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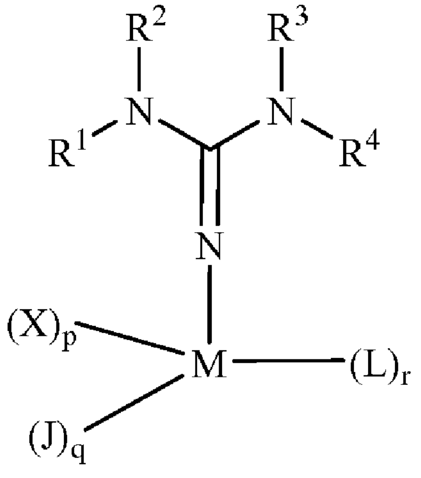
(54) Title: METAL-LIGAND COMPLEX, OLEFIN POLYMERIZATION CATALYST DERIVED THEREFROM, AND OLEFIN POLYMERIZATION METHOD UTILIZING THE CATALYST



(I)

(57) Abstract: A metal-ligand complex has formula (I): wherein J, L, M, R^1, R^2, R^3, R^4, X, p, q, and r are defined herein. The metal-ligand complex is useful as a catalyst or catalyst precursor for olefin polymerization.

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METAL-LIGAND COMPLEX, OLEFIN POLYMERIZATION CATALYST DERIVED THEREFROM, AND OLEFIN POLYMERIZATION METHOD UTILIZING THE CATALYST

FIELD

[0001] The present invention generally relates to metal-ligand complexes, catalysts comprising or prepared from the metal-ligand complexes, and processes of catalyzing olefin polymerization reactions with the catalysts to prepare polyolefins.

INTRODUCTION

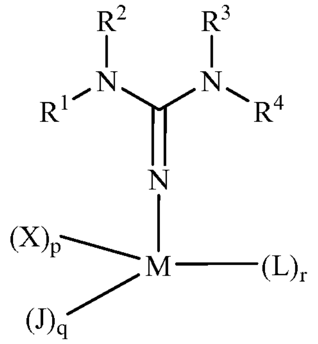
[0002] D. Shoken et al. "Mono(imidazolin-2-iminato) Titanium Complexes for Ethylene Polymerization at Low Amounts of Methylaluminoxane", *Journal of the American Chemical Society*, 2013, volume 135, number 34, pages 12592-12595, describes ethylene polymerization using catalyst precursors of the type $Im{=}N{-}Ti(Cl)_m(CH_3)_{3-m}$, where Im=N- is an imidazolin-2-iminato ligand, and m is 1, 2, or 3.

[0003] M. Sharma et al., "Bis(1,3-di-tert-butylimidazolin-2-iminato) Titanium Complexes as Effective Catalysts for the Monodisperse Polymerization of Propylene", *Journal of the American Chemical Society*, 2012, volume 134, number 41, pages 17234-17244, describes propylene polymerization using catalyst precursors of the type $(Im{=}N{-})_2Ti(CH_3)_2$, where Im=N- is an imidazolin-2-iminato ligand.

[0004] Chemical industry desires new metal-ligand catalysts and catalyst precursors with improved stability under olefin polymerization reaction conditions. Preferably, the new catalysts would be useful for improving reaction yields, providing alternative substrate selectivities (e.g., providing a new relative selectivity for a monomer and co-monomer in making a polyolefin copolymer), exhibiting good thermal stability at high various reactor temperatures, producing polymers with high molecular weight, reducing manufacturing costs, improving process safety, or a combination thereof.

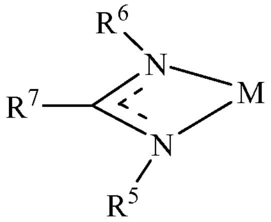
SUMMARY

[0005] One embodiment is a metal-ligand complex of formula (I):


(I)

wherein J is a monoanionic moiety selected from $(R^K)(R^L)(R^X)P{=}N$-, $(R^K)(R^L)C{=}N$-, $(R^K)((R^L)(R^X)N)C{=}N$-, $(R^K)(R^L)B$-O-, R^KO-, R^KS-, $R^KS(O)$-, $(R^K)(R^L)N$-, $(R^KN{=}C(R^L)$-$N(R^X)$-, $(R^K)(R^L)NO$-, $R^KC(O)O$-, $R^KC(O)NH$-, and $(R^K)(R^L)P$-, wherein each R^K, R^L, and R^X is independently is hydrogen, $(C_1$-$C_{40})$hydrocarbyl-, $((C_1$-$C_{15})$hydrocarbyl$)_3$Si-, $((C_1$-$C_{15})$hydrocarbyl$)_2$N-, or $(C_1$-$C_{40})$heterohydrocarbyl-; L is independently at each occurrence halogen, hydrogen, $((C_1$-$C_{40})$hydrocarbyl)C(O)N(H)-, $((C_1$-$C_{40})$hydrocarbyl)C(O)N(H)$(C_1$-$C_{20})$hydrocarbyl-, $((C_1$-$C_{40})$hydrocarbyl)C(O)O-, $(C_1$-$C_{40})$hydrocarbyl-, $(C_1$-$C_{40})$heterohydrocarbyl-, $R^K(R^L)N$-, R^LO-, R^LS-, or $R^K(R^L)P$-, wherein each of R^K and R^L independently is as defined above; and each occurrence of L is a monoanionic moiety that is bonded to M; M is a metal of any one of Groups 3, 4, 5, and 6 of a Periodic Table of the Elements, the metal being in a formal oxidation state of +2, +3, +4, +5, or +6; R^1, R^2, R^3, and R^4 are independently at each occurrence hydrogen, $(C_1$-$C_{40})$hydrocarbyl-, $((C_1$-$C_{40})$hydrocarbyl)O-, $((C_1$-$C_{40})$hydrocarbyl)S-, $((C_1$-$C_{40})$hydrocarbyl$)_3$Si-, or $(C_1$-$C_{40})$heterohydrocarbyl-; X is a neutral Lewis base group selected from $R^XN(R^K)(R^L)$, $R^X{=}N(R^K)$, $R^KO(R^L)$, $R^KS(R^L)$, and $R^XP(R^K)(R^L)$, wherein each of R^K , R^L, and R^X independently is as defined above; p is 0, 1, 2, or 3 (specifically 0 or 1), and q is 0 or 1, provided that the sum of p and q is at least 1; r is 2 or 3; two occurrences of L are optionally taken together to form a $(C_2$-$C_{40})$hydrocarbylene or $(C_1$-$C_{40})$heterohydrocarbylene, or $(R^D)_2C{=}C(R^D)$-$C(R^D){=}C(R^D)_2$, wherein each R^D independently is hydrogen, unsubstituted $(C_1$-$C_6)$alkyl, phenyl, or naphthyl; J and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2$-$C_{40})$hydrocarbylene or $(C_1$-$C_{40})$heterohydrocarbylene; one occurrence of L and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2$-$C_{40})$hydrocarbylene or

$(C_1\text{-}C_{40})$heterohydrocarbylene; one occurrence of X and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_1\text{-}C_{40})$heterohydrocarbylene; any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; X and J are optionally taken together to form a monoanionic bidentate moiety X-J, provided that when X-J is bound to M to form a fragment having the structure



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then R^5, R^6, and R^7 are each independently hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})$hydrocarbyl)O-, $((C_1\text{-}C_{40})$hydrocarbyl)S-, $((C_1\text{-}C_{40})$hydrocarbyl$)_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-; and provided that when X-J is bound to M via an anionic nitrogen and a Lewis base nitrogen, X-J and M form a four-membered metallocycle or a six-membered metallocycle; and each of the above-mentioned $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$heterohydrocarbyl, $(C_2\text{-}C_{40})$hydrocarbylene, and $(C_1\text{-}C_{40})$heterohydrocarbylene independently is the same or different and is unsubstituted or substituted with one or more substituents R^S selected from halogen, unsubstituted $(C_1\text{-}C_{18})$hydrocarbyl, F_3C-, FCH_2O-, F_2HCO-, F_3CO-, oxo, R_3Si-, RO-, RS-, RS(O)-, $RS(O)_2$-, R_2P-, R_2N-, $R_2C{=}N$-, NC-, RC(O)O-, ROC(O)-, RC(O)N(R)-, and $R_2NC(O)$-, wherein each R independently is an unsubstituted $(C_1\text{-}C_{18})$hydrocarbyl.

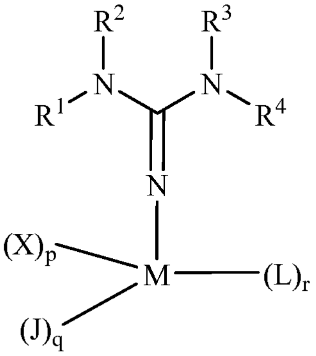
[0006] Another embodiment is a catalyst comprising, or comprising the reaction product of, one or more metal-ligand complexes of the preceding paragraph, and one or more activating cocatalysts, wherein a ratio of total number of moles of the one or more metal-ligand complexes to total number of moles of the one or more activating cocatalyst is 1:10,000 to 100:1. Another embodiment is a process for preparing a polyolefin, the process comprising contacting at least one polymerizable olefin with the aforementioned catalyst under conditions sufficient to polymerize at least some of the at least one polymerizable olefin, thereby producing a polyolefin.

[0007] These and other embodiments are described in detail below.

DETAILED DESCRIPTION

[0008] As summarized previously, the present invention generally relates to metal-ligand complexes, catalysts comprising or prepared from the metal-ligand complexes, processes of catalyzing olefin polymerization reactions with the catalysts to prepare polyolefins. The present inventors have determined that the metal-ligand complexes described herein are precursors to active catalysts for olefin polymerization. Preferably, the catalyst comprises, or is prepared from, three or fewer, more preferably two, and still more preferably one metal-ligand complex of formula (I). Preferred catalysts show beneficial catalyst efficiencies (e.g., higher grams of polymer produced per gram of metal-ligand complex of formula (I)) and produce polyolefins, including polyolefin copolymers, having beneficially high weight average molecular weights (M_w), number average molecular weights (M_n), or both.

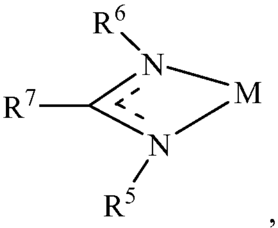
[0009] One embodiment is a metal-ligand complex of formula (I):



(I)

wherein J is a monoanionic moiety selected from $(R^K)(R^L)(R^X)P{=}N-$, $(R^K)(R^L)C{=}N-$, $(R^K)((R^L)(R^X)N)C{=}N-$, $(R^K)(R^L)B{-}O-$, R^KO-, R^KS-, $R^KS(O)-$, $(R^K)(R^L)N-$, $(R^KN{=}C(R^L)-N(R^X))-$, $(R^K)(R^L)NO-$, $R^KC(O)O-$, $R^KC(O)NH-$, and $(R^K)(R^L)P-$, wherein each R^K, R^L, and R^X is independently is hydrogen, (C_1-C_{40})hydrocarbyl-, $((C_1-C_{15})\text{hydrocarbyl})_3Si-$, $((C_1-C_{15})\text{hydrocarbyl})_2N-$, or (C_1-C_{40})heterohydrocarbyl-; L is independently at each occurrence halogen, hydrogen, $((C_1-C_{40})\text{hydrocarbyl})C(O)N(H)-$, $((C_1-C_{40})\text{hydrocarbyl})C(O)N(H)(C_1-C_{20})$hydrocarbyl-, $((C_1-C_{40})\text{hydrocarbyl})C(O)O-$, (C_1-C_{40})hydrocarbyl-, (C_1-C_{40})heterohydrocarbyl-, $R^K(R^L)N-$, R^LO-, R^LS-, or $R^K(R^L)P-$, wherein each of R^K and R^L independently is as defined above; and each occurrence of L is a monoanionic moiety that is bonded to M; M is a metal of any one of Groups 3, 4, 5, and 6 of a Periodic Table of the Elements, the metal being in a formal oxidation state of +2, +3, +4, +5, or +6; R^1, R^2, R^3, and R^4 are independently at each occurrence hydrogen,

$(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})$hydrocarbyl)O-, $((C_1\text{-}C_{40})$hydrocarbyl)S-, $((C_1\text{-}C_{40})$hydrocarbyl$)_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-; X is a neutral Lewis base group selected from $R^XN(R^K)(R^L)$, $R^X{=}N(R^K)$, $R^KO(R^L)$, $R^KS(R^L)$, and $R^XP(R^K)(R^L)$, wherein each of R^K , R^L, and R^X independently is as defined above; p is 0, 1, 2, or 3 (specifically 0 or 1), and q is 0 or 1, provided that the sum of p and q is at least 1; r is 2 or 3; two occurrences of L are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, or $(R^D)_2C{=}C(R^D)\text{-}C(R^D){=}C(R^D)_2$, wherein each R^D independently is H, unsubstituted $(C_1\text{-}C_6)$alkyl, phenyl, or naphthyl; J and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; one occurrence of L and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; one occurrence of X and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_1\text{-}C_{40})$heterohydrocarbylene; any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; X and J are optionally taken together to form a monoanionic bidentate moiety X-J, provided that when X-J is bound to M to form a fragment having the structure



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then R^5, R^6, and R^7 are each independently hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})$hydrocarbyl)O-, $((C_1\text{-}C_{40})$hydrocarbyl)S-, $((C_1\text{-}C_{40})$hydrocarbyl$)_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-; and provided that when X-J is bound to M via an anionic nitrogen and a Lewis base nitrogen, X-J and M form a four-membered metallocycle or a six-membered metallocycle; and each of the above-mentioned $(C_1\text{-}C_{40})$hydrocarbyl, $(C_1\text{-}C_{40})$heterohydrocarbyl, $(C_2\text{-}C_{40})$hydrocarbylene, and $(C_1\text{-}C_{40})$heterohydrocarbylene independently is the same or different and is unsubstituted or substituted with one or more substituents R^S selected from halogen, unsubstituted $(C_1\text{-}C_{18})$hydrocarbyl, F_3C-, FCH_2O-,

F_2HCO-, F_3CO-, oxo, R_3Si-, RO-, RS-, RS(O)-, $RS(O)_2$-, R_2P-, R_2N-, R_2C=N-, NC-, RC(O)O-, ROC(O)-, RC(O)N(R)-, and $R_2NC(O)$-, wherein each R independently is an unsubstituted (C_1-C_{18})hydrocarbyl.

[0010] As used herein, the term "(C_1-C_{40})hydrocarbyl" means a hydrocarbon radical of 1 to 40 carbon atoms and the term "(C_1-C_{40})hydrocarbylene" means a hydrocarbon diradical of from 1 to 40 carbon atoms, wherein each hydrocarbon radical and diradical independently is 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, or a combination of two or more of the foregoing; and each hydrocarbon radical and diradical is the same as or different from another hydrocarbon radical and diradical, respectively, and independently is unsubstituted or substituted by one or more R^S.

[0011] Preferably, a (C_1-C_{40})hydrocarbyl independently is an unsubstituted or substituted (C_1-C_{40})alkyl, (C_3-C_{40})cycloalkyl, (C_3-C_{20})cycloalkyl-(C_1-C_{20})alkylene, (C_6-C_{40})aryl, or (C_6-C_{20})aryl-(C_1-C_{20})alkylene. More preferably, a (C_1-C_{40})hydrocarbyl independently is an unsubstituted or substituted (C_1-C_{20})hydrocarbyl, e.g., (C_1-C_{20})alkyl, (C_3-C_{20})cycloalkyl, (C_3-C_{10})cycloalkyl-(C_1-C_{10})alkylene, (C_6-C_{20})aryl, or (C_6-C_{18})aryl-(C_1-C_{10})alkylene. Still more preferably, a (C_1-C_{40})hydrocarbyl independently is an unsubstituted or substituted (C_1-C_{18})hydrocarbyl, e.g., (C_1-C_{18})alkyl, (C_3-C_{18})cycloalkyl, (C_3-C_{12})cycloalkyl-(C_1-C_6)alkylene, (C_6-C_{18})aryl, or (C_6-C_{12})aryl-(C_1-C_6)alkylene. Preferably, any (C_3-C_{18})cycloalkyl independently is an unsubstituted or substituted (C_3-C_{10})cycloalkyl.

[0012] The term "(C_1-C_{40})alkyl" means a saturated straight or branched hydrocarbon radical of from 1 to 40 carbon atoms that is unsubstituted or substituted by one or more R^S. Examples of unsubstituted (C_1-C_{40})alkyl are unsubstituted (C_1-C_{20})alkyl; unsubstituted (C_1-C_{10})alkyl; unsubstituted (C_1-C_5)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 (C_1-C_{40})alkyl are substituted (C_1-C_{20})alkyl, substituted (C_1-C_{10})alkyl, trifluoromethyl, and (C_{45})alkyl. Preferably, each (C_1-C_5)alkyl independently is methyl, trifluoromethyl, ethyl, 1-propyl, or 2-methylethyl.

[0013] The term "(C_1-C_{20})alkylene" means a saturated straight or branched chain diradical of from 1 to 20 carbon atoms that is unsubstituted or substituted by one or more R^S. Preferably, (C_1-C_{20})alkylene, together with atoms of formula (I) through which the (C_1-C_{20})alkylene is bonded, comprise a 5- or 6-membered ring. Examples of unsubstituted

$(C_1\text{-}C_{20})$alkylene are unsubstituted $(C_1\text{-}C_{10})$alkylene, including unsubstituted 1,2-$(C_1\text{-}C_{10})$alkylene; $-CH_2-$, $-CH_2CH_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$, $-(CH_2)_7-$, $-(CH_2)_8-$, and $-(CH_2)_4C(H)(CH_3)-$. Examples of substituted $(C_1\text{-}C_{20})$alkylene are substituted $(C_1\text{-}C_{10})$alkylene, $-CF_2-$, $-C(O)-$, and $-(CH_2)_{14}C(CH_3)_2(CH_2)_5-$ (i.e., a 6,6-dimethyl substituted normal-1,20-eicosylene).

[0014] The term "$(C_6\text{-}C_{40})$aryl" means an unsubstituted or substituted (by one or more R^S) mono-, bi- or tricyclic aromatic hydrocarbon radical of from 6 to 40 total carbon atoms, of which at least from 6 to 14 carbon atoms are ring carbon atoms, and the mono-, bi- or tricyclic radical comprises 1, 2 or 3 rings (first, second, and third rings, respectively), wherein any second or third ring independently is fused or non-fused to a first ring or each other, and the first ring is aromatic and, preferably, at least one of any second or third rings is aromatic. Examples of unsubstituted $(C_6\text{-}C_{40})$aryl are unsubstituted $(C_6\text{-}C_{20})$aryl; unsubstituted $(C_6\text{-}C_{18})$aryl; unsubstituted $(C_6\text{-}C_{12})$aryl; phenyl; fluorenyl; tetrahydrofluorenyl; indacenyl; hexahydroindacenyl; indenyl; dihydroindenyl; naphthyl; tetrahydronaphthyl; and phenanthrene. Examples of substituted $(C_6\text{-}C_{40})$aryl are substituted $(C_6\text{-}C_{20})$aryl; substituted $(C_6\text{-}C_{18})$aryl; substituted $(C_6\text{-}C_{12})$aryl; 2-$(C_1\text{-}C_5)$alkyl-phenyl; 2,4-bis$(C_1\text{-}C_5)$alkyl-phenyl; 2,4-bis[(C_{20})alkyl]-phenyl; polyfluorophenyl; pentafluorophenyl; and fluoren-9-one-1-yl. A preferred substituted $(C_6\text{-}C_{12})$aryl is a substituted (C_6)aryl, more preferably 2,6-bis(1-methylethyl)phenyl.

[0015] The term "$(C_3\text{-}C_{40})$cycloalkyl" means a saturated cyclic hydrocarbon radical of from 3 to 40 carbon atoms that is unsubstituted or substituted by one or more R^S. Examples of unsubstituted $(C_3\text{-}C_{40})$cycloalkyl are unsubstituted $(C_3\text{-}C_{20})$cycloalkyl, unsubstituted $(C_3\text{-}C_{10})$cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted $(C_3\text{-}C_{40})$cycloalkyl are substituted $(C_3\text{-}C_{20})$cycloalkyl, substituted $(C_3\text{-}C_{10})$cycloalkyl, cyclopentanon-2-yl, and 1-fluorocyclohexyl.

[0016] Examples of $(C_1\text{-}C_{40})$hydrocarbylene are unsubstituted or substituted $(C_6\text{-}C_{40})$arylene, $(C_3\text{-}C_{40})$cycloalkylene, and $(C_1\text{-}C_{40})$alkylene (e.g., $(C_1\text{-}C_{20})$alkylene). In some embodiments, the diradicals are on adjacent carbon atoms (i.e., 1,2-diradicals), or spaced apart by one, two, or more intervening carbon atoms (e.g., respective 1,3-diradicals, 1,4-diradicals, etc.). Preferred is a 1,2-, 1,3-, 1,4-, or an alpha,omega-diradical (i.e., having maximum spacing between the radical carbons), more preferably a 1,2-diradical. More preferred are 1,2-diradical versions of $(C_6\text{-}C_{18})$arylene, $(C_3\text{-}C_{20})$cycloalkylene, and

(C_2-C_{20})alkylene.

[0017] The term "(C_1-C_{40})heterohydrocarbyl" means a heterohydrocarbon radical of from 1 to 40 carbon atoms and one or more heteroatoms N (when comprising —N=, as in certain nitrogen containing heteroaryl groups, e.g., an isoxazolyl); O; S; S(O); $S(O)_2$; $Si(R^C)_2$; $P(R^P)$; and $N(R^N)$, wherein independently each R^c is unsubstituted (C_1-C_{18})hydrocarbyl, each R^P is unsubstituted (C_1-C_{18})hydrocarbyl; and each R^N is unsubstituted (C_1-C_{18})hydrocarbyl. The term "(C_1-C_{40})heterohydrocarbylene" means a heterohydrocarbon diradical of from 1 to 40 carbon atoms and one or more heteroatoms $Si(R^C)_2$, $P(R^P)$, $N(R^N)$, N, O, S, S(O), and $S(O)_2$ as defined above. The heterohydrocarbon radical and each of the heterohydrocarbon diradicals independently are on a carbon atom or heteroatom thereof. Each heterohydrocarbon radical and diradical independently is 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, or a combination of two or more thereof; and each heterohydrocarbon is the same as or different from another heterohydrocarbon radical and diradical, respectively.

