatalysts. Inventive Metal–ligand Complex 1 to Inventive Metal–ligand Complex 10 (MLC-1 to MLC-10) were synthesized from various ligands disclosed hererin. One or more features of the present disclosure are illustrated in view of the examples as follows:

[00104] **Example 1 –For the Synthesis of MLC-2**

[00105] **3-bromo-1-(3,5-dimethylphenyl)-1H-indazole** – For the synthesis of MLC-2

[00106] 3-bromo-1H-indazole (600 mg, 3.05 mmol, 100 mol%), 1-iodo-3,5-dimethylbenzene (1060 mg, 4.57 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (139 mg, 1.22 mmol, 40 mol%), CuI (116 mg, 0.61 mmol, 20 mol%), and K₂CO₃ (631 mg, 4.57 mmol, 150 mol%) were weighted in a vial. Toluene (3 mL) was added and the mixture was allowed to stir overnight at

110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was removed *in vacuo*. The residue was subjected to column chromatography on silica (Hex → Hex/EtOAc 3:7) to furnish the product (599.2 mg) in 65% yield.

[00107] ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.67 (m, 2H), 7.47 (ddd, *J* = 8.4, 6.9, 1.2 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.02 (s, 1H), 2.41 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 139.98, 139.55, 139.52, 128.94, 128.32, 125.00, 123.57, 122.27, 120.79, 120.62, 110.98, 21.51.

[00108] **3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,5-dimethylphenyl)-1H-indazole** – For the synthesis of MLC-2

[00109] 3-bromo-1-(3,5-dimethylphenyl)-1H-indazole (99 mg, 0.33 mmol, 100 mol%), 2-(2,7-di-tert-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (234 mg, 0.41 mmol, 125 mol%, 85% pure), Pd(PPh₃)₄ (38 mg, 0.03 mmol, 10 mol%), and K₃PO₄ (210 mg, 0.99 mmol, 300 mol%) were weighted in a vial. Dioxane (5 mL) and H₂O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H₂O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex → Hex/DCM 7:3) to furnish the product (82.7 mg) in 44% yield as a yellow solid.

[00110] ¹H NMR (400 MHz, CDCl₃) δ 9.50 (s, 1H), 8.40 (s, 1H), 8.24 (dt, *J* = 8.1, 1.0 Hz, 1H), 8.08 (dt, *J* = 1.8, 0.8 Hz, 2H), 7.98 (d, *J* = 8.9 Hz, 2H), 7.82 – 7.77 (m, 1H), 7.57 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.50 (ddd, *J* = 8.4, 7.0, 1.1 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.20 (dd, *J* = 3.5, 2.6 Hz, 1H), 6.98 – 6.95 (m, 1H), 6.68 (dd, *J* = 3.5, 2.7 Hz, 1H), 2.40 (s, 6H), 1.38 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 148.11, 140.22, 140.13, 139.63, 139.33, 131.75, 129.92, 128.97, 128.20, 127.54, 127.35, 126.43, 125.44, 124.55, 122.28, 121.81, 121.73, 120.98, 120.47, 112.88, 110.93, 108.76, 35.31, 31.08, 21.54.

[00111] Example 2 – **For the Synthesis of MLC-3**

[00112] **3-bromo-1-(3,5-dimethoxyphenyl)-1H-indazole** – For the synthesis of MLC-3

[00113] 3-bromo-1H-indazole (600 mg, 3.05 mmol, 100 mol%), 1-iodo-3,5-dimethoxybenzene (1206 mg, 4.57 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (139 mg, 1.22 mmol, 40 mol%), CuI (116 mg, 0.61 mmol, 20 mol%), and K₂CO₃ (631 mg, 4.57 mmol, 150 mol%) were weighted in a vial. Toluene (3 mL) was added and the mixture was allowed to stir overnight at 110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was removed *in*

vacuo. The residue was subjected to column chromatography on silica (Hex → Hex/DCM 4:6) to furnish the product (462.1 mg) in 46% yield.

[00114] ¹H NMR (400 MHz, CDCl₃) δ 7.77 (dt, *J* = 8.7, 1.0 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.48 (ddd, *J* = 8.4, 7.0, 1.2 Hz, 1H), 7.29 (ddd, *J* = 8.0, 6.9, 0.8 Hz, 1H), 6.87 (d, *J* = 2.2 Hz, 2H), 6.47 (t, *J* = 2.3 Hz, 1H), 3.86 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 161.52, 141.25, 139.94, 128.55, 125.20, 124.03, 122.49, 120.86, 111.11, 101.16, 99.34, 55.80.

[00115] **3-(5-(2,6-di-*tert*-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,5-dimethoxyphenyl)-1H-indazole** – For the synthesis of MLC-3

[00116] 3-bromo-1-(3,5-dimethoxyphenyl)-1H-indazole (100 mg, 0.30 mmol, 100 mol%), 2-(2,6-di-*tert*-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (181 mg, 0.38 mmol, 125 mol%), Pd(PPh₃)₄ (35 mg, 0.03 mmol, 10 mol%), and K₃PO₄ (191 mg, 0.90 mmol, 300 mol%) were weighted in a vial. Dioxane (5 mL) and H₂O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H₂O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex/DCM 6:4) to furnish the product (139.3 mg) in 76% yield as a yellow solid.

[00117] ¹H NMR (400 MHz, CDCl₃) δ 9.68 (s, 1H), 8.37 (s, 1H), 8.16 (dt, *J* = 8.1, 1.0 Hz, 1H), 8.02 – 7.93 (m, 3H), 7.87 (d, *J* = 2.0 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.56 (dd, *J* = 8.9, 1.9 Hz, 1H), 7.48 (ddd, *J* = 8.4, 5.3, 1.6 Hz, 2H), 7.34 (ddd, *J* = 7.9, 6.9, 0.9 Hz, 1H), 7.16 (dd, *J* = 3.5, 2.6 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 2H), 6.62 (dd, *J* = 3.5, 2.7 Hz, 1H), 6.35 (t, *J* = 2.3 Hz, 1H), 3.77 (s, 6H), 1.44 (s, 9H), 1.35 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 161.38, 147.87, 147.28, 141.73, 140.09, 139.91, 131.41, 131.30, 130.47, 130.27, 129.24, 128.10, 127.58, 127.26, 126.90, 126.48, 125.39, 125.22, 124.71, 122.61, 122.48, 121.95, 121.85, 120.91, 112.88, 111.10, 109.04, 100.69, 98.68, 55.66, 35.24, 34.94, 31.10, 31.04. **HRMS** (ESI) [M+H]⁺ = 608.326

[00118] **Example 3 – For the Synthesis of MLC-7**

[00119] **3-bromo-1-(4-(*tert*-butyl)phenyl)-1H-pyrazole**

[00120] 3-bromo-1H-pyrazole (500 mg, 3.40 mmol, 100 mol%), 1-(*tert*-butyl)-4-iodobenzene (1327 mg, 5.10 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (163 μL, 1.36 mmol, 40 mol%), CuI (130 mg, 0.68 mmol, 20 mol%), and K₂CO₃ (705 mg, 5.10 mmol, 150 mol%) were weighted in a vial. Toluene (3.4 mL) was added, and the mixture was allowed to stir overnight at 110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was removed *in*

vacuo. The residue was subjected to column chromatography on silica (Hex → Hex/DCM 1:1) to furnish the product (193.6 mg) in 20% yield.

[00121] ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 2.5 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.48 – 7.43 (m, 2H), 6.46 (d, *J* = 2.4 Hz, 1H), 1.34 (s, 9H).

[00122] ¹³C NMR (101 MHz, CDCl₃) δ 150.35, 137.38, 128.74, 127.93, 126.48, 118.94, 110.42, 34.75, 31.46.