[0018] Preferably, a (C_1-C_{40})heterohydrocarbyl independently is unsubstituted or substituted (C_1-C_{40})heteroalkyl, (C_2-C_{40})heterocycloalkyl, (C_2-C_{40})heterocycloalkyl-(C_1-C_{20})alkylene, (C_3-C_{40})cycloalkyl-(C_1-C_{20})heteroalkylene, (C_2-C_{40})heterocycloalkyl-(C_1-C_{20})heteroalkylene, (C_1-C_{40})heteroaryl, (C_1-C_{20})heteroaryl-(C_1-C_{20})alkylene, (C_6-C_{20})aryl-(C_1-C_{20})heteroalkylene, or (C_1-C_{20})heteroaryl-(C_1-C_{20})heteroalkylene. More preferably, a (C_1-C_{40})heterohydrocarbyl independently is unsubstituted or substituted (C_1-C_{20})heterohydrocarbyl, e.g., (C_1-C_{20})heteroalkyl, (C_2-C_{20})heterocycloalkyl, (C_2-C_{20})heterocycloalkyl-(C_1-C_{20})alkylene, (C_3-C_{20})cycloalkyl-(C_1-C_{20})heteroalkylene, (C_2-C_{20})heterocycloalkyl-(C_1-C_{20})heteroalkylene, (C_1-C_{20})heteroaryl, (C_1-C_{20})heteroaryl-(C_1-C_{20})alkylene, (C_6-C_{20})aryl-(C_1-C_{20})heteroalkylene, or (C_1-C_{20})heteroaryl-(C_1-C_{20})heteroalkylene. Still more preferably, a (C_1-C_{40})heterohydrocarbyl independently is unsubstituted or substituted (C_1-C_{18})heterohydrocarbyl, e.g., (C_1-C_{18})heteroalkyl, (C_2-C_{18})heterocycloalkyl, (C_2-C_{12})heterocycloalkyl-(C_1-C_6)alkylene, (C_3-C_{12})cycloalkyl-(C_1-C_6)heteroalkylene, (C_2-C_{12})heterocycloalkyl-(C_1-C_6)heteroalkylene, (C_1-C_{12})heteroaryl, (C_1-C_{12})heteroaryl-(C_1-C_6)alkylene, (C_6-C_{18})aryl-(C_1-C_6)heteroalkylene, or (C_1-C_{12})heteroaryl-(C_1-C_6)heteroalkylene. Preferably, any (C_2-C_{18})heterocycloalkyl independently is unsubstituted or substituted (C_2-C_9)heterocycloalkyl.

[0019] Examples of (C_1-C_{40})heteroalkyl and (C_1-C_{20})heteroalkylene are saturated straight or branched chain radical or diradical, respectively, of from 1 to 40 or 1 to 20 carbon atoms, respectively, and one or more of the heteroatoms $Si(R^C)_2$, $P(R^P)$, $N(R^N)$, N, O, S, S(O), and $S(O)_2$ as defined above, wherein the $(C_1\text{-}C_{40})$heteroalkyl and $(C_1\text{-}C_{20})$heteroalkylene independently are unsubstituted or substituted by one or more R^S.

[0020] Examples of unsubstituted $(C_2\text{-}C_{40})$heterocycloalkyl are unsubstituted $(C_2\text{-}C_{20})$heterocycloalkyl, unsubstituted $(C_2\text{-}C_{10})$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-thia-cyclononyl, and 2-aza-cyclodecyl.

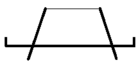
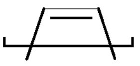
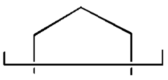
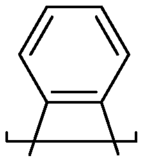
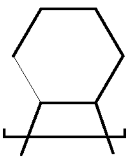
[0021] Examples of unsubstituted $(C_1\text{-}C_{40})$heteroaryl are unsubstituted $(C_1\text{-}C_{20})$heteroaryl, unsubstituted $(C_1\text{-}C_{10})$heteroaryl, pyrrol-1-yl; pyrrol-2-yl; furan-3-yl; thiophen-2-yl; pyrazol-1-yl; isoxazol-2-yl; isothiazol-5-yl; imidazol-2-yl; oxazol-4-yl; thiazol-2-yl; 1,2,4-triazol-1-yl; 1,3,4-oxadiazol-2-yl; 1,3,4-thiadiazol-2-yl; tetrazol-1-yl; tetrazol-2-yl; tetrazol-5-yl; pyridine-2-yl; pyrimidin-2-yl; pyrazin-2-yl; indol-1-yl; benzimidazole-1-yl; quinolin-2-yl; and isoquinolin-1-yl.

[0022] The terms "halogen" and "halogen atom" mean a fluoro (F), chloro (Cl), bromo (Br), or iodo (I) radical. Preferably, halogen or halogen atom is fluoro or chloro, more preferably fluoro.

[0023] Preferably, in the metal-ligand complex of formula (I), there are no O—O, S—S, or O—S bonds, other than O—S bonds in an S(O) or $S(O)_2$ diradical functional group.

[0024] Preferably, in the metal-ligand complex of formula (I), M is Ti, Zr, or Hf.

[0025] In some embodiments of the metal-ligand complex of formula (I), one of R^1 and R^2 and one of R^3 and R^4 are taken together to form

 ,  ,  ,  , or  .

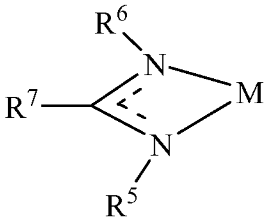
[0026] In some embodiments of formula (I), two occurrences of L are taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, or $(R^D)_2C{=}C(R^D)\text{-}C(R^D){=}C(R^D)_2$, wherein each R^D independently is H, unsubstituted $(C_1\text{-}C_6)$alkyl, phenyl, or naphthyl.

[0027] In some embodiments of formula (I), J and one of R^1, R^2, R^3, and R^4 are taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene.

[0028] In some embodiments of formula (I), one occurrence of L and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene.

[0029] In some embodiments of formula (I), one occurrence of X and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_1\text{-}C_{40})$heterohydrocarbylene.

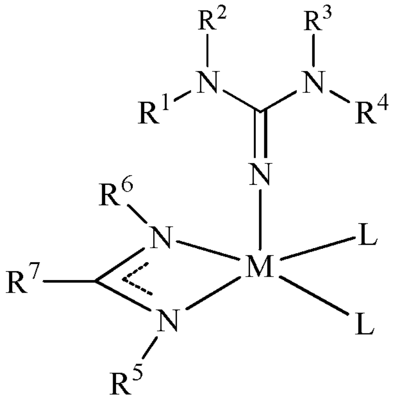
[0030] In some embodiments of formula (I), X and J are taken together to form a monoanionic bidentate moiety X-J, provided that when X-J is bound to M to form a fragment having the structure



,

then R^5, R^6, and R^7 are each independently hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})$hydrocarbyl)O-, $((C_1\text{-}C_{40})$hydrocarbyl)S-, $((C_1\text{-}C_{40})$hydrocarbyl$)_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-. In these embodiments, X-J can be bound to one of R^1, R^2, R^3, or R^4 via one of R^5, R^6, or R^7. Thus, one of R^1, R^2, R^3, R^4 is optionally taken together with one of R^5, R^6, and R^7 to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene. Also, when X and J are taken together to form the monoanionic bidentate moiety X-J, and X-J is bound to M via an anionic nitrogen and a Lewis base nitrogen, then X-J and M form a four-membered metallocycle (for example, that shown above in this paragraph) or a six-membered metallocycle (not a five-membered metallocycle).

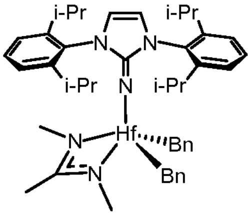
[0031] In some embodiments, the metal-ligand complex has formula (II)

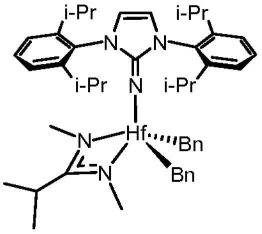


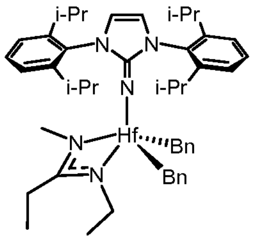
(II)

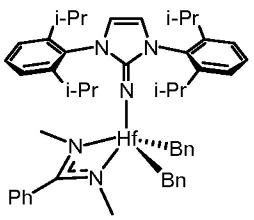
wherein L, M, R^1, R^2, R^3, and R^4 are as defined as for formula (I); R^5, R^6, and R^7 are each independently hydrogen, (C_1-C_{40})hydrocarbyl-, $((C_1-C_{40})$hydrocarbyl)O-, $((C_1-C_{40})$hydrocarbyl)S-, $((C_1-C_{40})$hydrocarbyl$)_3$Si-, or (C_1-C_{40})heterohydrocarbyl-; one occurrence of L and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene; any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene; one of R^5, R^6, and R^7 is optionally taken together with one of R^1, R^2, R^3, R^4, and L to form a (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene; and the two occurrences of L are optionally taken together to form a (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene, or $(R^D)_2C=C(R^D)-C(R^D)=C(R^D)_2$, wherein each R^D independently is H, unsubstituted (C_1-C_6)alkyl, phenyl, or naphthyl.

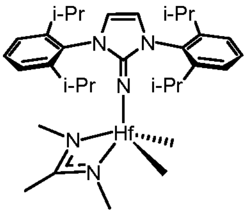
[0032] Specific examples of metal-ligand complexes of formula (II) include

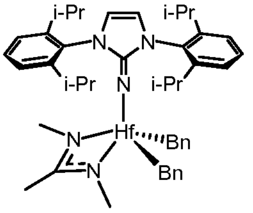


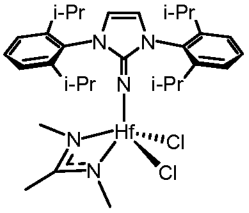


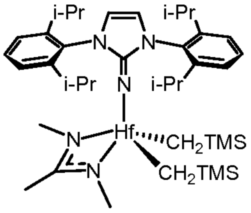


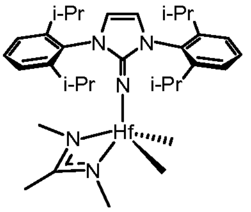


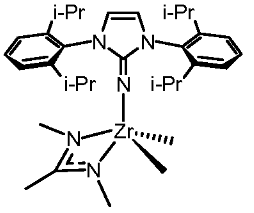


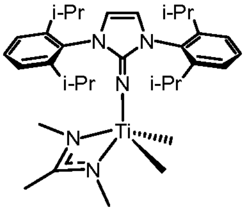


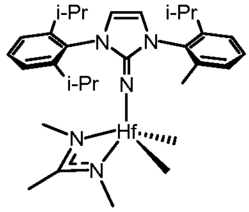


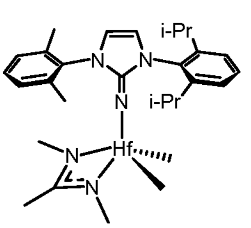


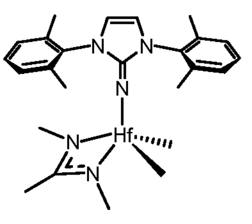


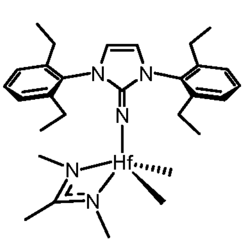


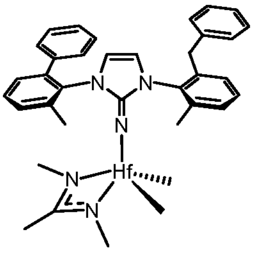


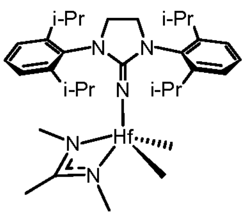


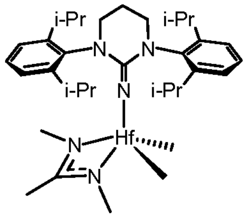


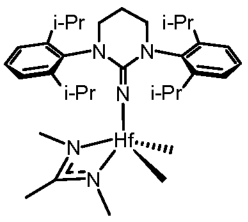


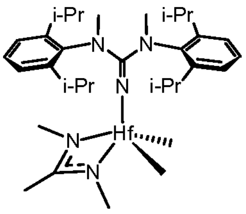


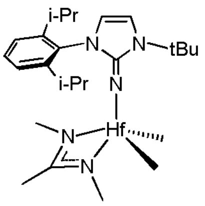


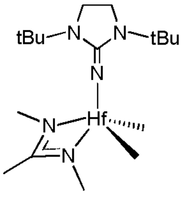


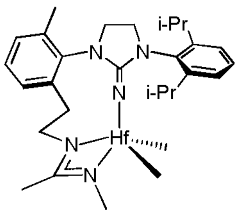


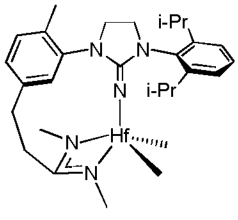


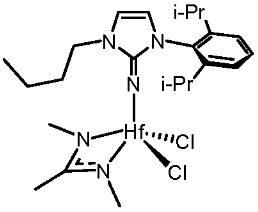


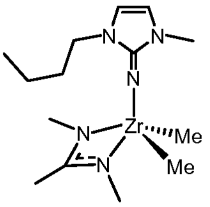


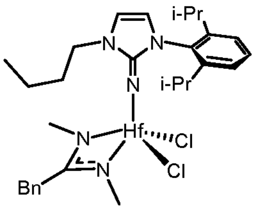


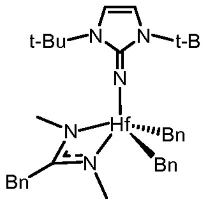


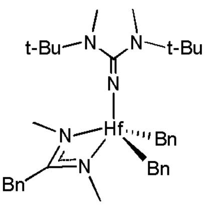


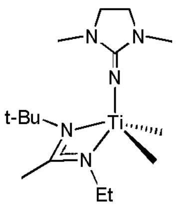


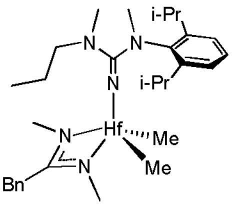






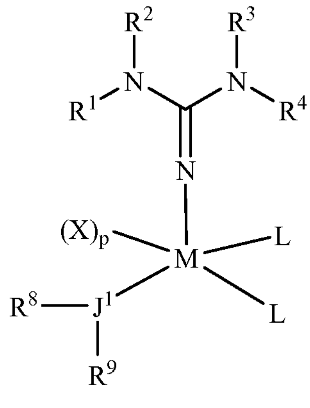






and combinations thereof, wherein Bn is benzyl, Et is ethyl, iPr is isopropyl, t-Bu is t-butyl, and TMS is trimethylsilyl.

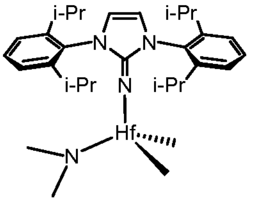
[0033] In some embodiments, the metal-ligand complex has formula (III)

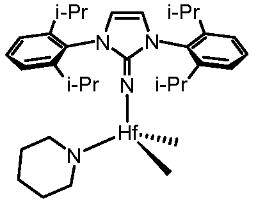


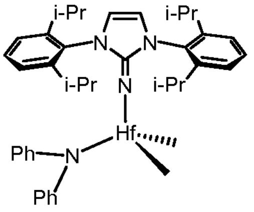
(III)

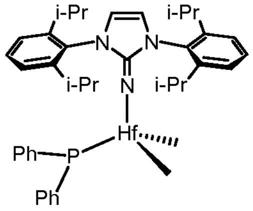
wherein L, M, p, R^1, R^2, R^3, R^4, and X are defined as for formula (I); J^1 is N or P; R^8 and R^9 are each independently hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})$hydrocarbyl)O-, $((C_1\text{-}C_{40})$hydrocarbyl)S-, $((C_1\text{-}C_{40})\text{hydrocarbyl})_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-; one occurrence of L and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; the two occurrences of L are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, or $(R^D)_2C{=}C(R^D)\text{-}C(R^D){=}C(R^D)_2$, wherein each R^D independently is H, unsubstituted $(C_1\text{-}C_6)$alkyl, phenyl, or naphthyl; any two of R^1, R^2, R^3, and R^4 optionally are taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; R^8 and R^9 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; R^8 and R^9 are optionally taken together to form a group double bonded to J^1; one of R^8 and R^9 is optionally taken together with one of R^1, R^2, R^3, R^4, and L to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; one of R^8 and R^9 is optionally covalently bonded to X; and X and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_1\text{-}C_{40})$heterohydrocarbylene.

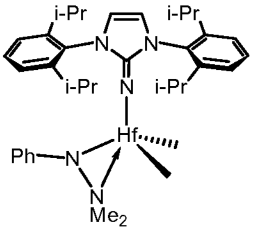
[0034] Specific examples of metal-ligand complexes of formula (III) include

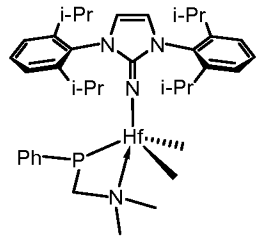


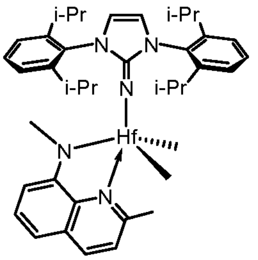


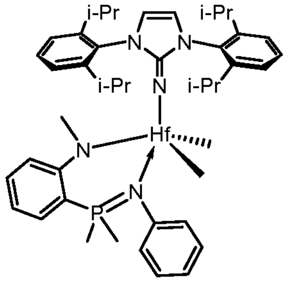


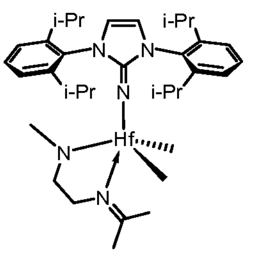


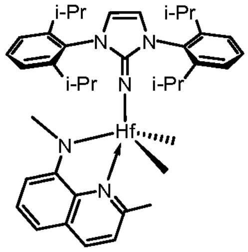


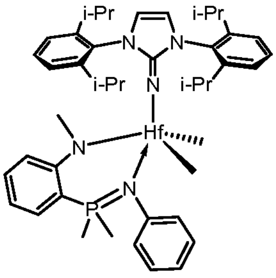


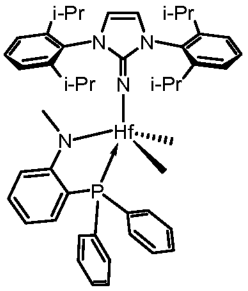


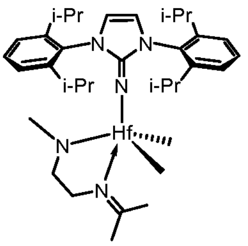


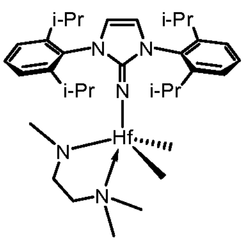


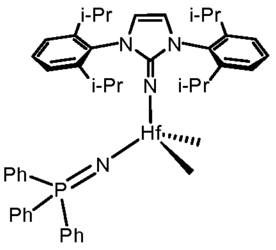


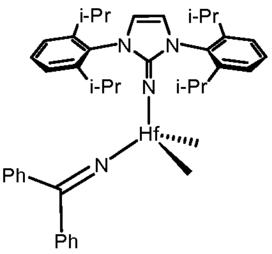


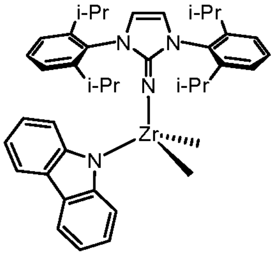


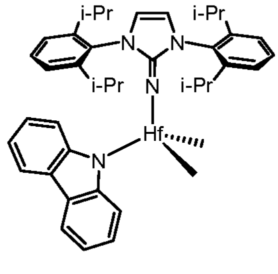


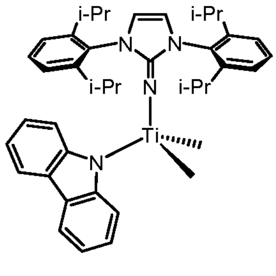


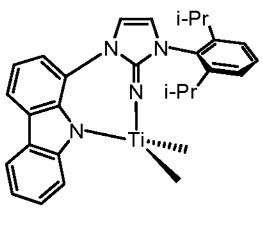


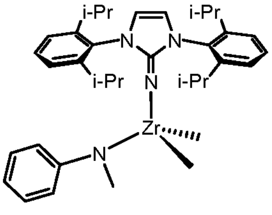


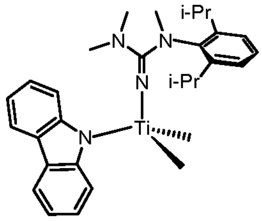


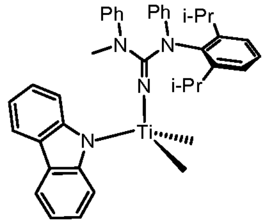


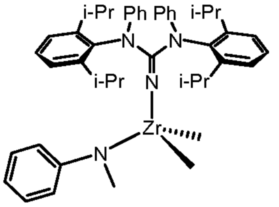






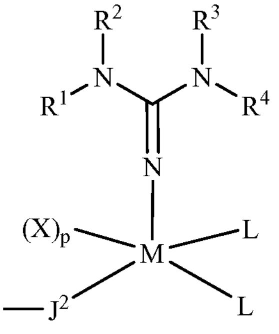






and combinations thereof.

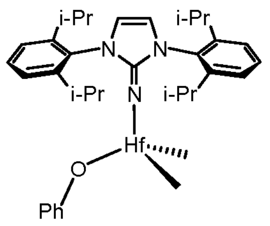
[0035] In some embodiments, the metal-ligand complex has formula (IV)

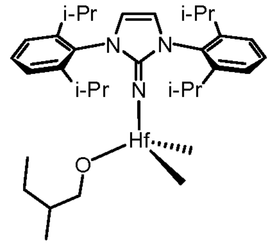


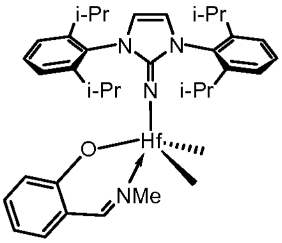
(IV)

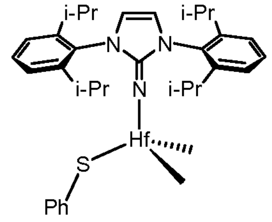
wherein L, M, p, R^1, R^2, R^3, R^4, and X are as defined as for formula (I); J^2 is O or S; and R^{10} is $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})\text{hydrocarbyl})_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-; one occurrence of L and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; any two of R^1, R^2, R^3, and R^4 optionally are taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; X and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_1\text{-}C_{40})$heterohydrocarbylene; and R^{10} is optionally taken together with one of R^1, R^2, R^3, R^4, and L to form a $(C_1\text{-}C_{40})$heterohydrocarbylene; and R^{10} is optionally covalently bonded to X.

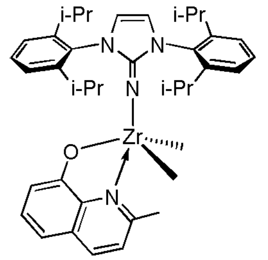
[0036] Specific examples of metal-ligand complexes of formula (IV) include

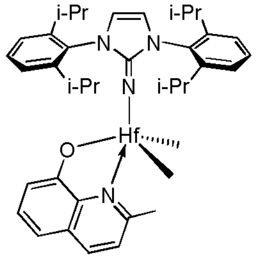


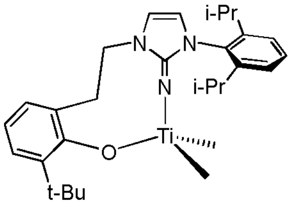


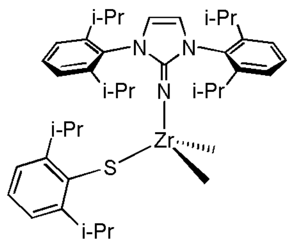


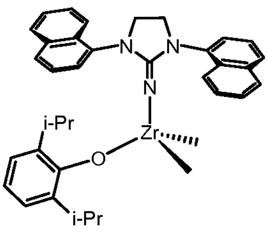


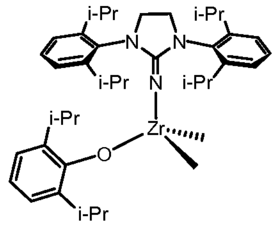


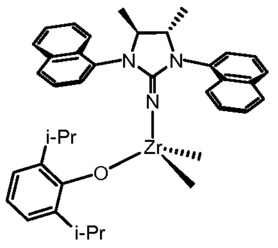


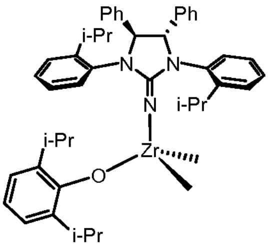


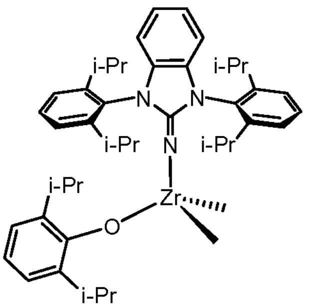






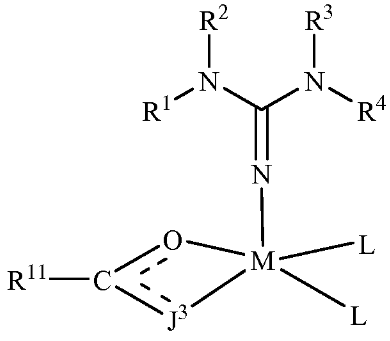






and combinations thereof.

[0037] In some embodiments, the metal-ligand complex has formula (V)

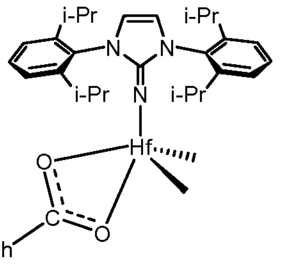


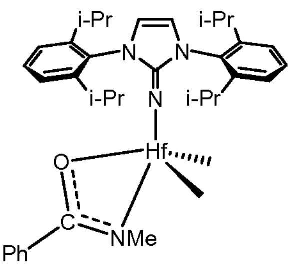
(V)

wherein L, M, R^1, R^2, R^3, and R^4 are as defined for formula (I); J^3 is O or NR^{12}; R^{11} and R^{12} are each independently hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})$hydrocarbyl)O-, $((C_1\text{-}C_{40})$hydrocarbyl)S-, $((C_1\text{-}C_{40})\text{hydrocarbyl})_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-; R^{11}

and R^{12} are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; one of R^{11} and R^{12} is optionally taken together with one of R^1, R^2, R^3, R^4, and L to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; two occurrences of L are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, or $(R^D)_2C{=}C(R^D)\text{-}C(R^D){=}C(R^D)_2$, wherein each R^D independently is H, unsubstituted $(C_1\text{-}C_6)$alkyl, phenyl, or naphthyl; one occurrence of L and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; and any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene.

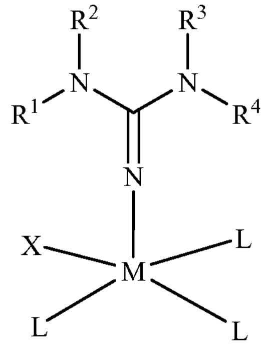
[0038] Specific examples of metal-ligand complexes of formula (V) include





and combinations thereof.

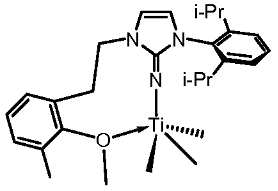
[0039] In some embodiments, the metal-ligand complex has formula (VI)

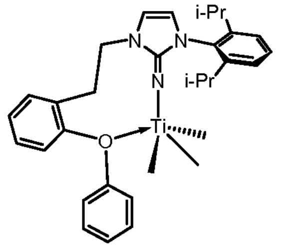


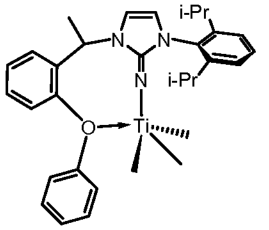
(VI)

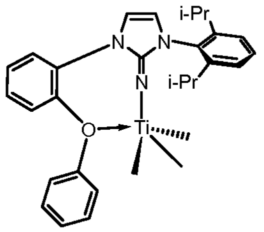
wherein L, M, R^1, R^2, R^3, R^4, and X are as defined for formula (I); two occurrences of L are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, or $(R^D)_2C{=}C(R^D)\text{-}C(R^D){=}C(R^D)_2$, wherein each R^D independently is H, unsubstituted $(C_1\text{-}C_6)$alkyl, phenyl, or naphthyl; one occurrence of L and one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; X and one of R^1, R^2, R^3, and R^4 are optionally taken together to form (C_1-C_{40})heterohydrocarbylene; and any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene.

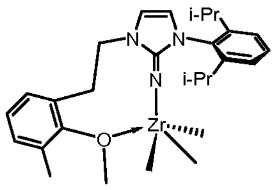
[0040] Specific examples of metal-ligand complexes of formula (VI) include

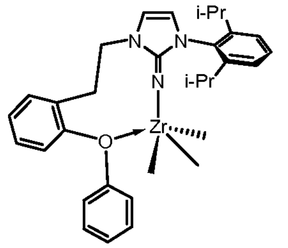


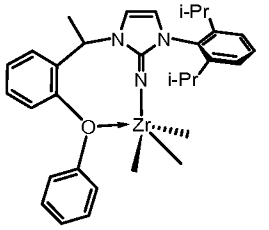


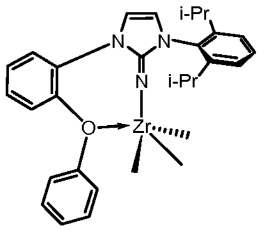


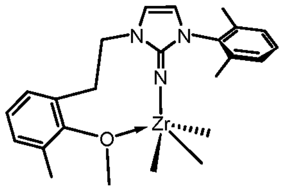


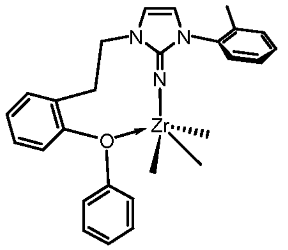


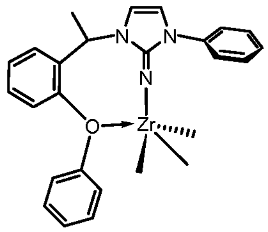


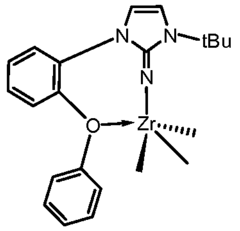


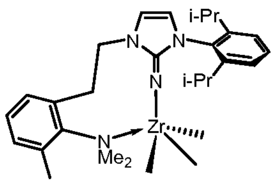


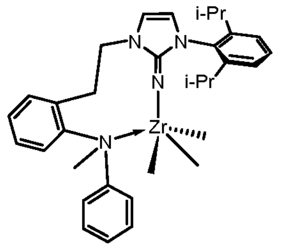


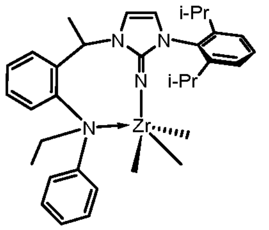


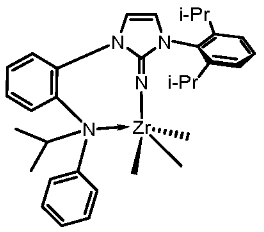


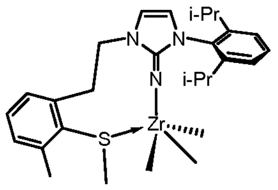


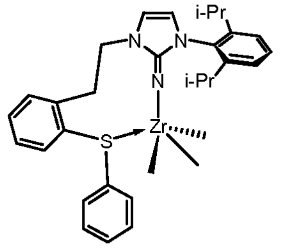


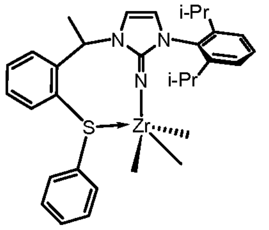


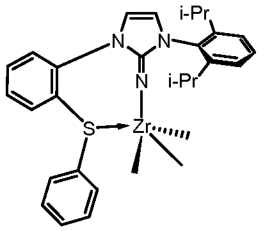


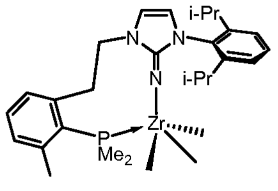


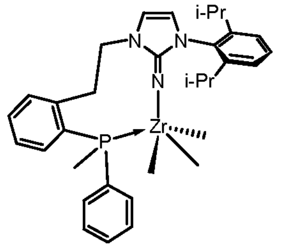


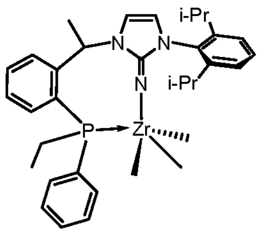


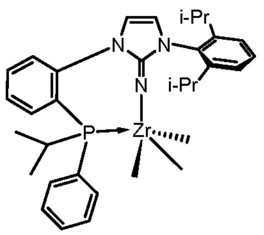


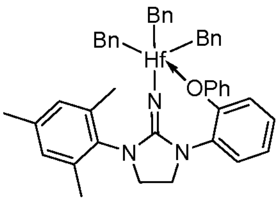






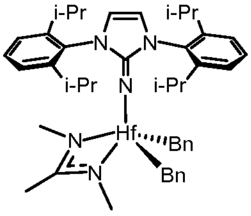


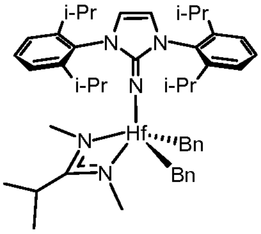


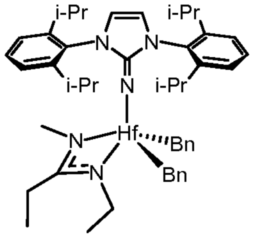


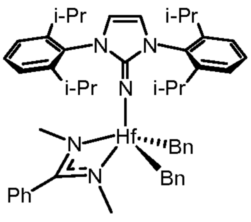
or a combination thereof.

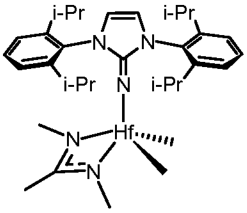
[0041] In some embodiments, the metal-ligand complex comprises

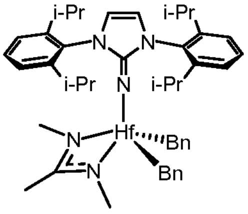


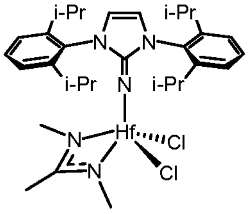


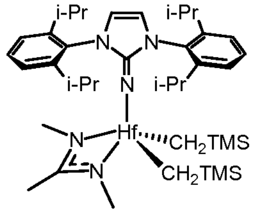


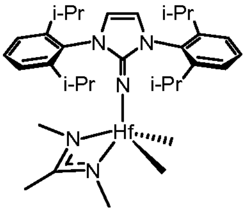


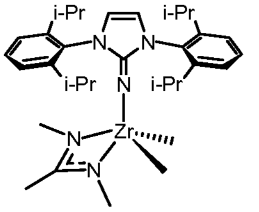


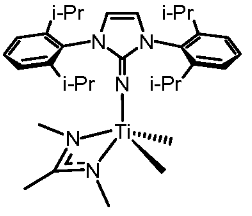


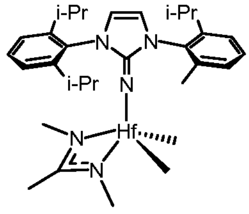


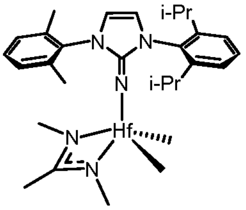


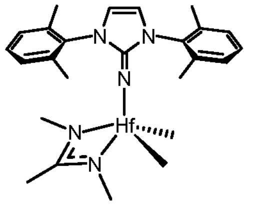


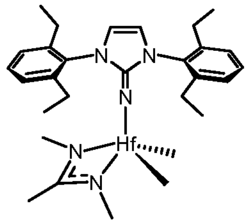


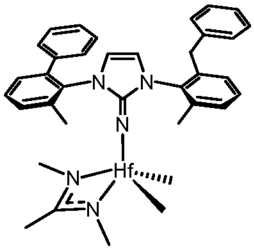


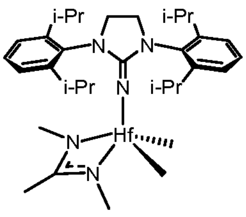


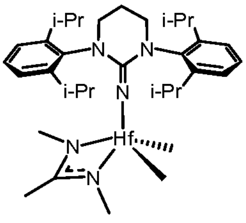


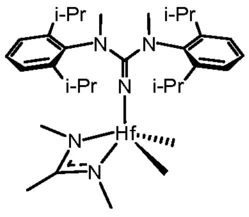


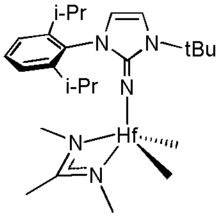


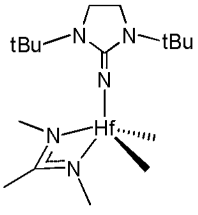


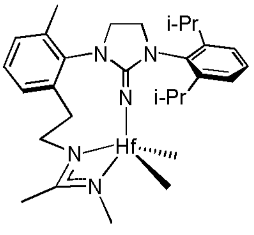


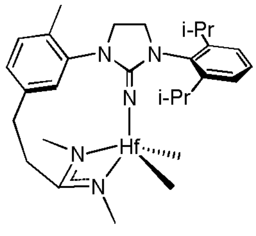


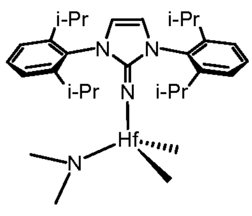








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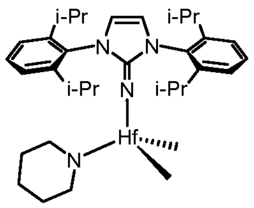
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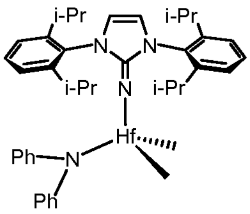
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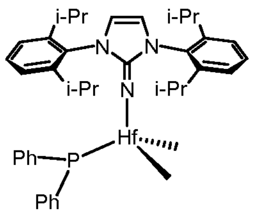
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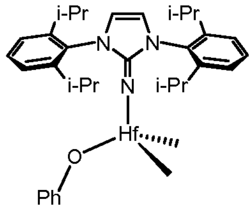
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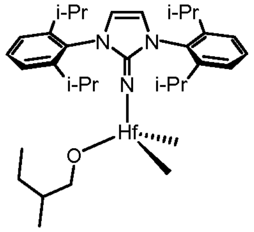
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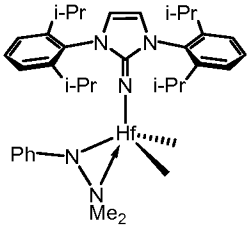
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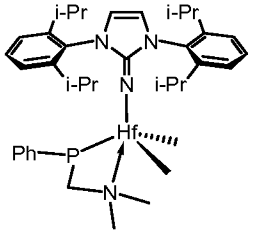
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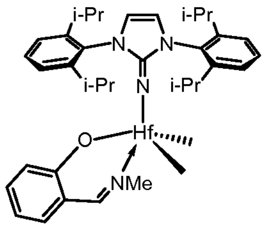
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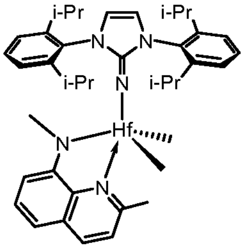
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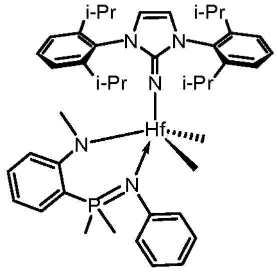
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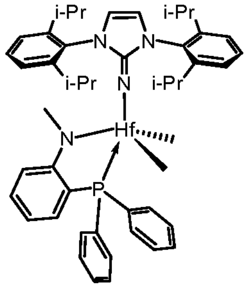
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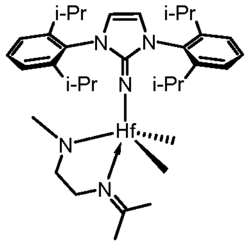
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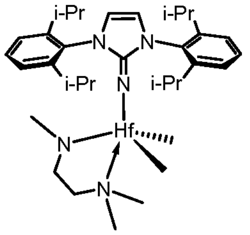
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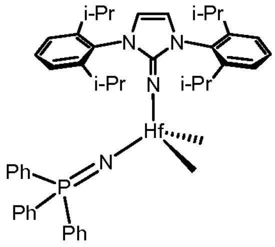
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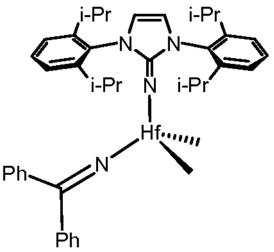
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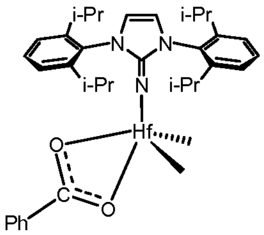
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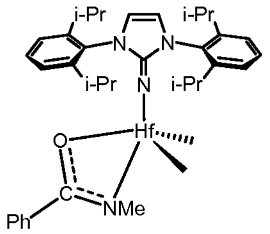
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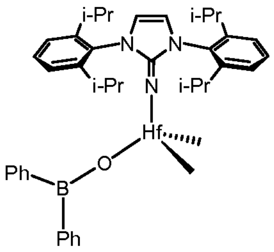
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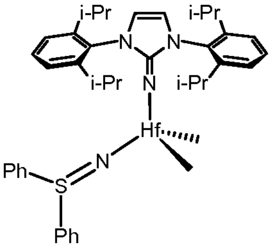
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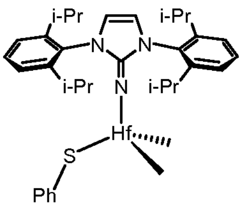
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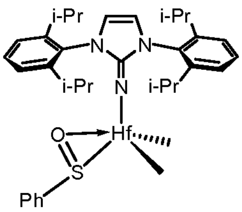
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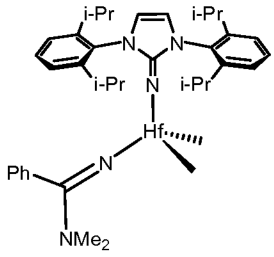
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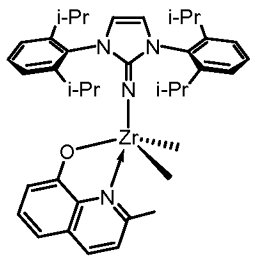
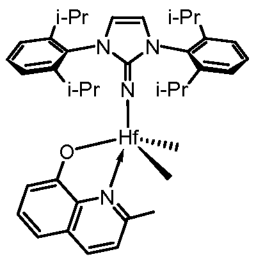
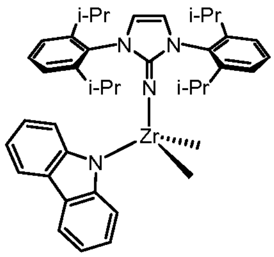
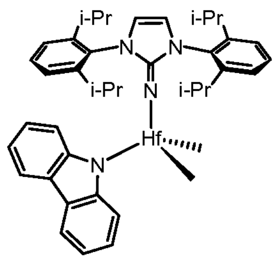
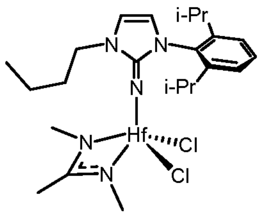
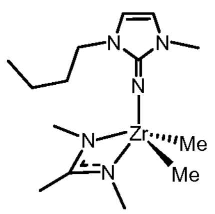
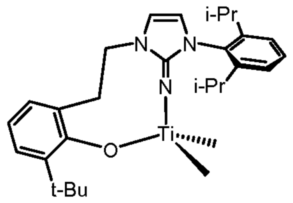
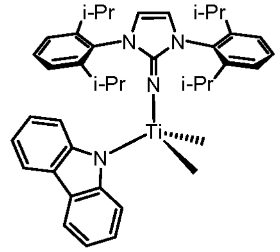
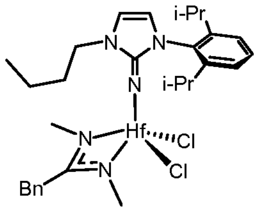
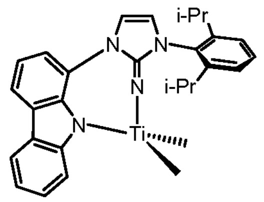
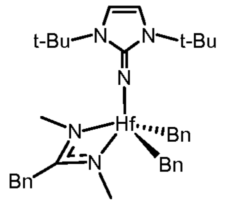
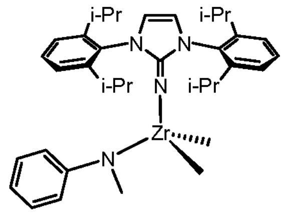
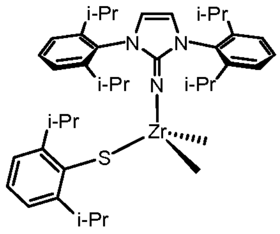
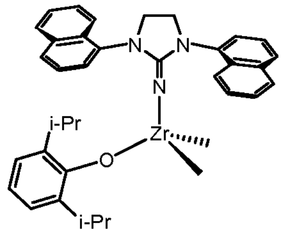
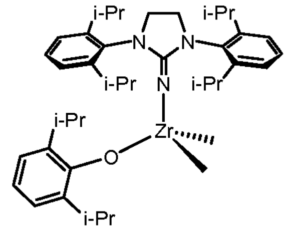
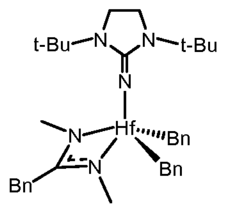
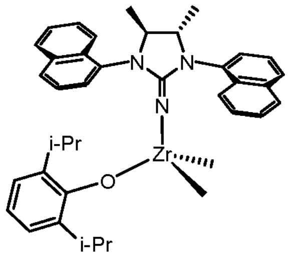
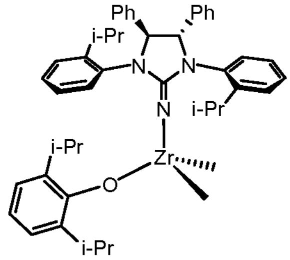
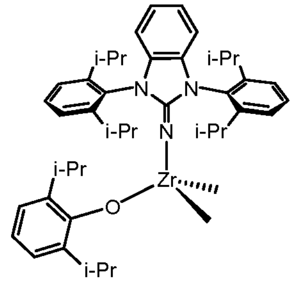
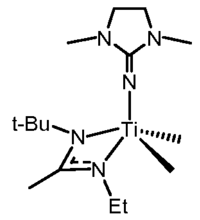
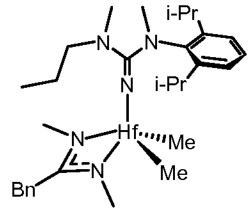
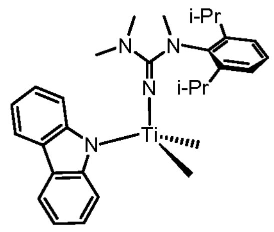
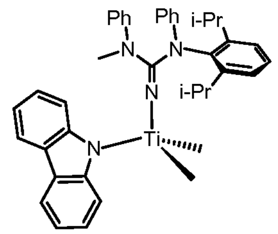
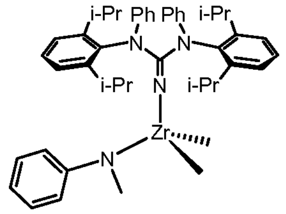
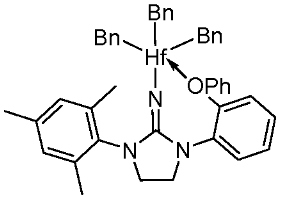


























or a combination thereof.