[00123] **1-(4-(tert-butyl)phenyl)-3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1H-pyrazole - For the Synthesis of MLC-7**

[00124] 3-bromo-1-(4-(tert-butyl)phenyl)-1H-pyrazole (83 mg, 0.30 mmol, 100 mol%), 2-(2,7-di-tert-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (179 mg, 0.37 mmol, 125 mol%), Pd(PPh₃)₄ (34 mg, 0.03 mmol, 10 mol%), and K₃PO₄ (189 mg, 0.89 mmol, 300 mol%) were weighted in a vial. 1,4-Dioxane (5 mL) and H₂O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H₂O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex/DCM 9:1) to furnish the product (85.8 mg) in 52% yield as a yellow solid.

[00125] ¹H NMR (400 MHz, CDCl₃) δ 9.24 (s, 1H), 8.38 (s, 1H), 8.02 (dd, *J* = 1.9, 0.9 Hz, 2H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.91 (d, *J* = 2.5 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.56 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.45 – 7.40 (m, 2H), 6.82 (dd, *J* = 3.5, 2.5 Hz, 1H), 6.71 (d, *J* = 2.5 Hz, 1H), 6.55 (dd, *J* = 3.5, 2.7 Hz, 1H), 1.36 (s, 18H), 1.33 (s, 9H).

[00126] ¹³C NMR (101 MHz, CDCl₃) δ 149.34, 148.08, 146.81, 137.85, 131.83, 129.93, 128.55, 128.16, 127.95, 127.81, 126.38, 126.32, 126.12, 124.53, 121.04, 118.61, 112.61, 107.67, 103.91, 35.30, 34.66, 31.48, 31.09.

[00127] **Example 4 – For the Synthesis of MLC-4**

[00128] **3-bromo-1-(4-methoxyphenyl)-1H-pyrazole**

[00129] 3-bromo-1H-pyrazole (500 mg, 3.40 mmol, 100 mol%), 1-iodo-4-methoxybenzene (1194 mg, 5.10 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (163 μL, 1.36 mmol, 40 mol%), CuI (130 mg, 0.68 mmol, 20 mol%), and K₂CO₃ (705 mg, 5.10 mmol, 150 mol%) were weighted in a vial. Toluene (3.4 mL) was added, and the mixture was allowed to stir overnight at 110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was removed *in*

vacuo. The residue was subjected to column chromatography on silica (Hex/DCM 1:1 → DCM) to furnish the product (136.8 mg) in 16% yield.

[00130] ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 2.4 Hz, 1H), 7.57 – 7.51 (m, 2H), 6.99 – 6.93 (m, 2H), 6.44 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H).

[00131] ¹³C NMR (101 MHz, CDCl₃) δ 158.76, 133.52, 128.89, 127.61, 120.98, 114.69, 110.23, 55.73.

[00132] 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(4-methoxyphenyl)-1H-pyrazole - For the Synthesis of MLC-4

[00133] 3-bromo-1-(4-methoxyphenyl)-1H-pyrazole (75 mg, 0.30 mmol, 100 mol%), 2-(2,7-di-tert-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (179 mg, 0.37 mmol, 125 mol%), Pd(PPh₃)₄ (34 mg, 0.03 mmol, 10 mol%), and K₃PO₄ (189 mg, 0.89 mmol, 300 mol%) were weighted in a vial. 1,4-Dioxane (5 mL) and H₂O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H₂O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex/DCM 8:2 → Hex/DCM 4:6) to furnish the product (103.0 mg) in 65% yield as a yellow solid.

[00134] ¹H NMR (400 MHz, CDCl₃) δ 9.21 (s, 1H), 8.38 (s, 1H), 8.03 – 8.00 (m, 2H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 2.5 Hz, 1H), 7.61 – 7.52 (m, 4H), 6.97 – 6.89 (m, 2H), 6.81 (dd, *J* = 3.5, 2.6 Hz, 1H), 6.69 (d, *J* = 2.5 Hz, 1H), 6.54 (dd, *J* = 3.5, 2.7 Hz, 1H), 3.82 (s, 3H), 1.36 (s, 18H).

[00135] ¹³C NMR (101 MHz, CDCl₃) δ 158.11, 148.05, 146.72, 134.08, 131.84, 129.93, 128.43, 128.16, 127.99, 127.84, 126.30, 126.19, 124.52, 121.05, 120.49, 114.65, 112.56, 107.49, 103.70, 55.71, 35.29, 31.09.

[00136] Example 5 – For the Synthesis of MLC-5

[00137] 3-bromo-1-(3,4-dimethoxyphenyl)-1H-pyrazole (EXP-21-CL5419-R3, DCI18651)

[00138] 3-bromo-1H-pyrazole (500 mg, 3.40 mmol, 100 mol%), 4-iodo-1,2-dimethoxybenzene (1347 mg, 5.10 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (163 μL, 1.36 mmol, 40 mol%), CuI (130 mg, 0.68 mmol, 20 mol%), and K₂CO₃ (705 mg, 5.10 mmol, 150 mol%) were weighted in a vial. Toluene (3.4 mL) was added, and the mixture was allowed to stir overnight at 110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was

removed *in vacuo*. The residue was subjected to column chromatography on silica (Hex/DCM 1:1 → DCM) to furnish the product (210.0 mg) in 22% yield.

[00139] ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 2.4 Hz, 1H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.06 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.45 (d, *J* = 2.4 Hz, 1H), 3.95 (s, 3H), 3.91 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.83, 148.33, 133.76, 129.03, 127.65, 111.31, 110.93, 110.33, 104.41, 56.35, 56.33.

[00140] 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,4-dimethoxyphenyl)-1H-pyrazole – For the Synthesis of MLC-5

[00141] 3-bromo-1-(3,4-dimethoxyphenyl)-1H-pyrazole (84 mg, 0.30 mmol, 100 mol%), 2-(2,7-di-tert-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (179 mg, 0.37 mmol, 125 mol%), Pd(PPh₃)₄ (34 mg, 0.03 mmol, 10 mol%), and K₃PO₄ (189 mg, 0.89 mmol, 300 mol%) were weighted in a vial. 1,4-Dioxane (5 mL) and H₂O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H₂O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex/EtOAc 8:2 → Hex/EtOAc 1:1 → DCM) to furnish the product (92.3 mg) in 55% yield as a green solid.

[00142] ¹H NMR (400 MHz, CDCl₃) δ 9.25 (s, 1H), 8.38 (s, 1H), 8.03 – 8.01 (m, 2H), 7.98 – 7.94 (m, 2H), 7.85 (d, *J* = 2.5 Hz, 1H), 7.55 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.09 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.82 (dd, *J* = 3.5, 2.6 Hz, 1H), 6.69 (d, *J* = 2.5 Hz, 1H), 6.55 (dd, *J* = 3.5, 2.7 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 1.36 (s, 18H).

[00143] ¹³C NMR (101 MHz, CDCl₃) δ 149.78, 148.06, 147.61, 146.76, 134.31, 131.83, 129.93, 128.46, 128.18, 128.12, 127.85, 126.33, 126.10, 124.53, 121.04, 112.59, 111.45, 110.32, 107.63, 103.97, 103.85, 56.34, 56.23, 35.29, 31.08.

[00144] Example 6 – For the Synthesis of MLC-6

[00145] 1-(benzo[d][1,3]dioxol-5-yl)-3-bromo-1H-pyrazole

[00146] 3-bromo-1H-pyrazole (500 mg, 3.40 mmol, 100 mol%), 5-iodobenzo[d][1,3]dioxole (1266 mg, 5.10 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (163 μL, 1.36 mmol, 40 mol%), CuI (130 mg, 0.68 mmol, 20 mol%), and K₂CO₃ (705 mg, 5.10 mmol, 150 mol%) were weighted in a vial. Toluene (3.4 mL) was added, and the mixture was allowed to stir overnight at 110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was removed *in*

vacuo. The residue was subjected to column chromatography on silica (Hex/DCM 1:1 → DCM) to furnish the product (154.8 mg) in 17% yield.

[00147] ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 2.4 Hz, 1H), 7.17 (d, *J* = 2.2 Hz, 1H), 7.05 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 6.03 (s, 2H).

[00148] ¹³C NMR (101 MHz, CDCl₃) δ 148.62, 146.84, 134.68, 129.05, 127.75, 112.71, 110.39, 108.43, 101.98, 101.98.