[0042] The invention includes a catalyst comprising, or comprising the reaction product of, one or more metal-ligand complexes of any of formulae (I), (II), (III), (IV), (V), and (VI), and one or more activating cocatalysts, wherein a ratio of total number of moles of the one or more metal-ligand complexes to total number of moles of the one or more activating cocatalysts is 1:10,000 to 100:1.

[0043] The invention further includes a process for preparing a polyolefin, the process comprising contacting at least one polymerizable olefin with the catalyst of the previous paragraph under conditions sufficient to polymerize at least some of the at least one polymerizable olefin, thereby producing a polyolefin.

[0044] The term "polymerizable olefin" means a carbon-carbon double or triple bond-containing monomer or carbon-carbon double or triple bond-containing oligomer or polyolefin prepared therefrom and independently has from 2 to 100,000 carbon atoms, preferably 50,000 carbon atoms or less, more preferably 10,000 carbon atoms or less. Preferably there is at least one carbon-carbon double bond in the polymerizable olefin, and more preferably the polymerizable olefin is a carbon-carbon double bond-containing monomer. Thus, polymerizable olefins include long chain macromolecular alpha-olefin units that are vinyl terminated polymeric remnants formed in situ during polymerization reactions. In some aspects of the polymer-forming process, such long chain macromolecular alpha-olefin units are readily polymerized along with ethylene and other short chain olefin monomers to give a polyolefin having long chain branching.

[0045] Preferably, the polyolefin prepared by the process is an ethylene homopolymer, an ethylene/alpha-olefin interpolymer (e.g., copolymer), or an ethylene/alpha-olefin/diene interpolymer (e.g., terpolymer). In some embodiments, the polyolefin is a copolymer of ethylene and 1-octene.

[0046] In some embodiments, the polyolefin-forming process further employs another polymerizable olefin (i.e., an olefin comonomer) so as to employ both an olefin monomer and olefin comonomer, a chain shuttling agent, and an associated olefin polymerization catalyst (which may be an invention catalyst, or a non-invention catalyst described later), the preferred process giving the polyolefin wherein the polyolefin comprises a poly(olefin monomer-olefin comonomer) interpolymer (e.g., copolymer), more preferably a poly(olefin monomer-olefin comonomer) block copolymer (i.e., an OBC), and in some embodiments a poly(ethylene/alpha-olefin) block copolymer. The poly(ethylene/alpha-olefin) block copolymer preferably comprises an ethylene-derived hard segment and a soft segment comprising residuals from the alpha-olefin and ethylene. The term “poly(ethylene/alpha-olefin) block copolymer” is used interchangeably herein with the terms “olefin block copolymer,” “OBC,” “ethylene/α-olefin block interpolymer,” and “ethylene/α-olefin block copolymer”. The terms “alpha-olefin” and “α-olefin” are used interchangeably herein.

[0047] Preferably, the polyolefin-forming process employs a solvent. The term “solvent” means a liquid, preferably aprotic, that is compatible with the polyolefin-forming process. Suitable solvents include aliphatic and aromatic hydrocarbons, ethers, and cyclic ethers, particularly branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; benzene and (C_1-C_5)alkyl-substituted benzenes such as toluene and xylenes; (C_1-C_5)alkyl-O-(C_1-C_5)alkyl; (C_4-C_5)heterocycloalkyl such as tetrahydrofuran, tetrahydropyran, and 1,4-dioxane; (C_1-C_5)alkyl ethers of (poly)alkylene glycols; and mixtures of the foregoing. In these embodiments, the catalyst preferably comprises a homogeneous catalyst.

[0048] In some embodiments, the catalyst further comprises, or is further prepared from, an inorganic or organic particulated solid support, wherein the catalyst is in supporting operative contact with the particulated solid support to give a particulated solid-supported catalyst. In these embodiments, the invention particulated solid-supported catalyst comprises a heterogeneous catalyst.

[0049] The particulated solid support is any material that is capable of supporting the catalyst and allows the resulting invention particulated solid-supported catalyst to catalyze polymerization of a polymerizable olefin. Examples of particulated solids are silica, alumina, clays, expanded clays (aerogels), aluminosilicates, trialkylaluminum compounds, and organic or inorganic polymeric materials, especially polyolefins such as, for example, a poly(tetrafluoroethylene). More preferably, the catalyst and solid support are employed in the invention particulated solid-supported catalyst in amounts that provide a ratio of (weight of the catalyst based on metal M) : (weight of the solid support) of from $1:10^6$ to $1:10^3$, more preferably from $1:10^6$ to $1:10^4$.

[0050] The metal-ligand complexes of formula (I) are rendered catalytically active by contacting them to, or combining them with, an activating cocatalyst or by using an activating technique such as those that are known in the art for use with metal (e.g., Group 4) olefin polymerization reactions. The present invention contemplates replacing one or more of the activating cocatalysts with the activating technique, although use of activating cocatalysts is preferred. Suitable activating cocatalysts 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 cocatalysts 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. Aluminoxanes and their preparations are known at, for example, U.S. Pat. No. 6,103,657. Examples of preferred polymeric or oligomeric alumoxanes are methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

[0051] Preferred Lewis acid activating cocatalysts are Group 13 metal compounds containing from 1 to 3 hydrocarbyl substituents as described herein. More preferred Group 13 metal compounds are tri(hydrocarbyl)-substituted-aluminum or tri(hydrocarbyl)-boron compounds, still more preferred are tri((C_1-C_{10})alkyl)aluminum or tri((C_6-C_{18})aryl)boron compounds and halogenated (including perhalogenated) derivatives thereof, even more especially tris(fluoro-substituted phenyl)boranes, still even more especially tris(pentafluorophenyl)borane.

[0052] Preferred combinations of neutral Lewis acid activating cocatalysts include mixtures comprising a combination of a tri((C_1-C_4)alkyl)aluminum and a halogenated tri((C_6-C_{18})aryl)boron compound, especially a tris(pentafluorophenyl)borane. Also preferred 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. Preferred ratios of numbers of moles of (metal-ligand complex):(tris(pentafluorophenyl)borane): (alumoxane) [e.g., (Group 4 metal-ligand complex):(tris(pentafluorophenyl)borane):(alumoxane)] are from 1:1:1 to 1:10:30, more preferably from 1:1:1.5 to 1:5:10.

[0053] Many activating cocatalysts and activating techniques have been previously taught with respect to different metal-ligand complexes in the following U.S. Pat. No. 5,064,802; U.S. Pat. No. 5,153,157; U.S. Pat. No. 5,296,433; U.S. Pat. No. 5,321,106; U.S. Pat. No. 5,350,723; U.S. Pat. No. 5,425,872; U.S. Pat. No. 5,625,087; U.S. Pat. No. 5,721,185; U.S. Pat. No. 5,783,512; U.S. Pat. No. 5,883,204; U.S. Pat. No. 5,919,983; U.S. Pat. No. 6,696,379; and U.S. Pat. No. 7,163,907. Examples of suitable hydrocarbyloxides are disclosed in U.S. Pat. No. 5,296,433. Examples of suitable Bronsted acid salts for addition to polymerization catalysts are disclosed in U.S. Pat. No. 5,064,802; U.S. Pat. No. 5,919,983; U.S. Pat. No. 5,783,512. Examples of suitable salts of a cationic oxidizing agent and a non-coordinating, compatible anion as activating cocatalysts for addition polymerization catalysts are disclosed in U.S. Pat. No. 5,321,106. Examples of suitable carbenium salts as activating cocatalysts for addition polymerization catalysts are disclosed in U.S. Pat. No. 5,350,723. Examples of suitable silylium salts as activating cocatalysts for addition polymerization catalysts are disclosed in U.S. Pat. No. 5,625,087. Examples of suitable complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are disclosed in U.S. Pat. No. 5,296,433. Some of these catalysts are also described in U.S. Pat. No. 6,515,155 B1.

[0054] In some embodiments, one or more of the foregoing activating cocatalysts are used in combination with each other. An especially preferred combination is a mixture of a tri((C_1-C_4)hydrocarbyl)aluminum, tri((C_1-C_4)hydrocarbyl)borane, or an ammonium borate with an oligomeric or polymeric alumoxane compound.

[0055] 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 activating cocatalyst is from 1:10,000 to 100:1. Preferably, the ratio is at least 1:5000, more preferably at least 1:1000; and 10:1 or less, more preferably 1:1 or less. When an alumoxane alone is used as an activating cocatalyst, preferably the number of moles of the alumoxane that are employed is at least 5 times the number of moles of the metal-ligand complex of formula (I). When tris(pentafluorophenyl)borane alone is used as an activating cocatalyst, preferably the ratio of 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) is 0.5:1 to 10:1, more preferably from 1:1 to 6:1, still more preferably from 1:1 to 5:1. The remaining activating cocatalysts are generally employed in approximately mole quantities equal to the total mole quantities of one or more metal-ligand complexes of formula (I).

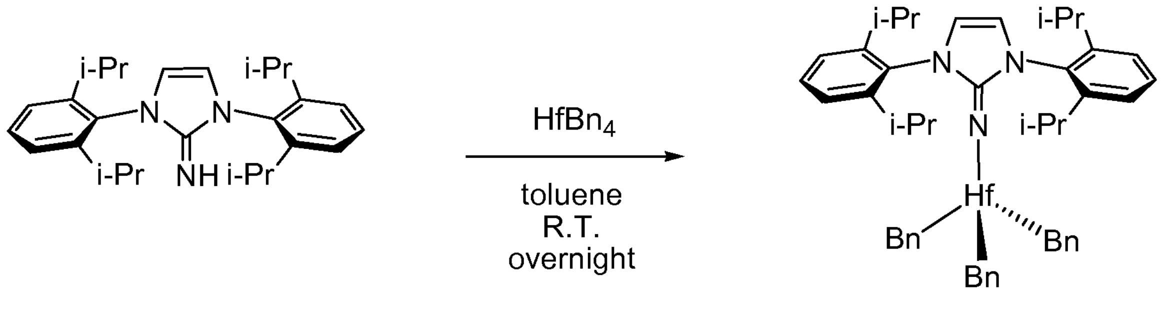
[0056] In some embodiments, a reducing agent is also employed so as to produce lower oxidation state forms (e.g., +2) of the metal-ligand complexes of formula (I) from higher oxidation state forms (e.g., +4) of the metal-ligand complexes of formula (I). As used herein, the term "reducing agent" means a metal-containing substance or compound, organic reductant, or technique (e.g., electrolysis) which, under reducing conditions, causes the metal, M, to be reduced from a higher to a lower oxidation state (e.g., from a +6 formal oxidation state to a +4 formal oxidation state). Examples of suitable reducing agents are alkali metals, alkaline earth metals, aluminum and zinc, and alloys of alkali metals or alkaline earth metals such as sodium/mercury amalgam and sodium/potassium alloy. Examples of other suitable reducing agents are sodium naphthalenide, potassium graphite, lithium alkyls, lithium or potassium alkadienyls, and Grignard reagents (e.g., alkyl magnesium halides). Most preferred reducing agents are the alkali metals or alkaline earth metals, especially lithium and magnesium metal. Suitable techniques that may be adapted by an ordinarily skilled artisan for preparing the metal-ligand complexes of the present invention are known and preferably are derived from techniques taught, for example, in U.S. Pat. No. 5,866,704; U.S. Pat. No. 5,959,047; and U.S. Pat. No. 6,268,444.

[0057] The term “olefin-polymerizing conditions” means reaction parameters such as, for example, temperature, pressure, concentration of olefin monomer(s), solvent(s), if any, reaction time, and reaction atmosphere sufficient to produce at least 5 mole percent yield of a polyolefin. In some embodiments, polymerization of olefins is accomplished using known conditions for Ziegler-Natta or Kaminsky-Sinn type olefin polymerization reactions. The process occurs under olefin-polymerizing conditions sufficient to polymerize at least some of the at least one polymerizable olefin and produce a polyolefin therefrom. The process can be performed at or with any temperature, pressure, or other condition (e.g., solvent, atmosphere, and absolute and relative amounts of ingredients) at which the polymerization reaction occurs. Preferably the conditions comprise a temperature of about -100° C to about 300° C. Within this range, the temperature is preferably at least about 0° C, more preferably at least about 20° C, still more preferably at least about 50° C. Also within this range, the temperature is preferably about 250° C or less, more preferably about 200° C or less, still more preferably about 150° C or less. Preferably the conditions include a pressure of about 0.5 atmosphere (50 kilopascals (kPa)) to 10,000 atmospheres (1,010,000 kPa). Within this range, the pressure is preferably at least about 1 atmosphere (101 kPa), more preferably at least about 10 atmospheres (1010 kPa). Also within this range, the pressure is preferably 1000 atmospheres (101,000 kPa) or less, more preferably 500 atmospheres (50,500 kPa) or less. The conditions preferably include a substantially inert atmosphere (e.g., a dry (i.e., substantially free from water) atmosphere consisting essentially of nitrogen gas, a noble gas (e.g., argon gas and helium gas), or a mixture of two or more thereof), with mixing (e.g., agitating, stirring, or shaking) for a time sufficient to produce the polyolefin (e.g., as determined by assaying an aliquot of a reaction mixture).

[0058] In some embodiments, the polymer-forming process employs one or more of the inventive catalysts and at least one additional homogeneous or heterogeneous polymerization catalyst, which may be a same or different inventive catalyst or a prior art olefin polymerization catalyst such as that referenced previously, either in the same reactor or in separate reactors, preferably connected in series or in parallel, to prepare polymer blends having desirable properties. A general description of such a process is disclosed in PCT International Patent Application Publication Number WO 94/00500.

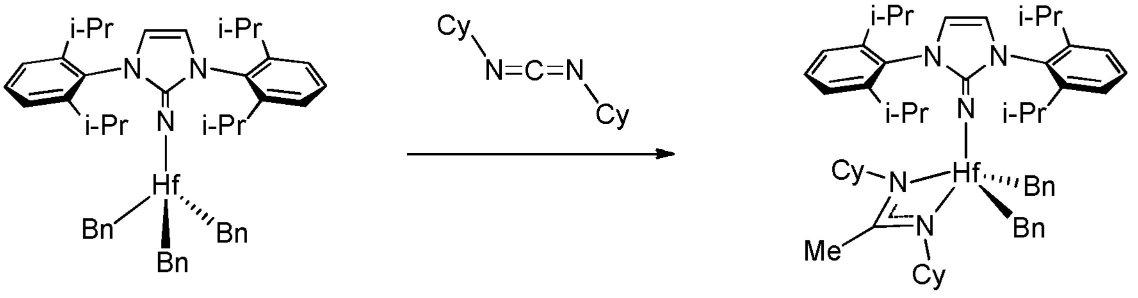
[0059] Polyolefins prepared by the process are useful, among other things, as synthetic lubricants (synthetic motor oils) and as materials for use in manufacturing foams, films, coatings, fibers, fabrics, extruded articles, and molded articles.

EXAMPLES



Complex **1**

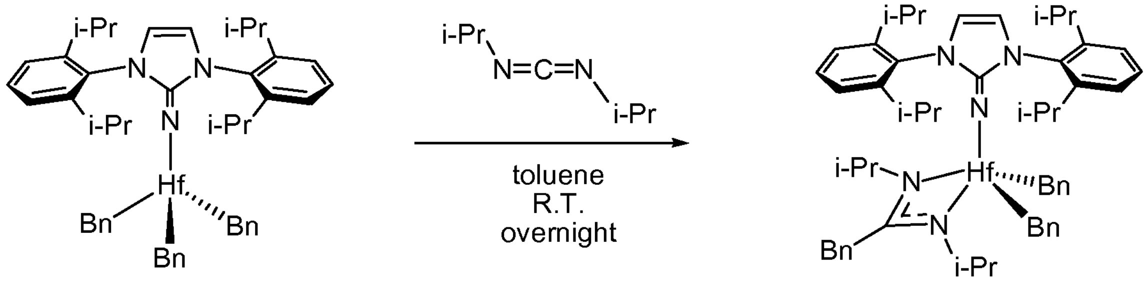
[0060] **Preparation of Complex 1**. In a glovebox under a nitrogen atmosphere, a glass jar was charged with a magnetic stirbar, $HfBn_4$ (0.600 g, 1.11 mmol) and toluene (10 mL). The resulting solution was cooled to -40 °C, and then 1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-2(3H)-imine (0.446 g, 1.11 mmol) was added to the cold solution. The resulting solution was allowed warm to room temperature, and stirred overnight. The solvent volume was reduced to about 5 mL. Hexane (5 mL) was then added to the solution, which was cooled to -40 °C. After 1 day, crystals were collected and dried, providing the desired species in high purity (0.91 g, 97%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.25 (dd, J = 8.5, 6.9 Hz, 2H), 7.18 – 7.12 (m, 4H), 7.06 (t, J = 7.6 Hz, 6H), 6.89 (m, 3H), 6.38 (dd, J = 7.6, 1.3 Hz, 6H), 5.95 (s, 2H), 3.13 (sp, J = 6.9 Hz, 4H), 1.40 (d, J = 6.9 Hz, 12H), 1.21 (s, 6H), 1.15 (d, J = 6.9 Hz, 12H).



Complex **1**

Complex **2**

[0061] **Preparation of Complex 2**. Complex **1** (0.500 g, 0.585 mmol) and N,N′-dicyclohexylcarbodiimide (0.121 g, 0.585 mmol) were combined in a small vial. Toluene (10 mL) was added and the reaction was allowed to stir overnight. The reaction mixture was concentrated and hexane was added until approximately a 1:2 ratio (toluene:hexane) was reached and the vial was placed in the freezer to induce crystallization. The resulting off white solid was isolated by filtration yielding the desired compound (0.148 g, 22 %). ^{1}H NMR (400 MHz, C_6D_6) δ 7.27 – 7.19 (m, 6H), 7.17-7.15 (m, 6H), 7.14 – 7.07 (m, 2H), 7.07 – 6.97 (m, 5H), 6.90 (tt, *J* = 7.3, 1.3 Hz, 2H), 5.96 (s, 2H), 3.52 (s, 2H), 3.31 (p, *J* = 6.8 Hz, 4H), 2.81 (td, *J* = 10.8, 5.3 Hz, 2H), 2.26 (d, *J* = 10.8 Hz, 2H), 1.88 (d, *J* = 10.8 Hz, 2H), 1.54 – 1.46 (m, 4H), 1.43 (d, *J* = 6.8 Hz, 12H), 1.30 – 1.21 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 12H), 1.11 – 0.82 (m, 14H).

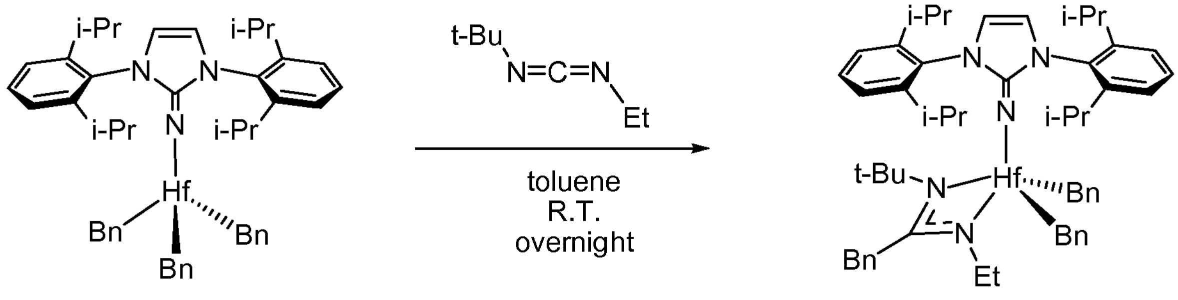


Complex **1**

Complex **3**

[0062] **Preparation of Complex 3**. In a glovebox under a nitrogen atmosphere, a glass jar was charged with a magnetic stirbar, complex **1** (0.505 g, 0.591 mmol) and toluene (10 mL). The resulting solution was cooled to -40 °C, and then 1,3-diisopropyl-carbodiimide (0.097 mL, 0.621 mmol) was added to the cold solution. The resulting solution was stirred and allowed warm to room temperature. After 1 h the solvent volume was reduced to about 5 mL. Hexane (5 mL) was then added to the solution, which was cooled to -40 °C. After 1 day, yellow crystals were collected and dried, providing the desired species in high purity (0.47 g, 81%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.27 – 7.11 (m, 13H), 7.07 (dd, *J* = 8.2, 1.4 Hz, 4H), 6.95

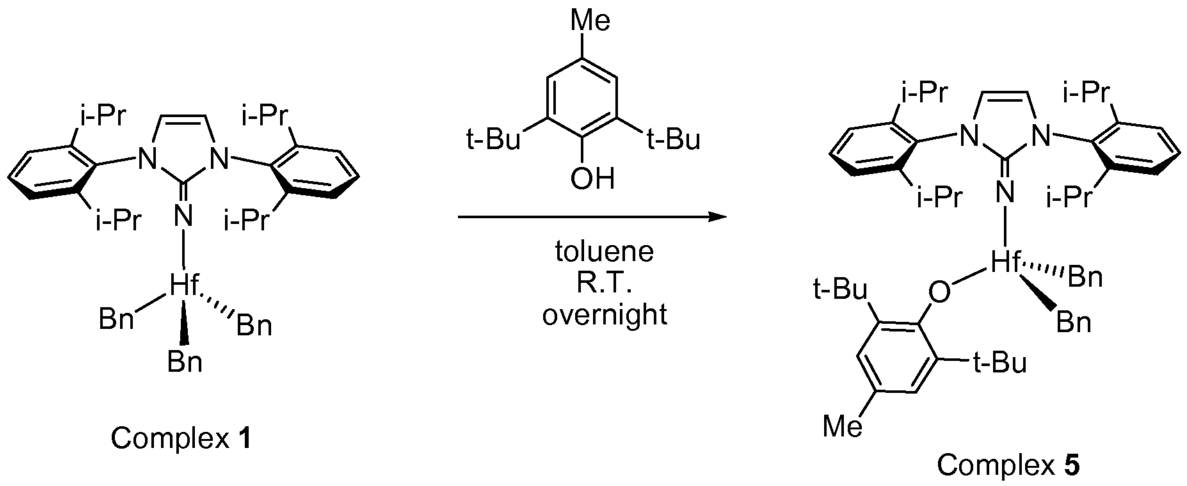
– 6.83 (m, 4H), 6.06 (s, 2H), 3.38 (sp, *J* = 6.8 Hz, 4H), 3.35 (s, 2H), 3.32 (sp, *J* = 6.5 Hz, 2H), 1.91 (d, *J* = 11.4 Hz, 2H), 1.64 (d, *J* = 11.4 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 12H), 1.18 (d, *J* = 6.8 Hz, 12H), 0.70 (d, *J* = 6.5 Hz, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 176.04, 149.53, 147.49, 145.49, 135.93, 134.63, 129.79, 128.91, 128.47, 128.13, 126.66, 124.39, 120.70, 114.69, 73.67, 47.76, 32.60, 29.06, 25.42, 24.76, 23.37.