[00149] **1-(benzo[d][1,3]dioxol-5-yl)-3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1H-pyrazole – For the Synthesis of MLC-6**

[00150] 1-(benzo[d][1,3]dioxol-5-yl)-3-bromo-1H-pyrazole (79 mg, 0.30 mmol, 100 mol%), 2-(2,7-di-tert-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (179 mg, 0.37 mmol, 125 mol%), Pd(PPh₃)₄ (34 mg, 0.03 mmol, 10 mol%), and K₃PO₄ (189 mg, 0.89 mmol, 300 mol%) were weighted in a vial. 1,4-Dioxane (5 mL) and H₂O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H₂O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex/DCM 8:2 → Hex/DCM 4:6) to furnish the product (114.0 mg) in 70% yield as a yellow solid.

[00151] ¹H NMR (400 MHz, CDCl₃) δ 9.21 (s, 1H), 8.38 (s, 1H), 8.01 (dt, *J* = 1.8, 0.8 Hz, 2H), 7.96 (dt, *J* = 8.9, 0.6 Hz, 2H), 7.81 (d, *J* = 2.5 Hz, 1H), 7.55 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.20 (d, *J* = 2.2 Hz, 1H), 7.09 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.84 – 6.79 (m, 2H), 6.68 (d, *J* = 2.5 Hz, 1H), 6.54 (dd, *J* = 3.5, 2.7 Hz, 1H), 5.99 (s, 2H), 1.36 (s, 16H).

[00152] ¹³C NMR (101 MHz, CDCl₃) δ 148.54, 148.08, 146.75, 146.11, 135.25, 131.84, 129.92, 128.59, 128.20, 128.16, 127.76, 126.33, 126.00, 124.52, 121.02, 112.59, 112.12, 108.43, 107.67, 103.86, 101.78, 101.56, 35.29, 31.08.

[00153] **Example 7 – For the Synthesis of MLC-8**

[00154] **3-bromo-1-(3,5-dimethylphenyl)-1H-pyrazole (EXP-21-CL5446-R1, DCI19068)**

[00155] 3-bromo-1H-pyrazole (500 mg, 3.40 mmol, 100 mol%), 1-iodo-3,5-dimethylbenzene (1184 mg, 5.10 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (163 μL, 1.36 mmol, 40 mol%), CuI (130 mg, 0.68 mmol, 20 mol%), and K₂CO₃ (705 mg, 5.10 mmol, 150 mol%) were weighted in a vial. Toluene (3.4 mL) was added and the mixture was allowed to stir overnight at 110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was removed *in*

vacuo. The residue was subjected to column chromatography on silica (Hex → Hex/DCM 4:6) to furnish the product (208 mg) in 24% yield.

[00156] ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 2.5$ Hz, 1H), 7.26 (s, 2H), 6.94 (s, 1H), 6.45 (d, $J = 2.5$ Hz, 1H), 2.36 (s, 6H).

[00157] ^{13}C NMR (101 MHz, CDCl_3) δ 139.62, 139.53, 128.82, 128.78, 127.94, 116.99, 110.38, 21.46.

[00158] 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,5-dimethylphenyl)-1H-pyrazole – For the Synthesis of MLC-8

[00159] 3-bromo-1-(3,5-dimethylphenyl)-1H-pyrazole (76 mg, 0.30 mmol, 100 mol%), 2-(2,7-di-tert-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (179 mg, 0.37 mmol, 125 mol%), $\text{Pd}(\text{PPh}_3)_4$ (34 mg, 0.03 mmol, 10 mol%), and K_3PO_4 (189 mg, 0.89 mmol, 300 mol%) were weighted in a vial. 1,4-Dioxane (5 mL) and H_2O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H_2O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex → Hex/DCM 4:6) to furnish the product (93.3 mg) in 59% yield as a yellow solid.

[00160] ^1H NMR (500 MHz, CDCl_3) δ 9.26 (s, 1H), 8.38 (s, 1H), 8.05 – 8.03 (m, 2H), 7.96 (d, $J = 8.9$ Hz, 2H), 7.91 (d, $J = 2.5$ Hz, 1H), 7.56 (dd, $J = 8.9, 1.9$ Hz, 2H), 7.31 (dt, $J = 1.5, 0.7$ Hz, 2H), 6.88 (tt, $J = 1.6, 0.8$ Hz, 1H), 6.82 (dd, $J = 3.4, 2.6$ Hz, 1H), 6.70 (d, $J = 2.5$ Hz, 1H), 6.55 (dd, $J = 3.5, 2.7$ Hz, 1H), 2.34 (s, 6H), 1.37 (s, 18H).

[00161] ^{13}C NMR (126 MHz, CDCl_3) δ 148.05, 146.80, 140.13, 139.35, 131.79, 129.94, 128.55, 128.18, 128.00, 127.86, 127.80, 126.30, 126.13, 124.52, 121.07, 116.68, 112.58, 107.65, 103.91, 35.30, 31.09, 21.51.

[00162] Example 8 – For the Synthesis of MLC-9

[00163] 3-bromo-1-(3,5-dimethoxyphenyl)-1H-pyrazole

[00164] 3-bromo-1H-pyrazole (500 mg, 3.40 mmol, 100 mol%), 1-iodo-3,5-dimethoxybenzene (1347 mg, 5.10 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (163 μL , 1.36 mmol, 40 mol%), CuI (130 mg, 0.68 mmol, 20 mol%), and K_2CO_3 (705 mg, 5.10 mmol, 150 mol%) were weighted in a vial. Toluene (3.4 mL) was added and the mixture was allowed to stir overnight at 110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was

removed *in vacuo*. The residue was subjected to column chromatography on silica (Hex → Hex/DCM 4:6) to furnish the product (308 mg) in 32% yield.

[00165] ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 2.5 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 2H), 6.46 (d, *J* = 2.5 Hz, 1H), 6.39 (t, *J* = 2.2 Hz, 1H), 3.84 (s, 6H).

[00166] ¹³C NMR (101 MHz, CDCl₃) δ 161.58, 141.32, 129.00, 128.22, 110.69, 99.15, 97.69, 55.80.

[00167] 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,5-dimethoxyphenyl)-1H-pyrazole – For the Synthesis of MLC-9

[00168] 3-bromo-1-(3,5-dimethoxyphenyl)-1H-pyrazole (86 mg, 0.30 mmol, 100 mol%), 2-(2,7-di-tert-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (179 mg, 0.37 mmol, 125 mol%), Pd(PPh₃)₄ (34 mg, 0.03 mmol, 10 mol%), and K₃PO₄ (189 mg, 0.89 mmol, 300 mol%) were weighted in a vial. 1,4-Dioxane (5 mL) and H₂O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H₂O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex/DCM 8:2 → Hex/DCM 4:6) to furnish the product (111.1 mg) in 66% yield as a yellow solid.

[00169] ¹H NMR (500 MHz, CDCl₃) δ 9.31 (s, 1H), 8.39 (s, 1H), 8.01 – 7.99 (m, 2H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.88 (d, *J* = 2.6 Hz, 1H), 7.55 (dd, *J* = 8.9, 1.9 Hz, 2H), 6.84 (d, *J* = 2.2 Hz, 2H), 6.82 (dd, *J* = 3.5, 2.6 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 6.54 (dd, *J* = 3.5, 2.7 Hz, 1H), 6.32 (t, *J* = 2.2 Hz, 1H), 3.80 (s, 6H), 1.36 (s, 18H).

[00170] ¹³C NMR (126 MHz, CDCl₃) δ 161.52, 148.08, 146.95, 141.73, 131.83, 129.92, 128.76, 128.21, 128.17, 127.77, 126.36, 125.83, 124.54, 121.01, 112.64, 108.04, 104.27, 98.43, 97.20, 55.73, 35.29, 31.08.

[00171] Example 9– For the Synthesis of MLC-10

[00172] 4-(3-bromo-1H-pyrazol-1-yl)-N,N-dimethylaniline

[00173] 3-bromo-1H-pyrazole (500 mg, 3.40 mmol, 100 mol%), 4-iodo-N,N-dimethylaniline (1000 mg, 4.05 mmol, 120 mol%), trans-cyclohexane-1,2-diamine (163 μL, 1.36 mmol, 40 mol%), CuI (130 mg, 0.68 mmol, 20 mol%), and K₂CO₃ (705 mg, 5.10 mmol, 150 mol%) were weighted in a vial. Toluene (3.4 mL) was added and the mixture was allowed to stir overnight at 110 °C. The reaction was diluted with hexanes (3 mL), filtered, and the solvent was removed *in*

vacuo. The residue was subjected to column chromatography on silica (Hex → Hex/DCM 4:6) to furnish the product (182 mg) in 20% yield.

[00174] ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 2.4 Hz, 1H), 7.49 – 7.44 (m, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 2.4 Hz, 1H), 2.99 (s, 6H).

[00175] ¹³C NMR (101 MHz, CDCl₃) δ 149.77, 128.76, 126.93, 120.95, 112.74, 109.73, 40.82.

[00176] **4-(3-(5-(2,7-di-*tert*-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1H-pyrazol-1-yl)-N,N-dimethylaniline – For the Synthesis of MLC-10**

[00177] 4-(3-bromo-1H-pyrazol-1-yl)-N,N-dimethylaniline (81 mg, 0.30 mmol, 100 mol%), 2-(2,7-di-*tert*-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (179 mg, 0.37 mmol, 125 mol%), Pd(PPh₃)₄ (34 mg, 0.03 mmol, 10 mol%), and K₃PO₄ (189 mg, 0.89 mmol, 300 mol%) were weighted in a vial. 1,4-Dioxane (5 mL) and H₂O (2 mL) were added, and the mixture was stirred at 90 °C for 16 h. The reaction was diluted with H₂O (6 mL), extracted with EtOAc (2 x 8 mL), and washed with brine (5 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was subjected to column chromatography on silica (Hex/DCM 8:2 → Hex/DCM 4:6) to furnish the product (90.6 mg) in 56% yield as a yellow solid.

[00178] ¹H NMR (500 MHz, CDCl₃) δ 9.20 (s, 1H), 8.37 (s, 1H), 8.04 – 8.02 (m, 2H), 7.96 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 2.5 Hz, 1H), 7.55 (dd, *J* = 8.9, 1.9 Hz, 2H), 7.51 (d, *J* = 9.0 Hz, 2H), 6.80 (dd, *J* = 3.4, 2.6 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.67 (d, *J* = 2.5 Hz, 1H), 6.54 (dd, *J* = 3.4, 2.7 Hz, 1H), 2.96 (s, 6H), 1.36 (s, 18H).

[00179] ¹³C NMR (126 MHz, CDCl₃) δ 148.01, 146.37, 131.84, 129.93, 128.16, 128.13, 127.96, 127.86, 126.51, 126.22, 124.51, 121.10, 120.51, 113.06, 112.51, 107.16, 103.26, 40.96, 35.28, 31.09.

[00180] **Example 10 – For the Synthesis of MLC-1**

[00181] **Synthesis of 3-bromo-1-(*p*-tolyl)-1H-indazole**

[00182] 3-bromo-1H-indazole (500 mg, 2.54 mmol, 100 mol%), 4-iodotoluene (830 mg, 3.81 mmol, 150 mol%), trans-cyclohexane-1,2-diamine (70 μL, 0.58 mmol, 23 mol%), CuI (53 mg, 0.28 mmol, 11 mol%), and K₂CO₃ (526 mg, 3.81 mmol, 150 mol%) were weighted in a vial. DMF (10 mL) was added and the mixture was allowed to stir overnight at 120 °C. The reaction was diluted with water (50 mL). The organics were extracted off with ethyl acetate (30 mL x 3). The combine organics were washed with water (30 mL x 3) and brine (30 mL). The organics were

dried over magnesium sulfate, filtered, and concentrated. The residue was subjected to column chromatography on silica (Hex/DCM 9:1 → Hex/DCM 6.5:3.5) to furnish the product (671 mg) in 92% yield.

[00183] ^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.62 (m, 2H), 7.59 – 7.54 (m, 2H), 7.47 (ddt, J = 8.8, 6.9, 1.0 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.29 (dq, J = 8.1, 1.0 Hz, 1H), 2.44 (s, 3H).

[00184] ^{13}C NMR (101 MHz, CDCl_3) δ 139.88, 137.12, 137.04, 130.03, 130.01, 128.18, 128.10, 124.82, 123.37, 122.80, 122.74, 122.09, 121.90, 120.65, 110.62, 110.49, 21.09, -0.01.

[00185] **3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(p-tolyl)-1H-indazole** –
For the Synthesis of MLC-1

[00186] 3-bromo-1-(p-tolyl)-1H-indazole (49 mg, 0.171 mmol, 100 mol%), 2-(2,7-di-tert-butylanthracen-9-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrrole (120 mg, 0.209 mmol, 123 mol%, 85% pure), $\text{Pd}(\text{PPh}_3)_4$ (12 mg, 0.010 mmol, 6 mol%), and K_3PO_4 (109 mg, 0.512 mmol, 300 mol%) were weighted in a vial. Dioxane (5 mL) and H_2O (2 mL) were added, and the mixture was stirred overnight at 90 °C. The reaction was diluted with H_2O (15 mL) and brine (15 mL), and extracted with EtOAc (2 x 30 mL). The combined organic layers were dried over MgSO_4 , filtered, and concentrated in vacuo. The residue was subjected to column chromatography on silica (Hex/DCM 9:1 → Hex/DCM 7:3) to furnish the product (83 mg) in 87% yield as a yellow solid.

[00187] ^1H NMR (400 MHz, Chloroform-*d*) δ 9.50 (s, 1H), 8.43 (s, 1H), 8.27 (d, J = 8.1 Hz, 1H), 8.12 (s, 2H), 8.01 (d, J = 8.9 Hz, 2H), 7.78 (d, J = 8.5 Hz, 1H), 7.68 – 7.55 (m, 4H), 7.54 – 7.46 (m, 1H), 7.42 – 7.28 (m, 3H), 7.26 (d, J = 3.5 Hz, 1H), 6.73 (t, J = 3.1 Hz, 1H), 2.43 (s, 3H), 1.41 (s, 18H).

[00188] ^{13}C NMR (101 MHz, CDCl_3) δ 148.04, 140.17, 139.57, 137.78, 136.19, 131.74, 129.95, 129.82, 128.85, 128.11, 127.48, 127.23, 126.35, 125.43, 124.45, 122.56, 122.17, 121.69, 121.59, 120.88, 112.78, 110.62, 108.63, 35.19, 30.98, 21.07.

[00189] **HRMS** (ESI) $[\text{M}+\text{H}]^+ = 562.325$

[00190] **Example 11– Synthesis of Metal–Ligand Complex 1 (MLC-1)**

[00191] In a glove box, a solution of 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(p-tolyl)-1H-indazole (15.0 mg, 0.03 mmol, 100 mol%) in C_6D_6 (500 μL) was added dropwise to solid HfBn_4 (14.0 mg, 0.03 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. 5 minutes after addition the solution was transferred to an NMR tube and checked by ^1H and ^{13}C NMR. Full conversion to the desired complex was observed.

[00192] ^1H NMR (400 MHz, C_6D_6) δ 8.41 (s, 1H), 8.36 - 8.31 (m, 2H), 7.94 (d, J = 9.0 Hz, 2H), 7.76 (dt, J = 8.2, 1.1 Hz, 1H), 7.46 (dd, J = 8.9, 1.9 Hz, 2H), 7.31 (d, J = 3.2 Hz, 1H), 7.25 (d, J = 1.9 Hz, 1H), 7.20 - 6.98 (m, 13H), 6.98 - 6.82 (m, 4H), 6.63 (t, J = 7.7 Hz, 4H), 6.56 - 6.50 (m, 1H), 6.39 (tt, J = 7.3, 1.3 Hz, 2H), 6.19 - 6.10 (m, 4H), 2.13 (s, 3H), 1.78 (d, J = 11.7 Hz, 2H), 1.36 (d, J = 11.7 Hz, 2H), 1.25 (s, 18H).