Complex **1**

Complex **4**

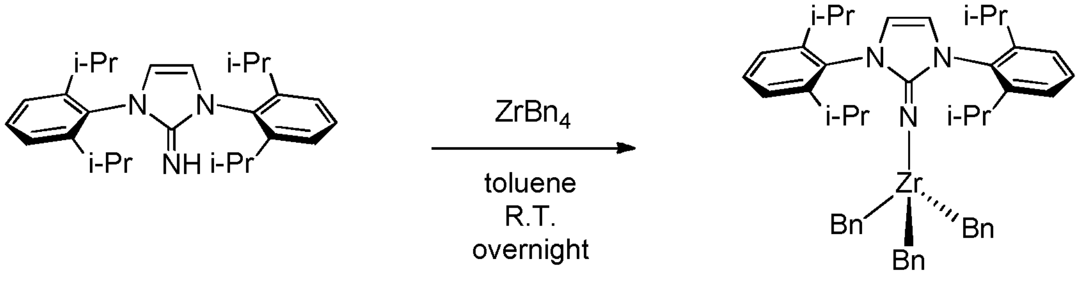
[0063] **Preparation of Complex 4**. In a glovebox under a nitrogen atmosphere, a glass jar was charged with a magnetic stirbar, complex **1** (0.250 g, 0.293 mmol) and toluene (10 mL). The resulting solution was cooled to -40 °C, and then 1-*tert*-Butyl-3-ethylcarbodiimide (0.048 mL, 0.307 mmol) was added to the cold solution. The resulting solution was stirred and allowed warm to room temperature. After 1 h the solvent volume was reduced to about 5 mL. Hexane (5 mL) was then added to the solution, which was cooled to -40 °C. After 1 day, off white colored crystals were collected and dried, providing the desired species in high purity (0.254 g, 89%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.30 – 7.06 (m, 13H), 7.02 (dd, *J* = 8.1, 1.3 Hz, 2H), 6.87 – 6.77 (m, 6H), 5.97 (s, 2H), 3.47 (s, 2H), 3.25 (sp, *J* = 6.8 Hz, 4H), 3.06 (q, *J* = 7.0 Hz, 2H), 1.74 (d, *J* = 11.5 Hz, 2H), 1.53 (d, *J* = 11.5 Hz, 2H), 1.45 (d, *J* = 6.8 Hz, 12H), 1.20 (d, *J* = 6.8 Hz, 12H), 0.70 (t, *J* = 7.0 Hz, 3H), 0.67 (s, 9H).



Complex **1**

Complex **5**

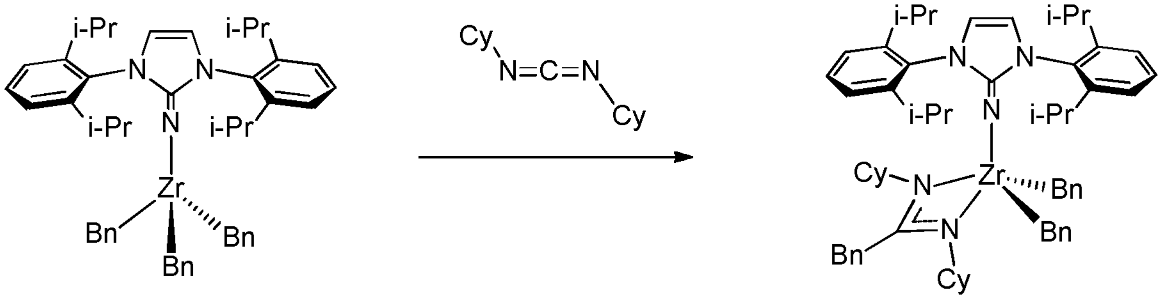
[0064] **Preparation of Complex 5**. In a glovebox under a nitrogen atmosphere, a glass jar was charged with a magnetic stirbar, complex **1** (0.250 g, 0.293 mmol) and toluene (10 mL). The resulting solution was cooled to -40 °C, and then 2,6-di-*tert*-butyl-4-methylphenol (0.068 g, 0.307 mmol) was added to the cold solution. The resulting solution was stirred and allowed warm to room temperature. After 1 h the solvent volume was reduced to about 5 mL. Hexane (5 mL) was then added to the solution, which was cooled to -40 °C. After 1 day, off-white colored crystals were collected and dried, providing the desired species in high purity (0.186 g, 65%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.21 (dd, J = 8.4, 7.1 Hz, 2H), 7.18 – 7.08 (m, 8H), 7.05 (s, 2H), 6.87 – 6.76 (m, 6H), 5.82 (s, 2H), 3.03 (sp, J = 6.9 Hz, 4H), 2.28 (s, 3H), 2.15 (d, J = 12.1 Hz, 2H), 1.85 (d, J = 12.1 Hz, 2H), 1.24 (s, 12H), 1.24 (d, J = 6.9 Hz, 12H), 1.09 (d, J = 6.9 Hz, 12H).



compelx **6**

[0065] **Preparation of Complex 6**. To a vial containing 1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-2(3H)-imine (0.172 g, 0.43 mmol) and $ZrBn_4$ (0.1942 g, 0.43 mmol) was added 2 mL of C_6D_6 which dissolved the components resulting in yellow-orange solution. Reaction mixture was stirred for 4 hr. To the reaction mixture was added 8 mL of hexane, solution was filtered through syringe filter and filtrate was put into freezer (-

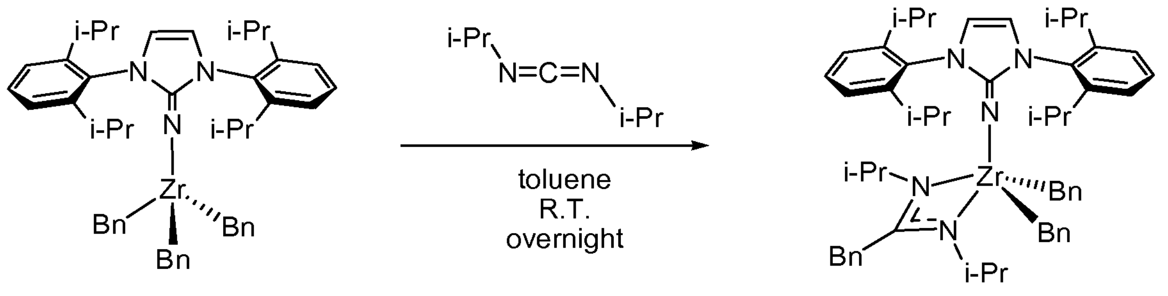
20 °C). Within minutes crystals appeared. After 24 hr in the freezer solution was decanted and yellow crystals were washed with hexane (2x3 mL) and dried under reduced pressure to give 0.268 mg of product. Yield 82%. ^{1}H NMR (500 MHz, C_6D_6) δ 7.24 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.16 (d, *J* = 7.3 Hz, 4H), 7.06 – 6.98 (m, 6H), 6.91 – 6.83 (m, 2H), 6.33 – 6.22 (m, 6H), 5.92 (s, 2H), 3.14 (hept, *J* = 6.9 Hz, 4H), 1.41 (d, *J* = 6.9 Hz, 12H), 1.35 (s, 6H), 1.15 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (126 MHz, C_6D_6) δ 147.38, 142.98, 142.55, 134.05, 130.18, 130.02, 127.27, 124.41, 121.92, 114.36, 60.28, 29.16, 24.46, 23.60.



complex **6**

complex **7**

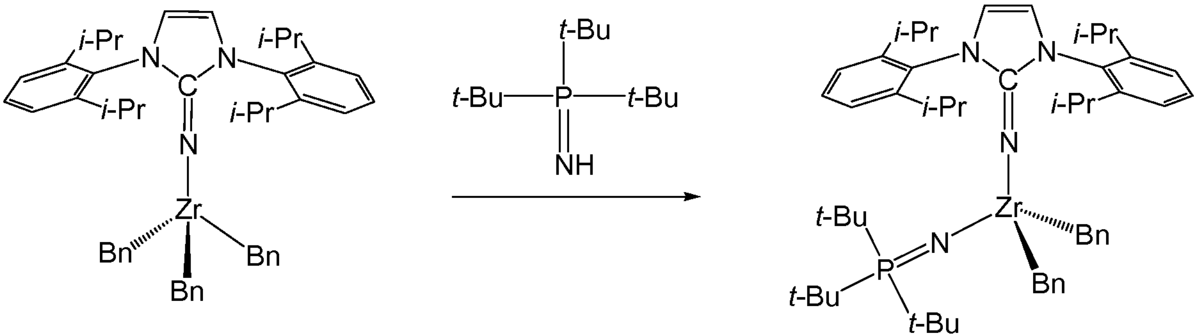
[0066] **Preparation of Complex 7.** Complex **6** (0.500 g, 0.652 mmol) and N,N′-dicyclohexylcarbodiimide (0.134 g, 0.652 mmol) were combined in a small vial. Toluene (10 mL) was added and the reaction was allowed to stir overnight. The reaction mixture was concentrated and hexane was added until approximately a 1:2 ratio (toluene:hexane) was reached and the vial was placed in the freezer to induce crystallization. The resulting off white solid was isolated by filtration yielding the desired compound (0.444 g, 70 %). ^{1}H NMR (400 MHz, C_6D_6) δ 7.27 – 7.19 (m, 7H), 7.17 (s, 2H), 7.14 – 7.07 (m, 2H), 7.07 – 6.97 (m, 6H), 6.90 (tt, *J* = 7.3, 1.3 Hz, 2H), 5.96 (s, 2H), 3.52 (s, 2H), 3.31 (p, *J* = 6.8 Hz, 4H), 2.81 (td, *J* = 10.8, 5.3 Hz, 2H), 2.26 (d, *J* = 10.8 Hz, 2H), 1.88 (d, *J* = 10.8 Hz, 2H), 1.54 – 1.46 (m, 5H), 1.43 (d, *J* = 6.8 Hz, 15H), 1.30 – 1.21 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 12H), 1.11 – 0.82 (m, 14H).



complex 6

complex 8

[0067] **Preparation of Complex 8**. In a glovebox under a nitrogen atmosphere, a glass jar was charged with a magnetic stirbar, complex **6** (0.525 g, 0.684 mmol) and toluene (10 mL). The resulting solution was cooled to -40 °C, and then 1,3-diisopropyl-carbodiimide (0.107 mL, 0.684 mmol) was added to the cold solution. The resulting solution was stirred and allowed warm to room temperature. After 1 h the solvent volume was reduced to about 5 mL. Hexane (5 mL) was then added to the solution, which was cooled to -40 °C. After 1 day, yellow crystals were collected and dried, providing the desired species in high purity (0.45 g, 73%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.40 – 7.11 (m, 13H), 7.08 – 7.02 (m, 4H), 6.94 – 6.82 (m, 4H), 6.04 (s, 2H), 3.39 (sp, *J* = 6.8 Hz, 4H), 3.36 (s, 2H), 3.19 (sp, *J* = 6.4 Hz, 2H), 2.23 (d, *J* = 10.5 Hz, 2H), 1.87 (d, *J* = 10.5 Hz, 2H), 1.39 (d, *J* = 6.8 Hz, 12H), 1.17 (d, *J* = 6.8 Hz, 12H), 0.72 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, C_6D_6) δ 176.24, 149.04, 147.42, 141.94, 136.25, 134.57, 129.87, 128.88, 128.47, 128.39, 127.38, 126.59, 124.44, 120.44, 114.80, 65.83, 47.92, 32.23, 29.10, 25.47, 24.90, 23.38.

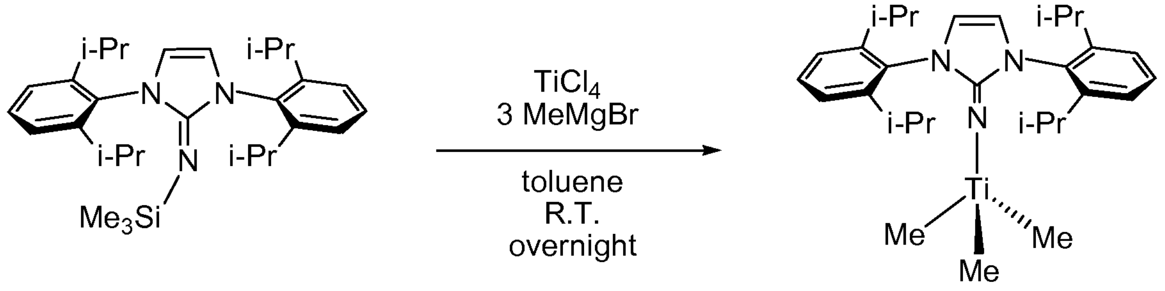


Complex 6

Complex 9

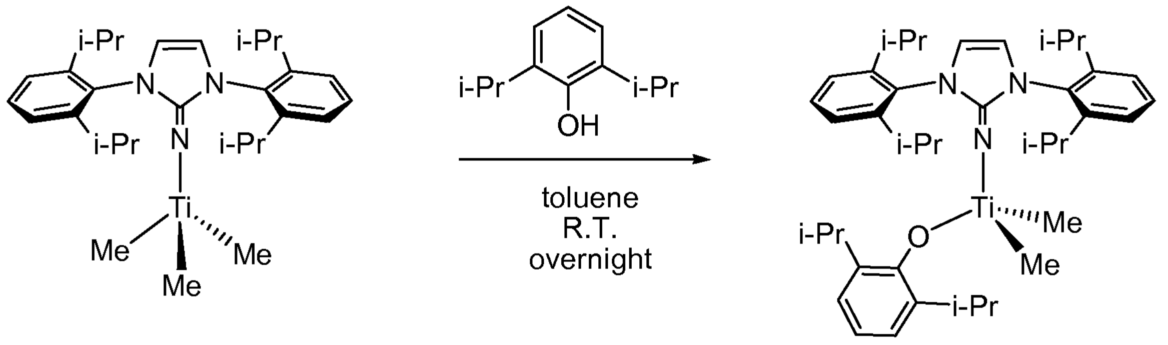
[0068] **Preparation of Complex 9**. To a vial containing 85 milligrams (mg) (0.11 mmol) of complex **6** and 24.1 mg (0.11 mmol) of *t*-Bu_3P=NH was added 1 mL of C_6D_6. Resulting yellow solution change color to virtually colorless within a few seconds. NMR taken after 10 min shows formation of the desired complex. Most of the solvent was removed under reduced pressure. To the residue (~100 microliters (µl)) was added 2 mL of hexane.

Within seconds white crystals started to form. After 30 min solvent was decanted and remaining crystals were washed with 3 mL of hexane and then dried under reduced pressure to give 28 mg. The filtrate was put into freezer overnight. Solvent was decanted and formed crystals were washed with 2 mL of cold hexane and dried under reduced pressure to give 27 mg of product. Combined yield 55 mg, 55.6%. ^{1}H NMR (500 MHz, C_6D_6) δ 7.26 – 7.21 (m, 2H), 7.21 – 7.17 (m, 4H), 7.13 (t, J = 7.7 Hz, 4H), 6.85 – 6.78 (m, 6H), 5.97 (s, 2H), 3.31 (hept, J = 6.8 Hz, 4H), 2.10 (d, J = 10.1 Hz, 2H), 1.54 (d, J = 10.1 Hz, 2H), 1.47 (d, J = 6.9 Hz, 12H), 1.22 (d, J = 6.9 Hz, 12H), 0.94 (d, J = 12.6 Hz, 27H). ^{13}C NMR (126 MHz, C_6D_6) δ 149.67, 147.62, 135.33, 129.53, 128.53, 126.62, 124.29, 119.89, 114.04, 57.73, 39.60 (d, J = 47.1 Hz), 29.70, 29.06, 24.43, 24.01. ^{31}P NMR (202 MHz, C_6D_6) δ 32.27.



Complex **10**

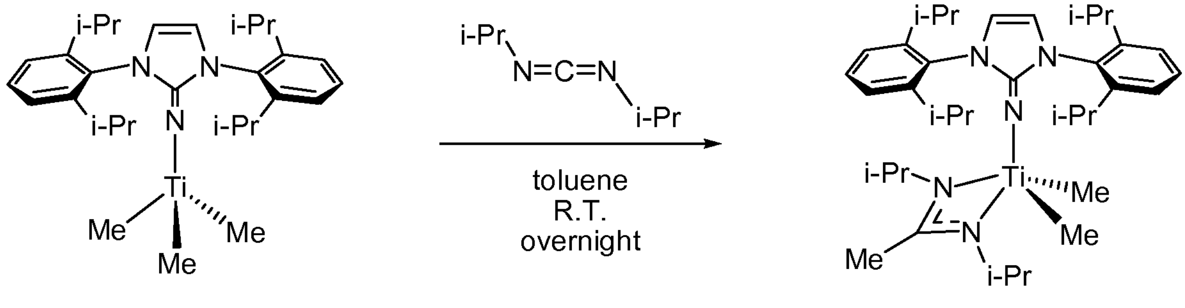
[0069] **Preparation of Complex 10**. In a glovebox under a nitrogen atmosphere, a solution of $TiCl_4$ (0.231 mL, 2.10 mmol) in toluene (10 mL) was treated with a solution of N-(1,3-bis(2,6-diisopropylphenyl)-1H-imidazol-2(3H)-ylidene)-1,1,1-trimethylsilanamine (1.00 g, 2.10 mmol) in toluene (5 mL). A dark orange precipitate formed immediately, and the resulting suspension was stirred for 0.5 h, at which point MeMgBr (4.20 mL of a 3M solution in diethyl ether, 6.73 mmol) was added and the reaction mixture was stirred overnight at ambient temperature. The volatiles were removed under vacuum, and the resulting brown residue was extracted with hexane (40 mL) and filtered. The filtrate was collected, concentrated to about 15 mL, and cooled to -40 °C. After 1 day, yellow/brown crystals were collected and dried, providing the desired species in high purity (0.94 g, 90%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.20 (dd, J = 8.4, 7.1 Hz, 2H), 7.11 (d, J = 7.4 Hz, 4H), 5.91 (s, 2H), 3.11 (sp, J = 6.9 Hz, 4H), 1.40 (d, J = 6.9 Hz, 12H), 1.16 (d, J = 6.9 Hz, 12H), 0.72 (s, 9H). ^{13}C NMR (101 MHz, C_6D_6) δ 147.31, 140.62, 133.46, 130.21, 124.13, 113.80, 53.14, 29.22, 24.20, 23.76.



Complex **10**

Complex **11**

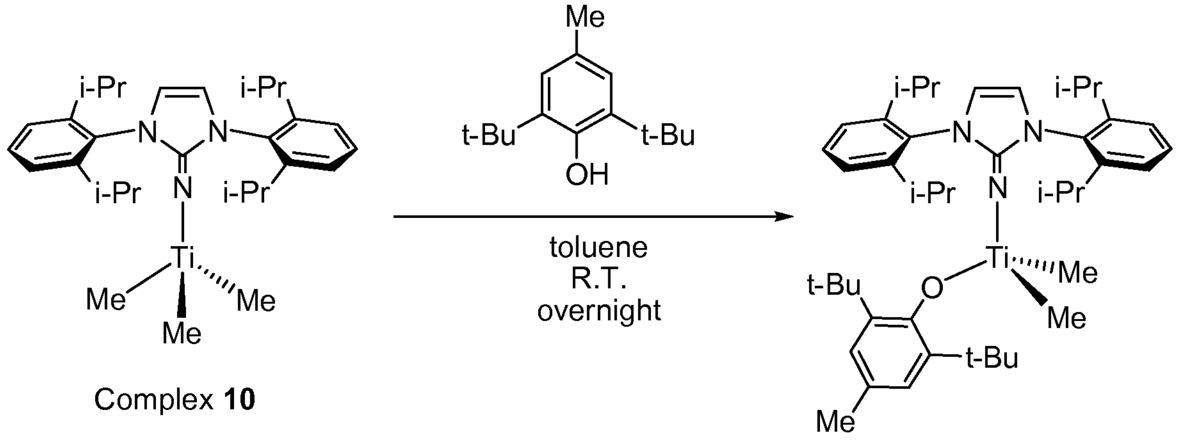
[0070] **Preparation of Complex 11**. In a glovebox under a nitrogen atmosphere, a glass jar was charged with a magnetic stirbar, complex **10** (0.200 gram (g), 0.404 millimole (mmol)) and toluene (5 milliliters (mL)). The resulting solution was stirred at ambient temperature, and then 2,6-diisopropylphenol (0.075 mL, 0.404 mmol) was added. The resulting solution was allowed to stir for 3 hours (h). The solvent volume was reduced to about 2 mL, and hexane (about 3 mL) was added and the mixture was cooled to -40 °C. After 1 day, pale yellow crystals were collected, providing the desired species in high purity (0.130 g, 49%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.20 (dd, J = 8.1, 7.1 Hz, 2H), 7.14 (d, J = 7.6 Hz, 2H), 7.06 (d, J = 7.6 Hz, 4H), 7.00 (dd, J = 8.1, 7.1 Hz, 1H), 5.77 (s, 2H), 3.29 (sp, J = 6.9 Hz, 2H), 3.04 (sp, J = 6.9 Hz, 4H), 1.31 (d, J = 6.9 Hz, 12H), 1.18 (d, J = 6.9 Hz, 12H), 1.11 (d, J = 6.9 Hz, 12H), 0.68 (s, 6H).