[00193] ^{13}C NMR (101 MHz, C_6D_6) δ 191.22, 148.19, 146.19, 145.78, 142.69, 139.56, 138.56, 137.58, 137.52, 137.32, 136.16, 133.32, 131.83, 130.87, 130.46, 130.18, 129.92, 129.31, 128.96, 128.61, 128.49, 128.27, 128.20, 127.00, 125.33, 124.81, 124.39, 122.98, 122.86, 121.80, 121.76, 119.32, 114.70, 111.87, 111.52, 110.98, 84.19, 34.94, 30.58, 21.07.

[00194] Example 12 – Synthesis of Metal–Ligand Complex 2 (MLC-2)

[00195] In a glove box, a solution of 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,5-dimethylphenyl)-1H-indazole (11.7 mg, 0.020 mmol, 100 mol%) in C_6D_6 (600 μL) was added dropwise to solid HfBn_4 (11.0 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. 5 minutes after addition the solution was transferred to an NMR tube and checked by ^1H and ^{13}C NMR. A mixture of [3,2] and mono-[2,1] complexes was observed. The solution was then heated for 2 h at 80 $^\circ\text{C}$ in the NMR tube.

[00196] ^1H NMR (400 MHz, C_6D_6) δ 8.45 (s, 1H), 8.42 – 8.40 (m, 2H), 7.99 (d, J = 9.0 Hz, 2H), 7.84 (dt, J = 8.2, 1.1 Hz, 1H), 7.47 (dd, J = 9.0, 1.9 Hz, 2H), 7.41 (d, J = 3.1 Hz, 1H), 7.35 (d, J = 8.9 Hz, 1H), 7.07 (q, J = 1.4 Hz, 1H), 6.99 (d, J = 3.1 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.81 (s, 1H), 6.62 – 6.56 (m, 4H), 6.51 – 6.42 (m, 5H), 6.24 – 6.16 (m, 2H), 2.29 (s, 3H), 2.17 (d, J = 11.9 Hz, 2H), 2.06 (s, 3H), 1.31 (d, J = 11.9 Hz, 2H), 1.24 (s, 18H). ^{13}C NMR (101 MHz, C_6D_6) δ 188.89, 148.51, 147.70, 145.76, 144.39, 142.82, 140.25, 137.44, 136.63, 136.04, 133.65, 131.28, 130.61, 130.09, 128.81, 128.45, 128.21, 127.27, 126.29, 125.24, 123.67, 122.84, 122.19, 122.01, 119.84, 114.74, 111.67, 111.51, 110.46, 86.44, 35.36, 30.83, 23.89, 21.69.

[00197] Example 13 – Synthesis of Metal–Ligand Complex 3 (MLC-3)

[00198] In a glove box, a solution of 3-(5-(2,6-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,5-dimethoxyphenyl)-1H-indazole (12.2 mg, 0.020 mmol, 100 mol%) in C_6D_6 (600 μL) was added dropwise to solid HfBn_4 (11.0 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. 5 minutes after addition the solution was transferred to an NMR tube and checked by ^1H and ^{13}C NMR.

[00199] ^1H NMR (400 MHz, C_6D_6) δ 8.55 – 8.52 (m, 1H), 8.43 (t, J = 4.5 Hz, 2H), 8.03 – 7.95 (m, 2H), 7.78 (dt, J = 8.2, 1.1 Hz, 1H), 7.50 (td, J = 9.1, 1.9 Hz, 2H), 7.36 (d, J = 3.2 Hz, 1H),

7.21 (d, $J = 8.7$ Hz, 1H), 6.96 (d, $J = 3.2$ Hz, 1H), 6.91 – 6.85 (m, 1H), 6.68 – 6.51 (m, 9H), 6.43 (d, $J = 1.6$ Hz, 1H), 6.32 (tt, $J = 6.3, 2.1$ Hz, 1H), 6.24 (tt, $J = 6.8, 1.9$ Hz, 1H), 5.99 (d, $J = 1.6$ Hz, 1H), 3.30 (s, 3H), 3.22 (s, 3H), 2.16 – 2.11 (m, 2H), 1.49 (d, $J = 6.4$ Hz, 1H), 1.42 (d, $J = 11.2$ Hz, 1H), 1.29 (s, 9H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6) δ 171.47, 167.78, 162.50, 148.62, 148.21, 147.67, 146.53, 143.17, 140.45, 138.46, 137.26, 136.50, 132.98, 132.38, 132.00, 131.17, 131.08, 130.35, 130.30, 128.98, 128.78, 127.63, 125.71, 125.36, 123.18, 122.97, 122.96, 122.26, 122.13, 119.98, 114.89, 111.96, 111.19, 91.95, 91.93, 88.64, 86.92, 54.79, 53.94, 35.37, 34.87, 30.93, 30.92.

[00200] Example 14 – Synthesis of Metal–Ligand Complex 4 (MLC-4)

[00201] In a glove box, a solution of 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(4-methoxyphenyl)-1H-pyrazole (10.6 mg, 0.020 mmol, 100 mol%) in C_6D_6 (600 μL) was added dropwise to solid ZrBn_4 (9.1 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. After addition, the solution was transferred to an NMR tube and the sample was allowed to react overnight at room temperature. *Two equivalents of toluene were evident in the NMR.*

[00202] ^1H NMR (400 MHz, C_6D_6) δ 8.35 (s, 1H), 8.26 – 8.14 (m, 2H), 7.91 (d, $J = 8.9$ Hz, 2H), 7.45 (dd, $J = 8.9, 1.9$ Hz, 2H), 6.80 (d, $J = 2.5$ Hz, 1H), 6.75 – 6.65 (m, 7H), 6.56 – 6.45 (m, 4H), 6.05 (d, $J = 2.5$ Hz, 1H), 5.93 – 5.87 (m, 4H), 3.32 (s, 3H), 2.05 (d, $J = 10.0$ Hz, 2H), 1.24 (s, 18H), 1.17 (d, $J = 10.0$ Hz, 2H).

[00203] ^{13}C NMR (101 MHz, C_6D_6) δ 181.58, 156.55, 151.57, 148.45, 140.16, 139.34, 138.30, 136.19, 133.64, 132.25, 130.52, 130.41, 129.15, 128.39, 127.32, 127.03, 125.18, 123.73, 122.30, 120.79, 113.73, 113.24, 111.51, 109.32, 100.16, 74.81, 54.95, 35.26, 30.94.

[00204] Example 15 – Synthesis of Metal–Ligand Complex 5 (MLC-5)

[00205] In a glove box, a solution of 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,4-dimethoxyphenyl)-1H-pyrazole (11.2 mg, 0.020 mmol, 100 mol%) in C_6D_6 (600 μL) was added dropwise to solid ZrBn_4 (9.1 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. After addition, the solution was transferred to an NMR tube and the sample was allowed to react overnight at room temperature. *Two equivalents of toluene were evident in the NMR.*

[00206] ^1H NMR (400 MHz, C_6D_6) δ 8.37 (s, 1H), 8.24 – 8.20 (m, 2H), 7.92 (d, $J = 9.0$ Hz, 2H), 7.47 (dd, $J = 8.9, 1.9$ Hz, 2H), 7.19 (d, $J = 3.1$ Hz, 1H), 6.76 (d, $J = 3.1$ Hz, 1H), 6.73 – 6.68 (m, 5H), 6.59 (d, $J = 2.5$ Hz, 1H), 6.58 – 6.52 (m, 2H), 6.17 (s, 1H), 6.05 (d, $J = 2.5$ Hz, 1H), 5.93

– 5.89 (m, 4H), 3.42 (s, 3H), 3.38 (s, 3H), 2.06 (d, $J = 10.1$ Hz, 2H), 1.25 (s, 18H), 1.19 (d, $J = 10.1$ Hz, 2H).

[00207] ^{13}C NMR (101 MHz, C_6D_6) δ 173.43, 151.86, 149.76, 148.44, 146.07, 140.29, 139.67, 138.76, 136.11, 133.67, 132.25, 130.53, 130.23, 129.09, 128.39, 127.44, 127.02, 125.19, 123.60, 122.37, 119.51, 113.73, 109.42, 100.18, 96.41, 74.43, 55.86, 55.82, 35.27, 30.94.

[00208] Example 16 – Synthesis of Metal–Ligand Complex 6 (MLC-6)

[00209] In a glove box, a solution of 1-(benzo[d][1,3]dioxol-5-yl)-3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1H-pyrazole (10.8 mg, 0.020 mmol, 100 mol%) in C_6D_6 (600 μL) was added dropwise to solid ZrBn_4 (9.1 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. After addition, the solution was transferred to an NMR tube and the sample was allowed to react overnight at room temperature. *Two equivalents of toluene were evident in the NMR.*

[00210] ^1H NMR (500 MHz, C_6D_6) δ 8.39 (s, 1H), 8.20 – 8.18 (m, 2H), 7.95 (d, $J = 9.0$ Hz, 2H), 7.45 (dd, $J = 8.9, 2.0$ Hz, 2H), 6.76 (d, $J = 2.5$ Hz, 1H), 6.70 (d, $J = 3.1$ Hz, 1H), 6.69 – 6.63 (m, 4H), 6.52 – 6.48 (m, 2H), 6.40 – 6.36 (m, 1H), 6.34 (d, $J = 8.1$ Hz, 1H), 6.22 – 6.17 (m, 4H), 6.06 (d, $J = 2.5$ Hz, 1H), 5.99 (d, $J = 8.1$ Hz, 1H), 5.13 (s, 2H), 1.86 (d, $J = 9.6$ Hz, 2H), 1.59 (d, $J = 9.5$ Hz, 2H), 1.23 (d, $J = 1.7$ Hz, 18H).

[00211] ^{13}C NMR (126 MHz, C_6D_6) δ 157.23, 151.32, 148.34, 143.49, 141.17, 140.78, 137.78, 135.88, 133.63, 132.63, 131.04, 130.60, 130.49, 128.95, 128.47, 128.35, 127.63, 126.74, 125.16, 124.16, 122.21, 114.05, 109.25, 106.50, 103.93, 100.27, 99.05, 74.79, 35.24, 30.93.

[00212] Example 17 – Synthesis of Metal–Ligand Complex 7 (MLC-7)

[00213] In a glove box, a solution of 1-(4-(tert-butyl)phenyl)-3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1H-pyrazole (11.1 mg, 0.020 mmol, 100 mol%) in C_6D_6 (600 μL) was added dropwise to solid ZrBn_4 (9.1 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. After addition, the solution was transferred to an NMR tube and the sample was allowed to react overnight at room temperature. *Two equivalents of toluene were evident in the NMR.*

[00214] ^1H NMR (500 MHz, C_6D_6) δ 8.37 (s, 1H), 8.21 – 8.18 (m, 2H), 7.92 (d, $J = 8.9$ Hz, 2H), 7.46 (dd, $J = 8.9, 1.9$ Hz, 2H), 7.22 (d, $J = 2.1$ Hz, 1H), 7.18 (d, $J = 3.1$ Hz, 1H), 6.94 (dd, $J = 8.3, 2.2$ Hz, 1H), 6.75 – 6.70 (m, 6H), 6.55 (t, $J = 7.4$ Hz, 2H), 6.51 (d, $J = 8.3$ Hz, 1H), 6.07 (d, $J = 2.5$ Hz, 1H), 5.91 (d, $J = 7.5$ Hz, 4H), 2.01 (d, $J = 10.0$ Hz, 2H), 1.24 (s, 18H), 1.22 (d, $J = 10.3$ Hz, 2H), 1.18 (s, 9H).

[00215] ^{13}C NMR (126 MHz, C_6D_6) δ 180.30, 151.87, 148.45, 146.26, 143.08, 140.38, 138.55, 136.21, 133.65, 132.94, 132.28, 130.53, 130.32, 129.05, 128.35, 127.69, 126.99, 125.20, 124.34, 123.62, 122.31, 113.69, 110.13, 109.43, 100.46, 74.51, 35.25, 34.61, 31.68, 30.92.

[00216] **Example 18 – Synthesis of Metal–Ligand Complex 8 (MLC-8)**

[00217] In a glove box, a solution of 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,5-dimethylphenyl)-1H-pyrazole (10.5 mg, 0.020 mmol, 100 mol%) in C_6D_6 (600 μL) was added dropwise to solid ZrBn_4 (9.1 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. After addition, the solution was transferred to an NMR tube and the sample was allowed to react overnight at room temperature. *Two equivalents of toluene were evident in the NMR.*

[00218] ^1H NMR (500 MHz, C_6D_6) δ 8.41 (s, 1H), 8.32 (s, 2H), 7.96 (dd, J = 8.9, 2.3 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H), 7.20 – 7.17 (m, 1H), 6.87 – 6.84 (m, 1H), 6.74 – 6.72 (m, 1H), 6.65 – 6.59 (m, 4H), 6.52 – 6.47 (m, 4H), 6.41 – 6.36 (m, 2H), 6.28 (s, 1H), 6.10 – 6.05 (m, 2H), 2.32 (d, J = 10.7 Hz, 2H), 1.98 (s, 3H), 1.94 (s, 3H), 1.57 (d, J = 10.8 Hz, 2H), 1.24 (s, 18H).

[00219] ^{13}C NMR (126 MHz, C_6D_6) δ 179.77, 150.86, 148.36, 144.20, 143.54, 140.55, 136.96, 136.84, 136.09, 133.68, 132.02, 130.61, 129.07, 128.68, 127.76, 127.63, 126.99, 126.65, 125.15, 123.58, 122.12, 113.34, 109.01, 108.65, 100.43, 76.71, 35.30, 30.84, 24.08, 21.20.

[00220] **Example 19 – Synthesis of Metal–Ligand Complex 9 (MLC-9)**

[00221] In a glove box, a solution of 3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1-(3,5-dimethoxyphenyl)-1H-pyrazole (11.2 mg, 0.020 mmol, 100 mol%) in C_6D_6 (600 μL) was added dropwise to solid ZrBn_4 (9.1 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. After addition, the solution was transferred to an NMR tube and the sample was allowed to react overnight at room temperature. *Two equivalents of toluene were evident in the NMR.*

[00222] ^1H NMR (500 MHz, C_6D_6) δ 8.40 (s, 1H), 8.31 (s, 2H), 7.95 (d, J = 8.6 Hz, 2H), 7.45 (dd, J = 9.0, 2.1 Hz, 2H), 7.20 – 7.17 (m, 1H), 6.84 – 6.81 (m, 1H), 6.71 – 6.60 (m, 5H), 6.50 – 6.44 (m, 2H), 6.40 – 6.35 (m, 4H), 6.06 – 6.02 (m, 1H), 5.79 (dd, J = 15.1, 2.6 Hz, 2H), 3.27 (s, 3H), 3.02 (s, 3H), 2.03 (d, J = 10.1 Hz, 2H), 1.87 (d, J = 10.2 Hz, 2H), 1.25 (s, 18H).

[00223] ^{13}C NMR (126 MHz, C_6D_6) δ 167.20, 162.47, 161.78, 151.64, 148.25, 145.85, 141.05, 137.92, 135.99, 133.71, 132.43, 130.62, 129.01, 128.59, 128.40, 128.35, 126.97, 125.09, 123.29, 122.27, 113.60, 109.33, 100.53, 93.06, 89.13, 76.45, 54.85, 53.51, 35.29, 30.91.