Complex **10**

Complex **12**

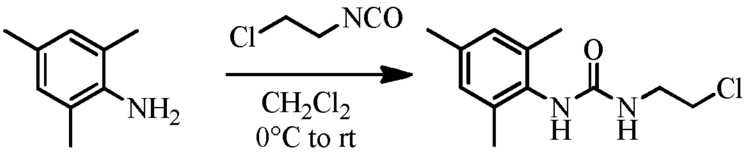
[0071] **Preparation of Complex 12**. In a glovebox under a nitrogen atmosphere, a glass jar was charged with a magnetic stirbar, complex **10** (0.045 g, 0.091 mmol) and toluene (2 mL). The resulting solution was stirred at ambient temperature, and then 1,3-diisopropylcarbodiimide (0.017 mL, 0.109 mmol) was added. The resulting solution was allowed to stir for 0.5 h, at which point volatiles were removed under vacuum, affording desired species in high purity (0.056 g, 100%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.23 (dd, *J* = 8.6, 6.7 Hz, 2H), 7.15 (d, *J* = 7.0 Hz, 4H), 5.90 (d, *J* = 0.6 Hz, 2H), 3.34 (sp, *J* = 6.8 Hz, 4H), 3.28 (sp, *J* = 6.4 Hz, 2H), 1.58 (s, 1H), 1.44 (d, *J* = 6.8 Hz, 12H), 1.19 (d, *J* = 6.8 Hz, 12H), 0.91 (d, *J* = 6.4 Hz, 12H), 0.69 (s, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ 173.52, 147.47, 138.75, 134.65, 129.89, 124.19, 114.30, 54.84, 48.08, 29.09, 24.77, 24.60, 23.70, 10.35.



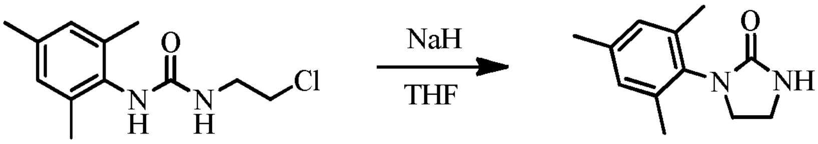
Complex **10**

Complex **13**

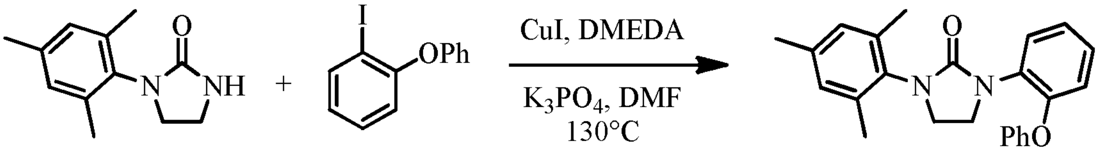
[0072] **Preparation of Complex 13**. In a glovebox under a nitrogen atmosphere, a glass jar was charged with a magnetic stirbar, complex **10** (0.030 g, 0.061 mmol) and toluene (5 mL). The resulting solution was stirred at ambient temperature, and then 2,6-di-*tert*-butyl-4-methylphenol (0.013 g, 0.061 mmol) was added. The resulting solution was allowed to stir for 0.5 h. The volatiles were removed under vacuum, and the residue was taken up in the minimal amount of hexane (ca. 1 mL). This solution was cooled to -40 °C. After 1 day, pale yellow crystals were collected, providing the desired species in high purity (0.021 g, 50%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.21 (dd, *J* = 8.3, 7.2 Hz, 2H), 7.14 (s, 2H), 7.07 (d, *J* = 7.7 Hz, 4H), 5.76 (s, 2H), 3.12 (p, *J* = 6.9 Hz, 4H), 2.30 (s, 3H), 1.39 (s, 18H), 1.27 (d, *J* = 6.9 Hz, 12H), 1.09 (d, *J* = 6.9 Hz, 12H), 0.83 (s, 6H).



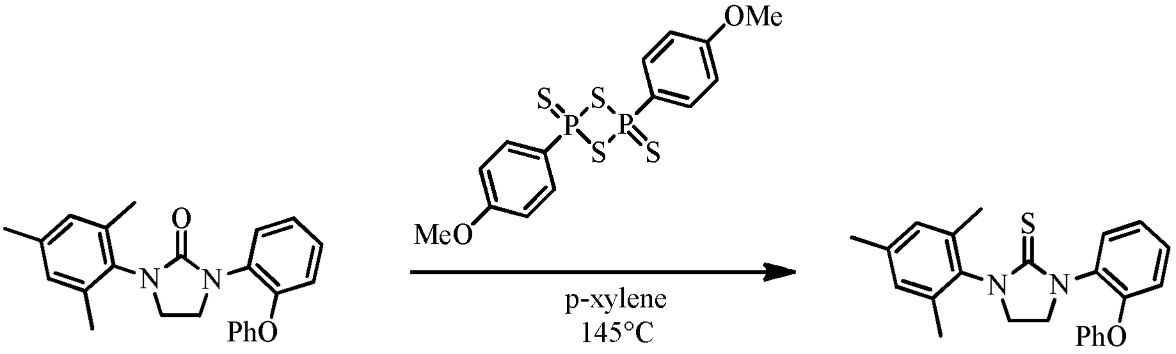
[0073] **Preparation of 1-(2-chloroethyl)-3-mesitylurea**. To a 500 mL round-bottom flask equipped with a magnetic stirbar was added dichloromethane (150 mL) and 2,4,6-trimethylaniline (10 mL, 71.2 mmol, 1 equiv.). The vessel was cooled to 0°C in a water/ice bath, after which 2-chloroethyl isocyanate (7.3 mL, 85.7 mmol, 1.2 equiv.) was added to the stirring solution drop-wise via syringe. The water/ice bath was removed and the reaction was allowed to warm to room temperature, stirring for a total of 20 hours. During this time, a significant amount of white solid precipitated from solution. All volatiles were removed via rotary evaporation. The solid was triturated with cold 10:1 hexanes:diethyl ether (2x100 mL). The slurry was filtered, further washed with room temperature 10:1 hexanes:diethyl ether (2x100 mL), and dried *in vacuo* to afford the product as a white powder (16.7 g, 97% yield) ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.48 (s, 1H), 6.81 (s, 2H), 6.17 (br s, 1H), 3.57 (t, J = 6.2 Hz, 2H), 3.32 (q, J = 6.3 Hz, 2H), 2.17 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.48, 135.93, 135.13, 133.49, 128.70, 44.84, 41.93, 20.90, 18.52. HRMS (ESI-MS+) calcd. For $C_{12}H_{17}ClN_2O$: $[M+H]^+$: 241.1102, found: 241.1105.



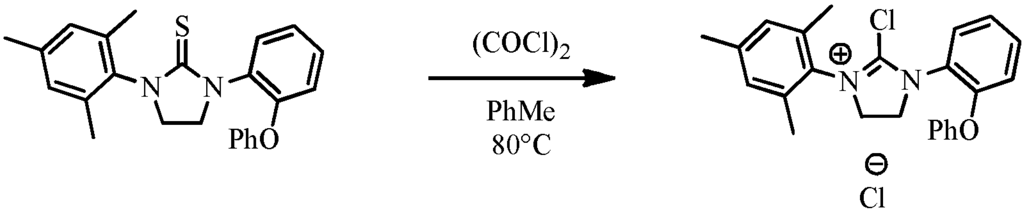
[0074] **Preparation of 1-mesitylimidazolidin-2-one.** In a nitrogen-filled glovebox, 1-(2-chloroethyl)-3-mesitylurea (4.81 g, 20 mmol, 1 equiv.) and tetrahydrofuran (50 mL) were added to a 250 mL round-bottom flask equipped with a magnetic stirbar. Dry sodium hydride (959 mg, 40 mmol, 2 equiv.) was added slowly to the stirring slurry, being careful to wait for hydrogen evolution to cease between additions. The sodium hydride vial was rinsed with tetrahydrofuran (5 mL), which was added to the reaction. By this point, all 1-(2-chloroethyl)-3-mesitylurea had dissolved in solution. The reaction was stirred at room temperature for 3 hours. The vessel was removed from the glove box, and water was slowly added. The solution was extracted with ethyl acetate (2x75 mL). The combined organic layers were washed with brine (1x75 mL), dried over $MgSO_4$, filtered, and concentrated via rotary evaporation to yield the product as a white solid (4.04 g, 99% yield). ^{1}H NMR (400 MHz, Chloroform-d) δ 6.89 (s, 2H), 6.01 (br s, 1H), 3.71 – 3.62 (m, 2H), 3.60 – 3.53 (m, 2H), 2.25 (s, 3H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 161.90, 137.60, 137.01, 132.88, 129.28, 46.41, 39.00, 20.93, 17.77. HRMS (ESI-MS+) calcd. For $C_{12}H_{16}N_2O$: $[M+H]^+$: 205.1335, found: 205.1343.



[0075] **Preparation of 1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-one.** To a 100 mL Schlenk flask equipped with a magnetic stirbar was added copper (I) iodide (0.520 g, 2.73 mmol, 0.3 equiv.), K_3PO_4 (3.86 g, 18.2 mmol, 2 equiv.), 1-iodo-2-phenoxybenzene (2.69 g, 9.09 mmol, 1 equiv.), and 1-mesitylimidazolidin-2-one (1.86 g, 9.09 mmol, 1 equiv.). The vessel was sealed with a septum and purged with nitrogen. Subsequently, *N*,*N'*-dimethylethylenediamine (0.59 mL, 5.46 mmol, 0.6 equiv.) and N,N-dimethylformamide (36 mL) were added via syringe. The reaction was placed into an aluminum heating block preheated to 130°C and stirred for 18 hours. After cooling to room temperature, the material was poured onto diethyl ether (200 mL) and washed with water (2x200 mL). The combined organic layers were washed with brine (1x400 mL), dried over $MgSO_4$, and filtered. The filter cake was washed with benzene (1x50 mL). The solution was concentrated via rotary evaporation. Adsorption onto silica gel, purification via flash column chromatography (1:4 to 1:1 hexanes:ethyl acetate eluent gradient), and concentration via rotary evaporation yielded the product as a white solid (2.64 g, 78% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.60 (m, 1H), 7.38 – 7.29 (m, 2H), 7.25 – 7.18 (m, 2H), 7.14 – 7.00 (m, 4H), 6.90 (s, 2H), 4.05 – 3.97 (m, 2H), 3.62 – 3.55 (m, 2H), 2.29 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.32, 157.28, 151.45, 137.47, 137.03, 133.40, 131.83, 129.76, 129.23, 128.65, 127.32, 124.48, 122.97, 120.89, 117.59, 45.13, 44.14, 21.01, 17.77. HRMS (ESI-MS+) calcd. For $C_{24}H_{24}N_2O_2$: $[M+H]^+$: 373.1911, found 373.1914.

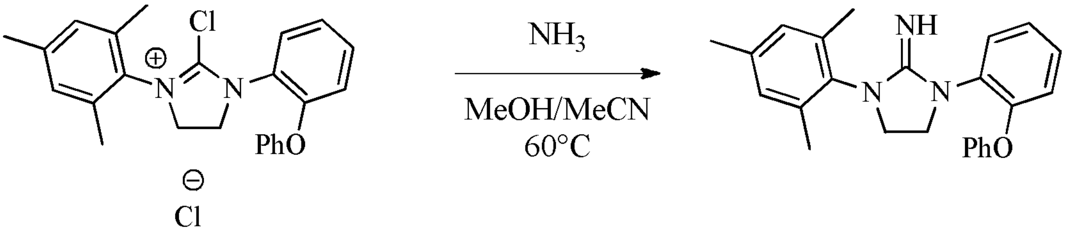


[0076] **Preparation of 1-mesityl-3-(2-phenoxyphenyl)imidazolidine-2-thione.** To a 50 mL three-neck round-bottom flask equipped with a magnetic stirbar and a reflux condenser was added 1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-one (1.2 g, 3.22 mmol, 1 equiv.) and Lawesson's reagent (2.60 g, 6.44 mmol, 2 equiv.). The vessel was sealed with a septum. The vessel was evacuated and backfilled with nitrogen three times. *P*-xylene (13 mL) was added via syringe, the vessel was placed into an aluminum heating block preheated to 145°C, and stirred for 23 hours. Upon cooling to room temperature, methanol (20 mL) and 1 M aqueous HCl (5.5 mL) were added via syringe, and the biphasic mixture was stirred at room temperature for 64 hours. The mixture was poured onto toluene (20 mL) and washed with water (2x30 mL). The combined aqueous layers were extracted with toluene (2x15 mL). The combined organic layers were washed with brine (1x40 mL), dried over $MgSO_4$, and concentrated via rotary evaporation. Adsorption onto silica gel, purification via flash column chromatography (15:85 to 50:50 hexanes:ethyl acetate eluent gradient), and concentration via rotary evaporation yielded the product as a white solid (1.16 g, 92% yield). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.36 – 7.30 (m, 3H), 7.27 – 7.21 (m, 1H), 7.13 – 7.07 (m, 3H), 7.05 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.91 (s, 2H), 4.16 (dd, *J* = 10.2, 8.1 Hz, 2H), 3.83 (dd, *J* = 10.2, 8.0 Hz, 2H), 2.29 (s, 3H), 2.11 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 182.36, 156.92, 152.79, 138.15, 136.53, 134.65, 132.29, 131.29, 129.73, 129.33, 129.15, 124.16, 123.28, 120.55, 118.09, 48.99, 47.82, 21.12, 17.65. HRMS (ESI-MS+) calcd. For $C_{24}H_{24}N_2OS$: $[M+H]^+$: 389.1682, found 389.1699.

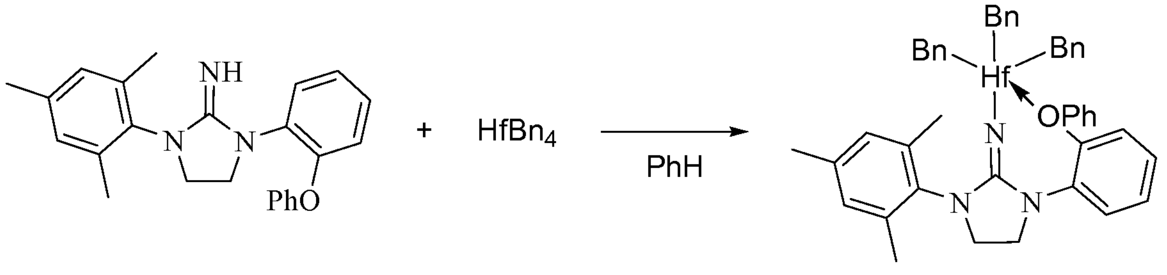


[0077] **Preparation of 2-chloro-3-mesityl-1-(2-phenoxyphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride.** To a 50-mL round-bottom flask equipped with a reflux condenser and a magnetic stirbar was added 1-mesityl-3-(2-phenoxyphenyl)imidazolidine-2-thione (1 g, 2.57 mmol, 1 equiv.). The vessel was evacuated and backfilled with nitrogen three times. Toluene (14 mL) and oxalyl chloride (2.1 mL, 23.2 mmol, 9 equiv.) were added via syringe. Upon addition of oxalyl chloride, the solution turned yellow. The vessel was placed into a room temperature aluminum heating block. The reaction was heated to 80°C and stirred for 38 hours. The volatile were removed *in vacuo* to yield a light brown solid. The vessel was transferred to a nitrogen-filled glovebox. The solid was triturated with toluene (10 mL), filtered, and further washed with toluene (3x5 mL). Drying *in vacuo* afforded a white solid (0.961 g, 87% yield). ^1H NMR (400 MHz, Chloroform-*d*) 8.18 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.43

– 7.29 (m, 3H), 7.24 – 7.11 (m, 2H), 7.02 – 6.93 (m, 2H), 6.94 – 6.86 (m, 3H), 5.00 (br s, 2H), 4.67 (br s, 2H), 2.26 (br s, 3H), 2.23 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.31, 154.94, 152.12, 141.23, 135.67 (br), 132.25, 130.38, 130.30, 130.06, 129.57, 125.03, 124.88, 124.63, 118.80, 118.14, 53.33, 51.68, 21.03, 17.60 (br). HRMS (ESI-MS+) calcd. For $C_{24}H_{24}Cl_2N_2O$: [M-Cl]$^+$: 391.1572, found 391.1580.



[0078] **Preparation of 1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-imine.** In a nitrogen-filled glovebox 2-chloro-3-mesityl-1-(2-phenoxyphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (0.9 g, 2.11 mmol, 1 equiv.) was added to a 25 mL round-bottom flask equipped with a magnetic stirbar. The vessel was sealed with a septum, removed from the glovebox, equipped with a reflux condenser, and the apparatus was evacuated and backfilled with nitrogen three times. Acetonitrile (6 mL) and 7 M ammonia in methanol (6 mL, 42 mmol, 20 equiv.) were added via syringe, and the reaction was placed in an aluminum block heated to 60°C and stirred for 16 hours. The vessel was allowed to cool to room temperature and poured onto 30 mL water. The aqueous phase was extracted with CH_2Cl_2 (3x20 mL). The combined organic phases were washed with brine (1x40 mL), dried over $MgSO_4$, and concentrated via rotary evaporation to yield the product as a white solid (0.754 g, 96% yield). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.32 – 7.25 (m, 1H), 7.14 – 7.04 (m, 2H), 6.90 – 6.85 (m, 1H), 6.83 – 6.77 (m, 2H), 6.77 – 6.72 (m, 2H), 6.69 – 6.64 (m, 1H), 6.60 (s, 2H), 4.60 (br s, 1H), 3.73 (t, *J* = 7.9 Hz, 2H), 3.40 (t, *J* = 7.9 Hz, 2H), 1.99 (s, 3H), 1.82 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d^6) δ 157.54, 156.54, 152.16, 137.53, 137.43, 133.05, 132.33, 130.13, 129.60, 129.44, 127.77, 124.53, 122.64, 120.82, 117.80, 47.28, 45.87, 20.61, 17.43. HRMS (ESI-MS+) calcd. For $C_{24}H_{25}CN_3O$: [M+H]$^+$: 372.2070, found 372.2076.



Complex **14**

[0079] **Preparation of Complex 14.** In a nitrogen-filled glovebox, 1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-imine (40 mg, 0.108 mmol, 1 equiv.) and tetrabenzylhafnium (58.5 mg, 0.108 mol, 1 equiv.) were each separately dissolved in benzene-d^6 (0.7 mL) in a reaction vial equipped with a magnetic stirbar. The solution of 1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-imine was added drop-wise to the stirring solution of tetrabenzylhafnium, and the material was allowed to stir for 1.5 hours, during which time the mixture changed from yellow colored to a clear, colorless solution. All volatiles were removed *in vacuo*, and hexanes (5 mL) was layered onto the material, resulting in the precipitation of a white solid. All volatiles were once again removed *in vacuo* to yield the product as an off-white solid (45 mg, 51% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.31 (ddd, J = 7.8, 1.5, 0.6 Hz, 1H), 7.13 – 6.78 (m, 17H), 6.69 (s, 2H), 6.46 (dd, J = 8.2, 1.2 Hz, 6H), 3.52 – 3.42 (m, 2H), 2.98 – 2.87 (m, 2H), 2.01 (s, 3H), 1.98 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d^6) δ 157.70, 151.83, 149.97, 142.64, 137.65, 137.32, 134.46, 132.45, 131.08, 129.68, 129.20, 129.07, 128.05, 127.46, 124.99, 122.72, 122.15, 121.32, 117.01, 71.41, 45.44, 44.26, 20.54, 17.42.

[0080] **Polymerization Procedure.** A one gallon (3.79 L) stirred autoclave reactor was charged with ISOPAR^{TM} E mixed alkanes solvent and the indicated amount of 1-octene (the total amount of ISOPAR^{TM} E and 1-octene was 1.60 kg). The reactor was then heated to 140 °C and charged with hydrogen (if desired) followed by an amount of ethylene to bring the total pressure to ca 450 psig (2.95 MPa). The ethylene feed was passed through an additional purification column prior to entering the reactor. The catalyst composition was prepared in a drybox under inert atmosphere by mixing the desired pro-catalyst and a cocatalyst (a mixture of 1.2 equiv of $[HNMe(C_{18}H_{37})_2][B(C_6F_5)_4]$ and 50 equivalents of triisobutylaluminum modified alumoxane (MMAO-3A)) with additional solvent to give a total volume of about 17 mL. The activated catalyst mixture was then quick-injected into the reactor. The reactor pressure and temperature were kept constant by feeding ethylene during the polymerization and cooling the reactor as needed. After 10 minutes, the ethylene feed was shut off and the solution transferred into a nitrogen-purged resin kettle. The polymer was thoroughly dried in a vacuum oven, and the reactor was thoroughly rinsed with hot ISOPAR^{TM} E between polymerization runs.

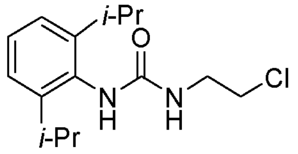
[0081] The results are summarized in the Table 1, where "**Poly.** (g)" is the polymer yield in grams, "**Cat. Amt.** (µmol)" is the catalyst amount in micromoles, "**Eff.** (MM g/g)" is catalyst efficiency expressed in units of millions of grams of catalyst per gram of metal in the catalyst, "**Octene** (g)" is the quantity of 1-octene co-monomer in grams, "**H_2** (mmol)" is the quantity of dihydrogen in millimoles, "**T_M** (° C)" is the polymer melting temperature in degrees centigrade, as measured by differential scanning calorimetry, "**Dens.** (g/cc)" is the polymer density in grams per cubic centimeter, "**Mn** (g/mol)" is the number average molecular weight in grams per mole, "**MWD**" is the molecular weight dispersity (ratio of weight average molecular weight to number average molecular weight), and "**Mw** (g/mol)" is the weight average molecular weight in grams per mole. The results show that new catalysts compositions are capable of polymerizing olefins at high efficiency at industrially relevant reactor temperatures for solution process giving polyolefins with high molecular weight. Depending on particular substitution pattern polyolefin properties such as molecular weight and polydispersity (Mw/Mn) can be altered which is needed feature for commercial applications.

Table 1

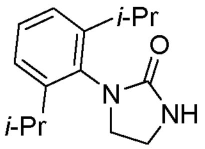
Metal Complex	**Poly.** (g)	**Cat. Amt.** (µmol)	**Eff.** (MM g/g)	**Octene** (g)	**H_2** (mmol)	**T_M** (°C)	**Dens.** (g/cc)	**Mn** (g/mol)	**MWD**	**Mw** (g/mol)
2	5.2	0.375	0.08	250	20	127.1	0.9233	83,085	2.44	202,894
2	4.0	0.31	0.07	250	40	116.4	0.9288	49,502	2.52	124,795
2	42.0	2.5	0.09	250	40	126.3	0.9262	48,405	2.44	117,842
2	54.4	2.5	0.12	250	0	124.3	0.9168	102,152	2.68	273,842
2	51.2	2.5	0.11	350	40	122.7	0.9243	44,581	2.63	117,322
2	54.7	2.5	0.12	450	40	121.5	0.9266	42,672	2.57	109,594
7	8.0	0.31	0.28	250	20	124.0	0.9294	6,185	14.92	92,293
7	5.1	0.24	0.23	250	40	123.1	0.9367	28,533	2.34	66,710
8	1.6	0.21	0.08	250	20	126.0	0.9372	7,480	10.67	79,819
8	7.6	0.25	0.33	250	20	125.8	0.9267	34,338	3.73	128,046
8	3.4	0.24	0.16	250	40	93.7	0.9403	8,580	9.25	79,339
8	29.5	0.9	0.36	250	0	123.2	0.9247	8,406	26.76	224,972
11	39.8	7.5	0.11	250	40	116.6	0.9164	6,220	8.33	51,818
11	51.9	7.5	0.14	250	0	113.2	0.9133	25,333	6.54	165,629

Table 1 (cont.)