[00224] **Example 20 – Synthesis of Metal–Ligand Complex 10 (MLC-10)**

[00225] In a glove box, a solution of 4-(3-(5-(2,7-di-tert-butylanthracen-9-yl)-1H-pyrrol-2-yl)-1H-pyrazol-1-yl)-N,N-dimethylaniline (10.8 mg, 0.020 mmol, 100 mol%) in C₆D₆ (600 μ L) was added dropwise to solid ZrBn₄ (9.1 mg, 0.020 mmol, 100 mol%) at room temperature. The vial was swirled after each drop to ensure mixing. After addition, the solution was transferred to an NMR tube and the sample was allowed to react overnight at room temperature. *Two equivalents of toluene were evident in the NMR.*

[00226] ¹H NMR (500 MHz, C₆D₆) δ 8.37 (s, 1H), 8.26 – 8.23 (m, 2H), 7.92 (d, J = 8.9 Hz, 2H), 7.46 (dd, J = 8.9, 1.9 Hz, 2H), 7.16 (s, 1H), 6.76 – 6.71 (m, 5H), 6.70 (d, J = 2.5 Hz, 1H), 6.62 (d, J = 2.7 Hz, 1H), 6.60 – 6.54 (m, 3H), 6.31 (dd, J = 8.7, 2.7 Hz, 1H), 6.05 (d, J = 2.5 Hz, 1H), 5.96 – 5.92 (m, 4H), 2.53 (s, 6H), 2.10 (d, J = 10.0 Hz, 2H), 1.25 (s, 18H), 1.19 (d, J = 10.0 Hz, 2H).

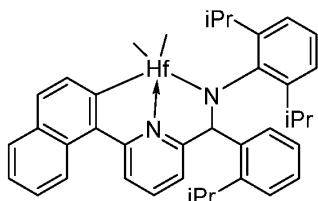
[00227] ¹³C NMR (126 MHz, C₆D₆) δ 181.54, 151.11, 148.39, 147.79, 139.89, 138.59, 136.86, 136.47, 133.71, 132.45, 130.55, 130.15, 129.30, 128.37, 126.99, 126.71, 125.16, 123.49, 122.44, 119.96, 113.65, 111.86, 111.21, 108.99, 99.81, 74.55, 40.89, 35.26, 30.96.

[00228] **Example 21 – Batch Reactor Screening of Metal–Ligand Complexes 1-3 and 4 to 10**

Table 3. Batch Reactor Results

Catalyst	Temp (°C)	Efficiency (gpoly/gM)	Yield (g)	Cat. Loading (μ mol)	Mw (g/mol)	PDI	Tm (°C)	Mol% octene
MCL-1	120	101,966	9.1	0.50	1,202,720	4.3	93.1	5.8
MCL-1	150	242,777	13.0	0.30	607,961	2.7	112.2	4.0
MCL-2	120	189,927	33.9	1.00	937,779	2.8	21.8	12.1
MCL-3	120	252,115	4.5	0.10	774,147	4.1	116.7	2.9
MCL-3	150	179,282	3.2	0.10	501,010	3.2	116.5	1.7
Comp. C1	120	187,686	6.7	0.20	641,421	8.3	-16.5	20.4
Comp. C1	150	60,508	10.8	1.00	586,088	11.3	-14.2	18.5

[00229] 120 °C semi-batch reactor conditions: 46 g ethylene, 300 g 1-octene, 610 g IsoparE, 1.2 eq, RIBS-II activator to catalyst, 10 μ mol MMAO-3A, 310 psi reactor pressure. 150 °C semi-batch reactor conditions: 43 g ethylene, 300 g 1-octene, 546 g IsoparE, 1.2 eq, RIBS-II activator to catalyst, 10 μ mol MMAO-3A, 360 psi reactor pressure. 190 °C semi-batch reactor conditions: 43 g ethylene, 300 g 1-octene, 520 g IsoparE, 1.2 eq, RIBS-II activator to catalyst, 10 μ mol MMAO-3A, 420 psi reactor pressure.



Comparative C1 (“Comp. C1”)

[00230] The polymers produced by the Comparative C1 have high levels of comonomer incorporation. Therefore, the expected melt temperature is very low, as indicated by the negative numbers in Table 1. The efficiency of Comparative C1 is not great at higher temperatures such as 150 °C when compared the inventive examples MLC-1 to MLC-3. The examples are more efficient at 150 °C. The inventive examples MLC-1 to MLC-3 also have a much higher reactivity ratio than Comparative C1.

Table 4: Batch Reactor Data for MLC-4 to MLC-10

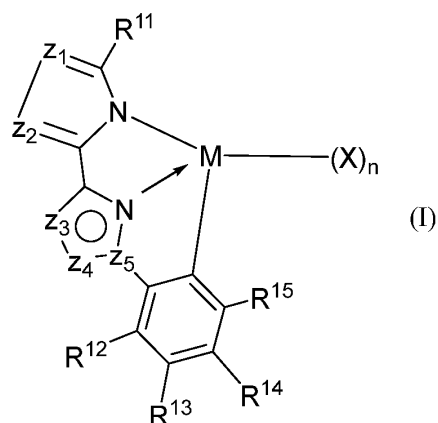
Catalyst	Temp. (°C)	Efficiency (gpoly/gM)	Yield (g)	Cat. Loading (μmol)	M _w (g/mol)	PDI	T _m (°C)	Mol% octene
MLC-4	120	1,534,684	14.0	0.10	460,538	5.9	93.4	8.4
MLC-4	150	317,899	2.9	0.10	341,152	4.6	91.3	5.9
MLC-4	190	54,810	0.5	0.10	151,927	3.6	91.1	7.1
MLC-5	120	1,282,557	11.7	0.10	514,370	15.9	114.4	3.6
MLC-5	150	657,722	6.0	0.10	316,949	61.3	115.0	7.6
MLC-5	190	54,810	0.5	0.10	153,042	12.8	102.7	5.9
MLC-6	120	1,326,405	12.1	0.10	509,402	6.5	114.4	6.4
MLC-6	150	602,912	5.5	0.10	419,080	6.7	102.2	4.5
MLC-6	190	65,772	0.6	0.10	181,505	7.9	116.4	5.7
MLC-7	120	1,699,114	15.5	0.10	468,268	4.5	115.6	6.4
MLC-7	150	690,608	6.3	0.10	345,723	5.6	113.6	5.9
MLC-7	190	65,772	0.6	0.10	165,611	5.7	88.5	6.4
MLC-8	150	328,861	3.0	0.10	359,603	2.9	111.1	5.8
MLC-8	190	51,156	1.4	0.30	128,202	2.6	105.2	8.9
MLC-9	150	1,140,051	10.4	0.10	606,135	4.3	115.5	2.1
MLC-9	190	93,177	1.7	0.20	252,309	5.7	42.1	2.6

MLC-10	150	328,861	3.0	0.10	395,857	7.9	97.9	6.6
MLC-10	190	47,502	1.3	0.30	211,386	5.1	93.7	5.3
Comp. C1	120	187,686	6.7	0.20	641,421	8.3	-16.5	20.4
Comp. C1	150	60,508	10.8	1.00	586,088	11.3	-14.2	18.5

[00231] At 120 °C, the semi-batch reactor conditions include: 46 g ethylene, 300 g 1-octene, 610 g IsoparE, 1.2 eq, RIBS-II activator to catalyst, 10 µmol MMAO-3A, 310 psi reactor pressure. 150 °C semi-batch reactor conditions: 43 g ethylene, 300 g 1-octene, 546 g IsoparE, 1.2 eq, RIBS-II activator to catalyst, 10 µmol MMAO-3A, 360 psi reactor pressure. At 190 °C, the semi-batch reactor conditions include: 43 g ethylene, 300 g 1-octene, 520 g IsoparE, 1.2 eq, RIBS-II activator to catalyst, 10 µmol MMAO-3A, 420 psi reactor pressure.