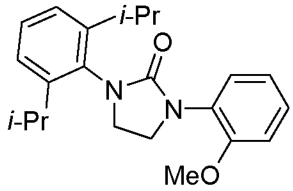
Metal Complex	**Poly.** (g)	**Cat. Amt.** (µmol)	**Eff.** (MM g/g)	**Octene** (g)	**H_2** (mmol)	**T_M** (°C)	**Dens.** (g/cc)	**Mn** (g/mol)	**MWD**	**Mw** (g/mol)
11	54.6	5.0	0.23	250	0	111.3	0.9058	15,019	23.02	345,666
11	41.6	5.0	0.09	250	0	112.1	0.9055	18,021	11.16	201,026
12	33.8	3.75	0.19	350	40	113.7	0.9119	1,774	4.94	8,771
12	41.0	4.1	0.21	450	40	112.4	0.9042	1,829	5.32	9,733
12	47.7	4.25	0.23	250	0	115.1	0.9162	3,080	47.38	145,934
13	18.5	5.0	0.08	250	40	116.6	0.9133	3,137	20.08	62,992
13	38.4	7.5	0.11	250	0	112.6	0.9053	21,212	9.78	207,392



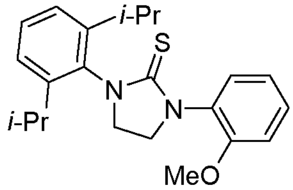
[0082] **Synthesis of 1-(2-chloroethyl)-3-(2,6-diisopropylphenyl)urea:** To a 500 mL round-bottom flask equipped with a magnetic stirbar was added dichloromethane (150 mL) and 2,6-di-*iso*-propylaniline (13 mL, 68.9 mmol, 1 equiv.). The vessel was cooled to 0°C in a water/ice bath, after which 2-chloroethyl isocyanate (7.1 mL, 82.7 mmol, 1.2 equiv.) was added to the stirring solution drop-wise *via* syringe. The water/ice bath was removed and the reaction was allowed to warm to room temperature, stirring for a total of 16 h. During this time, a significant amount of white solid precipitated from solution. All volatiles were removed *via* rotary evaporation. The solid was triturated with cold 10:1 hexanes:diethyl ether (2x100 mL). The slurry was filtered, further washed with room temperature 10:1 hexanes:diethyl ether (2x100 mL), and dried *in vacuo* to afford the product as a white powder (18.9 g, 97% yield). The ^{1}H NMR exhibited broad peaks at room temperature, but showed resolved peaks at 50°C. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.31 (t, $J = 7.7$ Hz, 1H), 7.19 (d, $J = 7.7$ Hz, 2H), 6.72 (br s, 1H), 4.65 (br s, 1H), 3.51 (t, $J = 5.6$ Hz, 2H), 3.44 (t, $J = 5.6$ Hz, 2H), 3.29 (hept, $J = 7.1$ Hz, 2H), 1.21 (d, $J = 7.0$ Hz, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.57, 147.96, 130.94, 128.88, 124.01, 44.29, 42.05, 28.36, 24.10 (br), 23.23(br). HRMS (ESI) Calculated for $C_{15}H_{23}ClN_2O$ $[M+H]^+$: 283.1572, found: 283.1572.



[0083] **Synthesis of 1-(2,6-diisopropylphenyl)imidazolidin-2-one:** In a nitrogen-filled glovebox, 1-(2-chloroethyl)-3-(2,6-diisopropylphenyl)urea (12.0 g, 42.4 mmol, 1 equiv.) and THF (100 mL) were added to a 250 mL round-bottom flask equipped with a magnetic stirbar. Dry sodium hydride (2.04 g, 84.9 mmol, 2 equiv.) was added slowly to the stirring slurry, being careful to wait for hydrogen evolution to cease between additions. The reaction was stirred at room temperature for 2 h. The vessel was removed from the glove box, and water (150 mL) was slowly added. The solution was extracted with ethyl acetate (2x100 mL). The combined organic layers were washed with brine (1x150 mL), dried over $MgSO_4$, filtered, and concentrated *via* rotary evaporation to yield the product as a white solid (10.3 g, 98% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 1H), 7.17 (d, $J =$ 7.7 Hz, 2H), 5.80 (br s, 1H), 3.77 – 3.64 (m, 2H), 3.63 – 3.51 (m, 2H), 3.06 (hept, $J = 6.9$ Hz, 2H), 1.24 (t, $J = 6.7$ Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.47, 148.07, 132.88, 128.72, 124.06, 49.00, 38.89, 28.52, 24.40, 24.32. HRMS (ESI) Calculated for $C_{15}H_{22}N_2O$: $[M+H]^+$: 247.1805, found: 247.1805.

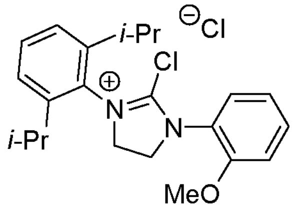


[0084] **Synthesis of 1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-one:** To a 200 mL Schlenk flask equipped with a magnetic stirbar was added copper (I) iodide (0.928 g, 4.87 mmol, 0.3 equiv.), K_3PO_4 (6.89 g, 32.5 mmol, 2 equiv.), 1-iodo-2-phenoxybenzene (2.11 mL, 16.2 mmol, 1 equiv.), and 1-(2,6-diisopropylphenyl)imidazolidin-2-one (4.0 g, 16.2 mmol, 1 equiv.). The vessel was sealed with a septum and purged with nitrogen. Subsequently, *N*,*N'*-dimethylethylenediamine (1.05 mL, 9.74 mmol, 0.6 equiv.) and *N*,*N*-dimethylacetamide (65 mL) were added *via* syringe. The reaction was placed into an aluminum heating block preheated to 130°C and stirred for 24 h. After cooling to room temperature, the material was poured onto diethyl ether (250 mL) and washed with water (2x250 mL). The combined aqueous layers were back extracted with diethyl ether (1x250 mL), dried over $MgSO_4$, and filtered. The solution was concentrated *via* rotary evaporation. Adsorption onto silica gel, purification *via* flash column chromatography (ISCO, 220 g silica, 20-30% EtOAc in hexanes gradient), and concentration *via* rotary evaporation yielded the product as a white solid (5.03 g, 92% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 1H), 7.31 (dd, $J = 8.3, 7.1$ Hz, 1H), 7.23 – 7.16 (m, 3H), 7.00 – 6.93 (m, 2H), 4.01 – 3.91 (m, 2H), 3.87 (s, 3H), 3.79 – 3.65 (m, 2H), 3.16 (hept, $J = 6.9$ Hz, 2H), 1.28 (d, $J = 6.1$ Hz, 6H), 1.26 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.72, 155.22, 148.25, 133.74, 129.23, 128.62, 128.54, 127.53, 123.97, 120.93, 112.33, 55.72, 46.73, 45.58, 28.62, 24.61, 24.27.HRMS (ESI) Calculated for $C_{22}H_{28}N_2O_2$: $[M+H]^+$: 353.2224, found 353.2229.

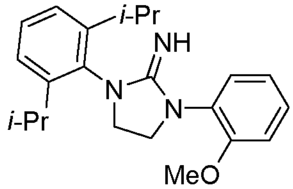


[0085] **Synthesis of 1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidine-2-thione:** To a 250 mL three-neck round-bottom flask equipped with a magnetic stirbar and a reflux condenser was added 1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-

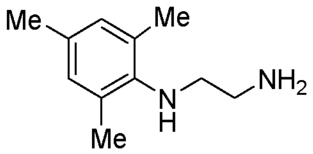
one (4.1 g, 11.6 mmol, 1 equiv.) and Lawesson's reagent (6.12 g, 15.2 mmol, 1.3 equiv.). The vessel was sealed with a septum. The vessel was evacuated and backfilled with nitrogen three times. *P*-xylene (50 mL) was added *via* syringe, the vessel was placed into an aluminum heating block preheated to 145°C, and stirred for 62 h. Upon cooling to room temperature, methanol (20 mL) and 1 M aqueous HCl (25 mL) were added *via* syringe, and the biphasic mixture was stirred at room temperature for 24 h. The mixture was poured onto toluene (75 mL) and washed with water (2x120 mL). The combined aqueous layers were extracted with toluene (3x75 mL). The combined organic layers were dried over $MgSO_4$, and concentrated *via* rotary evaporation. Adsorption onto silica gel, purification *via* flash column chromatography (ISCO, 330 g silica, 5-20% EtOAc in hexanes gradient), and concentration *via* rotary evaporation yielded the product as a white solid (2.96 g, 69% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.40 – 7.28 (m, 2H), 7.26 – 7.19 (m, 2H), 7.05 – 6.97 (m, 2H), 4.15 – 4.03 (m, 2H), 4.01 – 3.91 (m, 2H), 3.89 (s, 3H), 3.10 (hept, *J* = 6.9 Hz, 2H), 1.33 (d, *J* = 6.8 Hz, 6H), 1.28 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.86, 155.68, 147.49, 135.06, 130.70, 129.89, 129.32, 129.19, 124.37, 120.90, 112.57, 55.88, 50.72, 49.20, 28.66, 24.89, 24.55. HRMS (ESI) Calculated for $C_{22}H_{28}N_2OS$: $[M+H]^+$: 369.1995, found 369.1998.



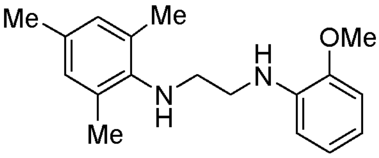
[0086] **Synthesis of 2-chloro-3-(2,6-diisopropylphenyl)-1-(2-methoxyphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride:** To a 50-mL round-bottom flask equipped with a reflux condenser and a magnetic stirbar was added 1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidine-2-thione (2.8 g, 7.60 mmol, 1 equiv.). The vessel was evacuated and backfilled with nitrogen three times. Toluene (36 mL) and oxalyl chloride (5.40 mL, 60.8 mmol, 8 equiv.) were added *via* syringe. Upon addition of oxalyl chloride, the solution turned yellow. The vessel was placed into a room temperature aluminum heating block. The reaction was heated to 80°C and stirred for 18 h. The volatile were removed *in vacuo* to yield a white solid. The vessel was transferred to a nitrogen-filled glovebox. The solid was triturated with toluene (10 mL), filtered, and further washed with toluene (3x5 mL). Drying *in vacuo* afforded a white solid (3.10 g, 87% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.47 – 7.37 (m, 2H), 7.27 – 7.19 (m, 2H), 7.07 – 6.96 (m, 2H), 4.67 (br s, 2H), 3.85 (s, 3H), 3.07 (br s, 2H), 1.28 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.88, 153.55, 146.48 (br), 132.42, 131.73, 129.48, 129.06, 125.26 (br), 122.78, 121.95, 111.94, 56.12, 54.05, 53.37, 28.76, 24.76, 24.30. HRMS (ESI) Calculated for $C_{22}H_{28}ClN_2O^+$: $[M]^+$: 371.1885, found 371.1885.



[0087] **Synthesis of 1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-imine:** In a nitrogen-filled glovebox 2-chloro-3-(2,6-diisopropylphenyl)-1-(2-methoxyphenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (2.6 g, 6.38 mmol, 1 equiv.) was added to a 100 mL round-bottom flask equipped with a magnetic stirbar. The vessel was sealed with a septum, removed from the glovebox, equipped with a reflux condenser, and the apparatus was evacuated and backfilled with nitrogen three times. Acetonitrile (18.2 mL) and 7 M ammonia in methanol (18.2 mL, 128 mmol, 20 equiv.) were added *via* syringe, and the reaction was placed in an aluminum block heated to 60°C and stirred for 18 h. The vessel was allowed to cool to room temperature. All volatiles were removed *in vacuo*. The material was dissolved in CH_2Cl_2 (50 mL) and washed with water (90 mL). The aqueous phase was extracted with CH_2Cl_2 (3x50 mL). The combined organic phases were washed with brine (1x50 mL), dried over $MgSO_4$, and concentrated *via* rotary evaporation to yield the HCl salt as a white solid. The material was dissolved in EtOH (5 mL), and 1 M aqueous NaOH (20 mL) was added. The solution was stirred at room temperature for 5 min, then poured onto 1 M aqueous NaOH (100 mL). The aqueous phase was extracted with CH_2Cl_2 (4x50 mL). The combined organic phases were washed with brine (150 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the free base as a white solid (2.14 g, 95% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.18 (m, 2H), 7.01 (s, 2H), 6.93 (dd, *J* = 7.7, 6.9 Hz, 3H), 4.78 (s, 1H), 3.84 (dd, *J* = 9.2, 6.8 Hz, 2H), 3.80 (s, 3H), 3.73 – 3.66 (m, 2H), 2.99 (hept, *J* = 6.8 Hz, 2H), 1.18 (d, *J* = 6.9 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.48, 155.75, 148.78, 132.77 (br), 130.11, 129.06, 128.05 (br), 124.10, 121.06, 112.24, 55.60, 48.70, 47.68, 28.19, 24.69, 24.07. HRMS (ESI) Calculated for $C_{22}H_{29}N_3O$: $[M+H]^+$: 352.2383, found 352.2394.

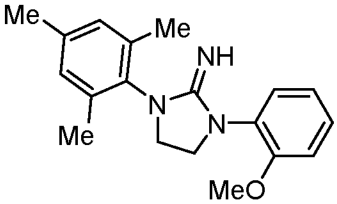


[0088] **Synthesis of *N*^{1}-mesitylethane-1,2-diamine:** In a 500 mL round-bottom flask, a suspension of 2-bromoethylamine hydrobromide (20.4 g, 99.7 mmol, 1 equiv.) and 2,4,6-trimethylaniline (28 mL, 199 mmol, 2 equiv.) was refluxed in toluene (150 mL) for 72 h. During the reaction, a significant amount of material crashed out of solution, forming a cake on the top of the liquid phase. The suspension was allowed to cool to room temperature, resulting in further precipitation of solid. Water (150 mL) was added, resulting in the majority of material dissolving in solution. A 50% w/w solution of NaOH in water (50 mL) was added slowly to the stirring biphasic mixture, causing all solids to dissolve. The organic phase was separated from the aqueous phase. The aqueous phase was further washed with toluene (2x100 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Adsorption onto silica gel, purification *via* flash column chromatography (ISCO, 330 g silica, 100% EtOAc followed by 9:1:0.1 DCM:MeOH:Et_3N isocratic), and concentration *via* rotary evaporation yielded the product as an amber oil (13.9 g, 78% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 6.83 (s, 2H), 3.01 – 2.94 (m, 2H), 2.93 – 2.86 (m, 2H), 2.29 (s, 6H), 2.24 (s, 3H), 1.95 (br s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.55, 131.21, 129.75, 129.41, 51.25, 42.57, 20.58, 18.39. HRMS (ESI) Calculated for $C_{11}H_{18}N_2$: $[M+H]^+$: 179.1543, found 179.1543.

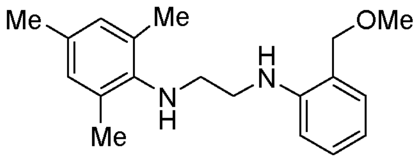


[0089] **Synthesis of *N*^{1}-mesityl-*N*^{2}-(2-methoxyphenyl)ethane-1,2-diamine:** In a nitrogen filled glovebox, BrettPhos palladacycle precatalyst (0.107 g, 0.118 mmol, 1 mol %), BrettPhos (63.4 mg, 0.118 mmol, 1 mol %), and sodium tert-butoxide (2.27 g, 23.6 mmol, 2 equiv.) were added to a reaction vial. *N*^{1}-mesitylethane-1,2-diamine (2.53 g, 14.2 mmol, 1.2 equiv.) and 2-chloroanisole (1.5 mL, 11.8 mmol, 1 equiv.) were added to a separate vial, dissolved in 12 mL dioxane, and the solution was subsequently added to the vial containing the catalyst. The vial was capped, and the reaction was stirred at 80°C for 18 h. The vial was removed from the glove box, poured onto water (100 mL), and extracted with ethyl acetate (2x100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Adsorption onto silica gel, purification *via* flash column chromatography

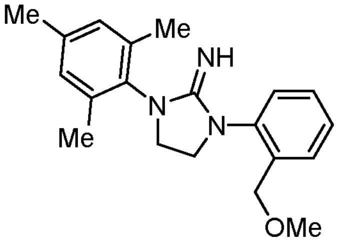
(ISCO, 220 g, 10-27% EtOAc in hexanes), and concentration *via* rotary evaporation yielded the product as a clear oil which turned to a light pink oil (3.296 g, 98% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (td, *J* = 7.6, 1.4 Hz, 1H), 6.81 (s, 2H), 6.78 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.70 – 6.67 (m, 1H), 6.67 – 6.62 (m, 1H), 3.84 (s, 3H), 3.34 (dd, *J* = 6.6, 4.9 Hz, 2H), 3.28 – 3.16 (m, 2H), 2.24 (s, 6H), 2.22 (s, 3H). ^{13}C NMR (101 MHz,Chloroform-*d*) δ 147.20, 143.24, 138.34, 131.54, 130.03, 129.64, 121.44, 116.86, 110.18, 109.67, 55.52, 47.92, 44.34, 20.73, 18.42. HRMS (ESI) Calculated for $C_{18}H_{24}N_2O$: $[M+H]^+$: 285.1961, found 285.1966.



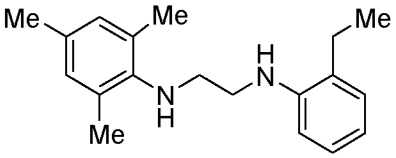
[0090] **Synthesis of 1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-imine**: Caution! Cyanogen bromide is highly toxic. All waste should be disposed of as a basic solution. Care should be taken during workups as to avoid possible contact with deadly cyanide! The excess nitrogen stream from reactions should be passed through 1 M aqueous NaOH solution to trap any possible cyanide-containing byproducts. *N*^{1}-mesityl-*N*^{2}-(2-methoxyphenyl)ethane-1,2-diamine (3.2 g, 11.3 mmol, 1 equiv.) was added to a 25 mL round bottom flask equipped with a reflux condenser. The vessel was evacuated and backfilled with nitrogen three times, after which anhydrous ethanol (4 mL) was added. The solution is cooled in an ice bath, and subsequently a solution of BrCN (1.31 g, 12.4 mmol, 1.1 equiv.) in anhydrous ethanol (3 mL) is added dropwise. The vial is rinsed with an additional anhydrous ethanol (1 mL), which is also added to the diamine solution. The ice bath is removed, and the vessel is allowed to warm to room temperature, then heated to reflux (105°C) for 19 h. The reaction was allowed to cool to room temperature, and 1 M aqueous NaOH (10 mL) was added to the reaction to quench the remaining cyanogen bromide. Mixture was stirred for 10 min, then poured onto 1 M aqueous NaOH solution (100 mL). The aqueous phase was extracted with CH_2Cl_2 (4x50 mL). The combined organic phases were washed with brine (1x150 mL), dried over $MgSO_4$, and concentrated *in vacuo* to yield a brown solid (4346-B, 3.48 g, 99% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.19 – 7.12 (m, 1H), 6.94 – 6.88 (m, 4H), 4.55 (br s, 1H), 3.89 – 3.84 (m, 3H), 3.83 (s, 3H), 3.72 – 3.66 (m, 2H), 2.25 (s, 3H), 2.24 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.61, 155.84, 137.90, 137.79, 133.37, 129.81, 129.42, 129.27, 128.29, 120.94, 112.24, 55.59, 47.46, 46.03, 20.97, 17.67. HRMS (ESI) Calculated for $C_{19}H_{23}N_3O$: $[M+H]^+$: 310.1914, found 310.1917.



[0091] **Synthesis of *N*^{1}-mesityl-*N*^{2}-(2-(methoxymethyl)phenyl)ethane-1,2-diamine:** In a nitrogen filled glovebox, $Pd(OAc)_2$ (25 mg, 0.111 mmol, 1 mol %), and Josiphos [(R), (S_p)-CyPF-*t*-Bu] (61.3 mg, 0.111 mmol, 1 mol %), were dissolved in DME (11 mL). *N*^{1}-mesitylethane-1,2-diamine (2.36 g, 13.3 mmol, 1.2 equiv.) and 1-bromo-2-(methoxymethyl)benzene (1.6 mL, 11.0 mmol, 1 equiv.), and sodium *tert*-butoxide (1.49 g, 15.5 mmol, 1.4 equiv.) were added to a separate vial. The catalyst and ligand solution was subsequently added to the vial containing the substrate. The vial was capped, and the reaction was stirred at 80°C for 17 h. The vial was removed from the glove box, poured onto water (100 mL), and extracted with ethyl acetate (2x100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Adsorption onto silica gel, purification *via* flash column chromatography (ISCO, 220 g, 10-20% EtOAc in hexanes), and concentration *via* rotary evaporation yielded the product as a thick light-brown oil (2.86 g, 87% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.21 (m, 1H), 7.10 (dd, J = 7.6, 1.6 Hz, 1H), 6.85 (s, 2H), 6.73 – 6.67 (m, 2H), 5.09 (br s, 1H), 4.49 (s, 2H), 3.42 – 3.36 (m, 2H), 3.34 (s, 3H), 3.25 – 3.20 (m, 2H), 2.29 (s, 6H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.66, 143.12, 131.63, 130.10, 130.04, 129.57, 129.46, 122.03, 116.59, 110.45, 74.12, 57.45, 47.72, 43.91, 20.57, 18.23.HRMS (ESI) Calculated for $C_{17}H_{26}N_2O$: $[M+H]^+$: 299.2118, found 299.2119.

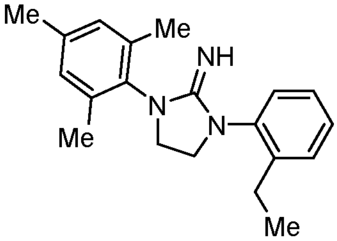


[0092] **Synthesis of 1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-imine:** Caution! Cyanogen bromide is highly toxic. All waste should be disposed of as a basic solution. Care should be taken during workups as to avoid possible contact with deadly cyanide! The excess nitrogen stream from reactions should be passed through 1 M aqueous NaOH solution to trap any possible cyanide-containing byproducts. *N*^{1}-mesityl-*N*^{2}-(2-(methoxymethyl)phenyl)ethane-1,2-diamine (2.81 g, 9.42 mmol, 1 equiv.) was added to a 25 mL round bottom flask equipped with a reflux condenser. The vessel was evacuated and backfilled with nitrogen three times, after which anhydrous ethanol (4 mL) was added. Subsequently a solution of BrCN (1.10 g, 10.4 mmol, 1.1 equiv.) in anhydrous ethanol (3 mL) is added dropwise. The vial is rinsed with an additional anhydrous ethanol (1 mL), which is also added to the diamine solution. The reaction was heated to reflux (100°C) for 15 h. The reaction was allowed to cool to room temperature, and 1 M aqueous NaOH (10 mL) was added to the reaction to quench the remaining cyanogen bromide. Mixture was stirred for 5 min, then poured onto 1 M aqueous NaOH solution (100 mL). The aqueous phase was extracted with CH_2Cl_2 (3x50 mL). The combined organic were dried over $MgSO_4$, and concentrated *in vacuo* to yield a yellow oil. Compared to other analogues, the crude product was not a single, clean species. The material was adsorbed onto basic alumina, purified *via* flash column chromatography (ISCO, 80 g basic alumina, 0-100% EtOAc in hexanes gradient), and concentrated *via* rotary evaporation yielded the product as an off-white solid (2.05 g, 67% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.49 (m, 1H), 7.38 – 7.34 (m, 2H), 7.33 – 7.26 (m, 1H), 6.94 (d, J = 0.7 Hz, 2H), 4.58 (br s, 2H), 4.02 (s, 1H), 3.95 – 3.81 (m, 2H), 3.73 – 3.64 (m, 2H), 3.42 (s, 3H), 2.36 – 2.25 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.47, 139.67, 137.77, 136.85, 133.73, 129.55, 128.87, 127.20, 126.83, 71.18, 58.40, 48.76, 45.84, 20.97, 17.80. HRMS (ESI) Calculated for $C_{20}H_{25}N_3O$: $[M+H]^+$: 324.2070, found 324.2071.