CLAIMS

1. A metal–ligand complex according to formula (I):



where:

M is a metal chosen from titanium, zirconium, or hafnium, the metal having a formal oxidation state of +2, +3, or +4;

each X is a monodentate or bidentate ligand independently chosen from (C₁–C₅₀)hydrocarbyl, halogen, $-(CH_2)_wSi(R^X)_3$, $-N(R^N)_2$, and $-NCOR^C$, where w is 1 to 10 and R^X is (C₁–C₂₀)alkyl;

when X is monodentate, n is 2, and when X is bidentate, n is 1 or 2;

z₁ is independently selected from N or C(R¹), and R¹ and R¹¹ are not covalently connected to form an aromatic ring or a non-aromatic ring;

z₂ is independently selected from N or C(R²), and R¹ and R² may be covalently connected to form an aromatic ring or a non-aromatic ring;

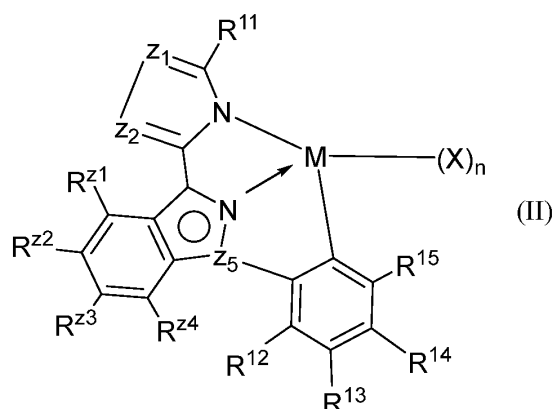
z₃ is independently selected from O, S, N, R^N or C(R³), and R³ and R⁴ may be covalently connected to form an aromatic ring or a non-aromatic ring;

z₄ is independently selected from O, S, N, NR^N or C(R⁴), and R⁴ and R³ may be covalently connected to form an aromatic ring or a non-aromatic ring;

z₅ is independently selected from N or C;

$R^1, R^2, R^3, R^4, R^{11}, R^{12}, R^{13}, R^{14}$, and R^{15} are independently selected from the group consisting of (C₁–C₅₀)hydrocarbonyl, (C₁–C₅₀)heterohydrocarbonyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, $-\text{Si}(\text{R}^{\text{C}})_3$, $-\text{Ge}(\text{R}^{\text{C}})_3$, $-\text{P}(\text{R}^{\text{P}})_2$, $-\text{N}(\text{R}^{\text{N}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $\text{R}^{\text{C}}\text{S}(\text{O})-$, $-\text{P}(\text{O})(\text{R}^{\text{P}})_2$, $\text{R}^{\text{C}}\text{S}(\text{O})_2-$, $(\text{R}^{\text{C}})_2\text{C}=\text{N}-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{O}-$, $\text{R}^{\text{C}}\text{OC}(\text{O})-$, $\text{R}^{\text{C}}\text{C}(\text{O})\text{N}(\text{R})-$, $(\text{R}^{\text{C}})_2\text{NC}(\text{O})-$, halogen, and $-\text{H}$, wherein R^{12} and R^{13} are optionally connected to form a ring, R^{13} and R^{14} are optionally connected to form a ring, and R^{14} and R^{15} are optionally connected to form a ring, wherein each R^{N} , R^{C} , and R^{P} is independently selected from the group consisting of (C₁–C₂₀)hydrocarbonyl, (C₁–C₂₀)heterohydrocarbonyl, and $-\text{H}$.

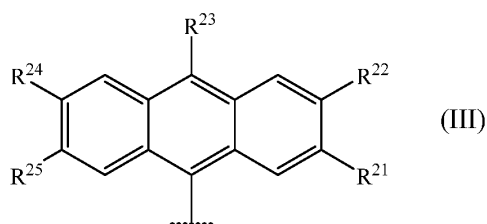
2. The metal–ligand complex of claim 1, wherein z_3 is CR^3 , z_4 is CR^4 , and R^3 and R^4 are connected to form an aromatic ring, and the metal–ligand structure has a structure according to formula (II):



where $z_1, z_2, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, X, n$, and M are defined as in formula (I), $R^{z1}, R^{z2}, R^{z3}, R^{z4}$ selected from the group consisting of hydrogen, (C₁–C₂₀)alkyl, (C₆–C₅₀)aryl, (C₁–C₁₀)heterohydrocarbonyl, $-\text{NR}^{\text{N}}$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, halogen, CF_3-NO_2 , or $-\text{CN}$, where R^{C} is (C₁–C₂₀)alkyl, (C₆–C₂₀)aryl; and z_5 is N.

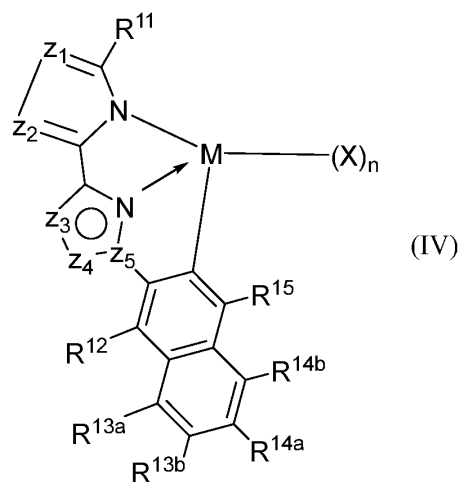
3. The metal–ligand complex of any one of the preceding claims, wherein X is benzyl, methyl, $-\text{CH}_2\text{Si}[(\text{C}_1-\text{C}_{20})\text{alkyl}]_3$, $-\text{N}[(\text{C}_1-\text{C}_{20})\text{alkyl}]_3$ or chloro.

4. The metal–ligand complex of any one of the preceding claims, wherein R^{11} is 2,4,6-triisopropylphenyl, mesityl, substituted and unsubstituted anthracenyl, 3,5-ditertbutylphenyl, naphthyl
5. The metal–ligand complex of any one of claims 1 – 3, wherein R^{11} is a radical of formula (III):



- wherein R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is independently chosen from (C_1-C_{10}) alkyl, (C_6-C_{10}) aryl, or $-H$.
6. The metal–ligand complex of claim 5, wherein R^{21} , R^{22} , R^{23} , R^{24} , and R^{25} is independently chosen from *tert*-butyl, 3,5-di-*tert*-butylphenyl, or $-H$.
7. The metal–ligand complex of any one of the preceding claims, wherein only one of z_1 and z_2 is N.
8. The metal–ligand complex of any one of the preceding claims, wherein when z_2 is N and z_1 is CR^1 , R^1 and R^{11} are not covalently connected to form an aromatic or non-aromatic ring.
9. The metal–ligand complex of any one of claims 1 to 8, wherein R^{12} , R^{13} , R^{14} and R^{15} are selected from the group consisting of hydrogen, chloro, fluoro, benzyl, (C_1-C_{10}) alkyl, cyclic (C_1-C_{10}) heteroalkyl, $-OR^C$, $-NR^N_2$, wherein R^C and R^N are (C_1-C_{12}) alkyl.
10. The metal–ligand complex of any one of claims 1 to 9, wherein R^{12} and R^{13} are connected to form a heterocyclic ring.
11. The metal–ligand complex of any one of claims 1 to 9, wherein R^{13} and R^{15} are chloro or fluoro, or (C_1-C_{10}) alkyl.
12. The metal–ligand complex of any one of claims 1 to 9, wherein R^{13} and R^{14} are $-OR^C$, wherein R^C is (C_1-C_8) alkyl.
13. The metal–ligand complex of any one of claims 1 to 9, wherein R^{14} is selected from the group consisting of (C_1-C_{10}) alkyl, cyclic (C_1-C_{10}) heteroalkyl, $-OR^C$, $-NR^N_2$, wherein R^C and R^N are (C_1-C_8) alkyl.

14. The metal–ligand complex of any one of the preceding claims, wherein R^{13} and R^{14} are covalently connected to form an aromatic ring, the metal–ligand has a structure according to formula (IV):



15. A polymerization process comprising contacting ethylene and optionally one or more α -olefin monomers in the presence of a catalyst system, wherein the catalyst system comprises one or more precatalyst and a cocatalyst, wherein the precatalyst is a metal–ligand complex according any one of claims 1 to 14, and producing an ethylene-based polymer.