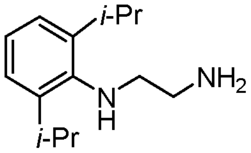
[0093] **Synthesis of *N*^{1}-(2-ethylphenyl)-*N*^{2}-mesitylethane-1,2-diamine:** In a nitrogen filled glovebox, $Pd(OAc)_2$ (26 mg, 0.116 mmol, 1 mol %), and Josiphos [(R), (S_p)-CyPF-*t*-Bu] (64.2 mg, 0.116 mmol, 1 mol %), were dissolved in DME (11 mL). *N*^{1}-mesitylethane-1,2-diamine (2.47 g, 13.9 mmol, 1.2 equiv.) and 1-bromo-2-ethylbenzene (1.6 mL, 11.6 mmol, 1 equiv.), and sodium *tert*-butoxide (1.56 g, 16.2 mmol, 1.4 equiv.) were added to a separate vial. The catalyst and ligand solution was subsequently added to the vial containing the substrate. The vial was capped, and the reaction was stirred at 80°C for 17 h. The vial was removed from the glove box, poured onto water (100 mL), and extracted with ethyl acetate (2x100 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Adsorption onto silica gel, purification *via* flash column chromatography (EXP-14-AK9305, ISCO, 120 g gold silica, 0-30% EtOAc in hexanes gradient), and concentration *via* rotary evaporation yielded the product as a pale yellow oil (2.97 g, 91%

yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (td, *J* = 7.8, 1.6 Hz, 1H), 7.15 – 7.12 (m, 1H), 6.88 (s, 2H), 6.77 (td, *J* = 7.4, 1.2 Hz, 1H), 6.72 – 6.69 (m, 1H), 3.42 – 3.37 (m, 2H), 3.30 – 3.26 (m, 2H), 2.54 (q, *J* = 7.5 Hz, 2H), 2.32 (d, *J* = 0.7 Hz, 6H), 2.28 (s, 3H), 1.30 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.70, 142.98, 131.92, 130.21, 129.57, 128.07, 127.98, 127.02, 117.46, 110.21, 47.79, 44.67, 23.95, 20.60, 18.28, 13.00. HRMS (ESI) Calculated for $C_{19}H_{26}N_2$: $[M+H]^+$: 283.2169, found 283.2169.

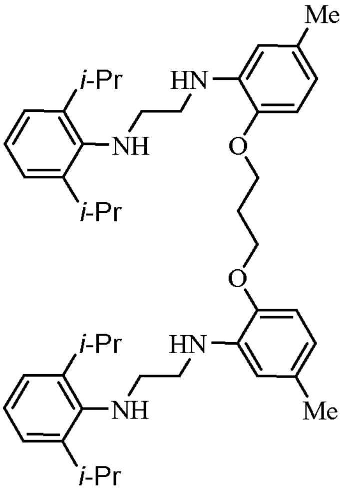


[0094] **Synthesis of 1-(2-ethylphenyl)-3-mesitylimidazolidin-2-imine:** Caution! Cyanogen bromide is highly toxic. All waste should be disposed of as a basic solution. Care should be taken during workups as to avoid possible contact with deadly cyanide! The excess nitrogen stream from reactions should be passed through 1 M aqueous NaOH solution to trap any possible cyanide-containing byproducts. *N*^{1}-(2-ethylphenyl)-*N*^{2}-mesitylethane-1,2-diamine (2.97 g, 10.5 mmol, 1 equiv.) was added to a 25 mL round bottom flask equipped with a reflux condenser. The vessel was evacuated and backfilled with nitrogen three times. Subsequently a solution of BrCN (1.23 g, 11.6 mmol, 1.1 equiv.) in anhydrous ethanol (8 mL) was added. The reaction was heated to reflux (100°C) for 15 h. The reaction was allowed to cool to room temperature, and 1 M aqueous NaOH (10 mL) was added to the reaction to quench the remaining cyanogen bromide. Mixture was stirred for 5 min, then poured onto 1 M aqueous NaOH solution (100 mL). The aqueous phase was extracted with CH_2Cl_2 (3x50 mL). The combined organic were dried over $MgSO_4$, and concentrated *in vacuo* to yield a yellow oil. The ^{1}H NMR spectrum looked clean, however extra peaks were present in the ^{13}C NMR spectrum. The material was adsorbed onto basic alumina, purified *via* flash column chromatography (ISCO, 80 g basic alumina, 0-93% EtOAc in hexanes gradient), and concentrated *via* rotary evaporation to yield a pale yellow oil (3.23 g, 77% yield), which still showed stray peaks in the ^{13}C NMR spectrum. NMR spectra at 50°C were cleaner, indicating that the compound is clean, albeit with different conformational isomers at room temperature. Over several days, the oil solidified. ^{1}H NMR (400 MHz, Chloroform-*d*, 25°C) δ 7.36 – 7.23 (m, 4H), 6.95 (s, 2H), 3.96 (br s, 1H), 3.86 – 3.76 (m, 2H), 3.75 – 3.62 (m, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 2.30 (s, 6H), 2.29 (s, 3H), 1.28 (t, *J* = 7.6 Hz, 3H). ^{13}C

NMR (101 MHz, Chloroform-*d*, 50°C) δ 158.70, 143.17, 139.58 (br), 137.65, 137.48, 134.20 (br), 129.47, 129.33, 127.57, 127.48, 127.04, 48.74, 45.77, 24.33, 20.87, 17.71, 14.66. HRMS (ESI) Calculated for $C_{20}H_{26}N_3$: $[M+H]^+$: 308.2121, found 308.2122.

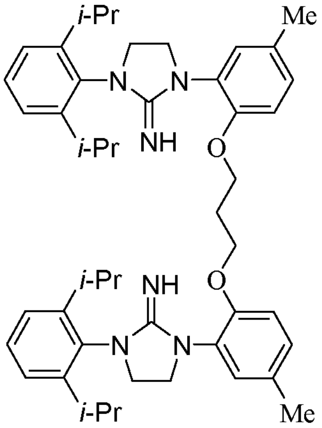


[0095] **Synthesis of *N*^{1}-(2,6-diisopropylphenyl)ethane-1,2-diamine:** In a round-bottom flask, 2,6-di-*iso*-propylaniline (15 mL, 79.5 mmol, 2 equiv.) was added to toluene (60 mL). 2-bromoethylamine hydrobromide (8.15 g, 39.8 mmol, 1 equiv.) was added and the reaction was heated at reflux until completion. The reaction was allowed to cool to room temperature, resulting in the solidification of the solution. Water (240 mL), toluene (200 mL), and 50% w/w aqueous NaOH solution (80 mL) were added, and the aqueous phase was saturated with NaCl. The organic phase was separated, and the aqueous phase was extracted with additional toluene. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. Adsorption onto silica gel, purification *via* flash column chromatography (ISCO, 330 g silica, 100% EtOAc followed by 9:1:0.1 DCM:MeOH:Et_3N isocratic), and concentration *via* rotary evaporation yielded the product as a yellow oil (6.06 g, 69% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.12 – 7.01 (m, 3H), 3.32 (hept, J = 6.9 Hz, 2H), 3.00 – 2.87 (m, 4H), 2.13 (br s, 2H), 1.24 (d, J = 6.9 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.26, 142.51, 123.69, 123.49, 54.25, 42.51, 27.57, 24.27. HRMS (ESI) Calculated for $C_{14}H_{24}N_2$: $[M+H]^+$: 221.2012, found 221.2012.

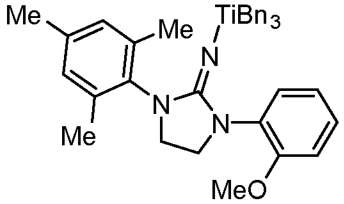


[0096] **Synthesis of *N*^{1},*N*$^{1\prime}$-((propane-1,3-diylbis(oxy))bis(5-methyl-2,1-phenylene))bis(*N*^{2}-(2,6-diisopropylphenyl)ethane-1,2-diamine):** In a nitrogen filled glovebox, $Pd(OAc)_2$ (11.4 mg, 0.051 mmol, 1 mol %), and Josiphos [(R), (S_p)-CyPF-*t*-Bu]

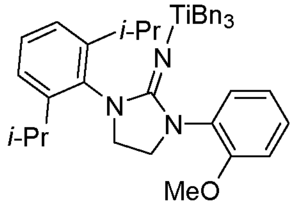
(28.1 mg, 0.051 mmol, 1 mol %), were dissolved in DME (5 mL). *N*[1]-(2,6-diisopropylphenyl)ethane-1,2-diamine (2.46 g, 11.2 mmol, 2.2 equiv.) and 1,3-bis(2-bromo-4-methylphenoxy)propane (2.10 g, 5.07 mmol, 1 equiv.), and sodium *tert*-butoxide (1.36 g, 1.36 mmol, 2.8 equiv.) were added to a separate vial. The catalyst and ligand solution was subsequently added to the vial containing the substrate. The vial was capped, and the reaction was stirred at 80°C for 15 h. The vial was removed from the glove box, poured onto water (100 mL), and extracted with ethyl acetate (3x50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Adsorption onto silica gel, purification *via* flash column chromatography (ISCO, 220 g, 1-16% EtOAc in hexanes), and concentration *via* rotary evaporation yielded the product as a thick oil which partially solidified over several days (2.40 g, 68% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.00 (m, 6H), 6.66 (d, J = 8.0 Hz, 2H), 6.49 (d, J = 2.0 Hz, 2H), 6.44 – 6.37 (m, 2H), 4.58 (br s, 2H), 4.18 (t, J = 6.2 Hz, 4H), 3.40 (t, J = 5.8 Hz, 4H), 3.25 (hept, J = 6.8 Hz, 4H), 3.12 (t, J = 5.8 Hz, 4H), 2.30 (p, J = 6.2 Hz, 2H), 2.24 (s, 6H), 1.19 (d, J = 6.8 Hz, 24H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.10, 142.84, 142.72, 137.85, 130.78, 123.97, 123.52, 116.87, 111.37, 110.71, 65.19, 50.62, 44.15, 29.64, 27.58, 24.25, 21.13. HRMS (ESI) Calculated for $C_{45}H_{64}N_4O_2$: $[M+H]^+$: 693.5102, found 693.5113.



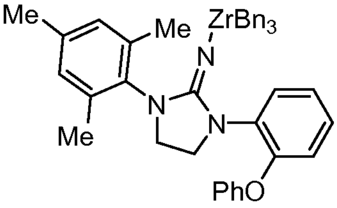
[0097] **Synthesis of 3,3'-((propane-1,3-diylbis(oxy))bis(5-methyl-2,1-phenylene))bis(1-(2,6-diisopropylphenyl)imidazolidin-2-imine):** Caution! Cyanogen bromide is highly toxic. All waste should be disposed of as a basic solution. Care should be taken during workups as to avoid possible contact with deadly cyanide! The excess nitrogen stream from reactions should be passed through 1 M aqueous NaOH solution to trap any possible cyanide-containing byproducts. *N*[1],*N*[1']-((propane-1,3-diylbis(oxy))bis(5-methyl-2,1-phenylene))bis(*N*[2]-(2,6-diisopropylphenyl)ethane-1,2-diamine) (2.23 g, 3.22 mmol, 1 equiv.) was added to a 50 mL round bottom flask equipped with a reflux condenser. The vessel was evacuated and backfilled with nitrogen three times. Anhydrous ethanol (9 mL) was added, however all tetraamine did not dissolve. Subsequently a solution of BrCN (0.682 g, 6.44 mmol, 2 equiv.) in anhydrous ethanol (6 mL) was added. The vial containing the BrCN solution was washed with additional ethanol (2 mL), and this was added to the tetraamine mixture. The reaction was heated to reflux (95°C) for 15 h. A small aliquot was analyzed *via* LC-MS, showing a mixture of starting material, monoaddition, and diaddition. A solution of BrCN (0.682 g, 6.44 mmol, 2 equiv.) in ethanol (5 mL) was added to the reaction, which was heated at reflux (105°C) for a further 16 h. The reaction was allowed to cool to room temperature, and 1 M aqueous NaOH (20 mL) was added to the reaction to quench the remaining cyanogen bromide. Mixture was stirred for 5 min, then poured onto 1 M aqueous NaOH solution (150 mL). The aqueous phase was extracted with CH_2Cl_2 (1x100 mL, 2x50 mL). The combined organic were dried over $MgSO_4$, and concentrated *in vacuo* to yield an off-white solid (2.6 g, 97% yield) (3.23 g, 77% yield). Despite drying *in* vacuo for several days, the material contained one equivalent of hexane. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.34 (dd, *J* = 8.2, 7.2 Hz, 2H), 7.29 (s, 2H), 7.20 (s, 4H), 6.98 (ddd, *J* = 8.3, 2.3, 0.8 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.24 (t, *J* = 6.2 Hz, 4H), 4.15 (br s, 2H), 3.85 (dd, *J* = 8.7, 6.4 Hz, 4H), 3.67 (dd, *J* = 8.3, 6.8 Hz, 4H), 3.17 (hept, *J* = 6.9 Hz, 4H), 2.33 (p, *J* = 6.2 Hz, 3H), 2.28 (s, 6H), 1.25 (d, *J* = 2.9 Hz, 12H), 1.24 (d, *J* = 2.8 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.77, 152.72, 149.16, 133.76 (br), 130.73, 130.25, 129.64, 128.87, 128.10, 124.40, 113.08, 65.21, 48.48, 47.09, 29.59, 28.34, 24.59, 24.52, 20.53. HRMS (ESI) Calculated for $C_{47}H_{62}N_6O_2$: $[M+H]^+$: 743.5007, found 743.5009.



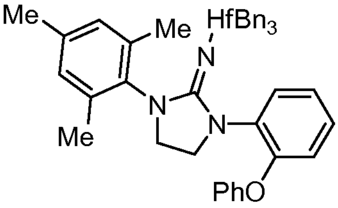
[0098] **Synthesis of Tribenzyl((1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)titanium:** In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-imine (0.150 g, 0.485 mmol, 1 equiv.) in benzene-d^6 (2 mL) was added to a vial containing a dark red solution of $TiBn_4$ (0.200 g, 0.485 mmol, 1 equiv.) in benzene-d^6 (2 mL) The solution was stirred at room temperature for 30 min, during which time the solution significantly lightened in color. All volatiles were removed *in vacuo*, yielding a thick oil. The oil was dissolved in toluene (1 ml). Hexanes (10 mL) was added to the stirring toluene solution, resulting in a hazy orange color. The vial was stored in a -30°C freezer for 4 days, during which time orange crystals precipitated from solution. The solid was filtered, washed with cold (-30°C) hexanes, and dried *in vacuo* to yield the product as orange crystals (0.158 g, 52% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.30 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.12 – 7.02 (m, 6H), 6.96 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 6.90 – 6.83 (m, 3H), 6.77 (td, *J* = 7.6, 1.3 Hz, 1H), 6.71 (s, 2H), 6.57 – 6.52 (m, 6H), 6.50 (dd, *J* = 8.3, 1.3 Hz, 1H), 3.55 – 3.43 (m, 2H), 3.33 (s, 3H), 3.17 – 3.07 (m, 2H), 2.23 (s, 6H), 2.01 (s, 3H), 1.99 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 155.73, 146.13, 145.23, 137.80, 137.24, 134.41, 130.73, 129.16, 128.89, 128.48, 128.45, 127.92, 121.72, 121.07, 111.67, 78.17, 54.95, 46.35, 45.02, 20.55, 17.60.



[0099] **Synthesis of Tribenzyl((1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)titanium:** In a nitrogen-filled glovebox, a solution of 1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-imine (0.150 g, 0.427 mmol, 1 equiv.) in toluene-d^8 (10 mL) was added dropwise over several minutes to a vial containing a dark red solution of $TiBn_4$ (0.176 g, 0.427 mmol, 1 equiv.) in toluene-d^8 (2 mL). The solution was stirred at room temperature for 1 h, during which time the solution significantly lightened in color. NMR shows a 3.5:1 ratio of tribenzyl:dibenzyl species. All volatiles were removed *in vacuo*, yielding a thick dark orange oil. The oil was dissolved in toluene (1 mL), and hexanes (10 mL) was added dropwise to the stirring toluene solution. The resulting dark orange solution was filtered through a 0.5 micron syringe filter and stored in a -30°C freezer for 16 h. The resulting orange crystalline material was filtered, washed with cold hexanes, and dried *in vacuo*. NMR showed a 5.7:1 tribenzyl:dibenzyl ratio. The material was dissolved in toluene (2 mL), hexanes (10 mL) was added, and the solution was again subjected to a 0.5 micron syringe filtration. The resulting clear orange solution was stored in a -30°C freezer for 16 h, resulting in the precipitation of an orange solid. The solid was filtered, washed with cold hexanes, and dried *in vacuo* to yield the product as an orange solid (0.150 g, 52% yield). Material still contains ~10% dibenzyl byproduct. ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.24 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.13 – 6.93 (m, 12H), 6.86 (t, *J* = 7.3 Hz, 3H), 6.73 (td, *J* = 7.6, 1.3 Hz, 1H), 6.57 (dd, *J* = 8.2, 1.4 Hz, 6H), 6.47 (dd, *J* = 8.3, 1.3 Hz, 1H), 3.52 – 3.46 (m, 2H), 3.34 (s, 3H), 3.36 – 3.24 (m, 2H), 2.00 (s, 6H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.16 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 155.89, 148.01, 147.33, 145.57, 134.43, 131.16, 129.09, 128.86, 128.79, 128.42, 127.77, 124.14, 121.66, 121.00, 111.50, 79.74, 54.91, 47.64, 46.35, 28.55, 24.81, 24.17.

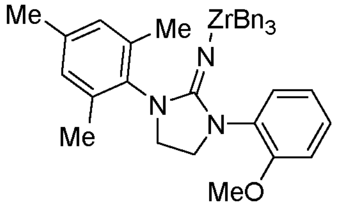


[0100] **Synthesis of Tribenzyl((1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-ylidene)amino)zirconium:** In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-imine (0.200 g, 0.538 mmol, 1 equiv.) in benzene-d^6 (3 mL) was added dropwise to a stirring solution of ZrBn$_4$ (0.245 g, 0.538 mmol, 1 equiv.) in benzene-d^6 (3 mL). The solution was stirred at room temperature for 1 h, resulting in a clear, yellow solution. All volatiles were removed *in vacuo*, yielding a thick oil. Hexane (15 mL) was added and the solution was stirred vigorously for 1 h, however the thick oil did not fully dissolve in the hexanes layer. The hexanes layer was decanted and stored in a -30°C freezer for 3 h, yielding a yellow precipitate. The remaining thick oil was dissolved in toluene (1 mL). Hexane (15 mL) was added to the stirring toluene solution, resulting in the formation of a yellow precipitate. The suspension was stored in a -30°C freezer for 3 h. The two batches of precipitated material were combined, filtered, washed with -30°C hexane, and dried *in vacuo* to yield a yellow solid (0.300 g, 76% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.44 – 7.39 (m, 1H), 7.14 – 6.77 (m, 17H), 6.69 (s, 2H), 6.38 – 6.29 (m, 6H), 3.50 – 3.44 (m, 2H), 2.96 – 2.89 (m, 2H), 2.01 (s, 3H), 2.00 (s, 6H), 1.42 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 157.63, 151.98, 146.83, 142.62, 137.66, 137.29, 134.53, 132.41, 131.15, 129.72, 129.71, 129.10, 128.13, 126.79, 124.88, 122.78, 121.70, 121.18, 117.17, 61.54, 45.71, 44.50, 20.54, 17.45.

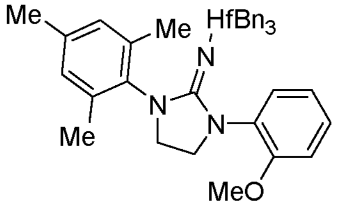


[0101] **Synthesis of Tribenzyl((1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-ylidene)amino)hafnium:** In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-

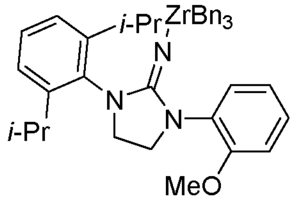
phenoxyphenyl)imidazolidin-2-imine (0.300 g, 0.808 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added dropwise to a stirring solution of $HfBn_4$ (0.245 g, 0.538 mmol, 1 equiv.) in benzene-d^6 (4 mL). The solution was stirred at room temperature for 1 h, resulting in a clear, colorless solution. All volatiles were removed *in vacuo*, yielding a thick oil. Hexane (15 mL) was added and the solution was stirred vigorously for 1 h. The vial was placed in a -30°C freezer for 4 h. The suspension was filtered, washed with -30°C hexane, and dried *in vacuo* to yield an off-white solid (0.550 g, 83% yield). ^1H NMR (400 MHz, Benzene-d_6) δ 7.31 (ddd, J = 7.8, 1.5, 0.6 Hz, 1H), 7.13 – 6.78 (m, 17H), 6.69 (s, 2H), 6.46 (dd, J = 8.2, 1.2 Hz, 6H), 3.52 – 3.42 (m, 2H), 2.98 – 2.87 (m, 2H), 2.01 (s, 3H), 1.98 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 157.70, 151.83, 149.97, 142.64, 137.65, 137.32, 134.46, 132.45, 131.08, 129.68, 129.20, 129.07, 128.05, 127.46, 124.99, 122.72, 122.15, 121.32, 117.01, 71.41, 45.44, 44.26, 20.54, 17.42.



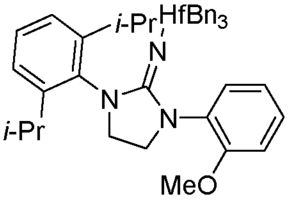
[0102] **Synthesis of Tribenzyl((1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)zirconium:** In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-imine (0.300 g, 0.970 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added dropwise to a stirring solution of $ZrBn_4$ (0.442 g, 0.970 mmol, 1 equiv.) in benzene-d^6 (4 mL). The solution was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*, yielding a thick oil. The oil was dissolved in toluene (2 mL). Hexane (15 mL) was added to the stirring toluene solution dropwise, resulting in the precipitation of a solid. The suspension was cooled in a -30°C freezer for 16 h. The solid was filtered, washed with -30°C hexane, and dried *in vacuo* to afford the product as a yellow solid (0.567 g, 87% yield). ^1H NMR (400 MHz, Benzene-d_6) δ 7.31 (dd, J = 7.7, 1.7 Hz, 1H), 7.04 – 6.96 (m, 7H), 6.89 – 6.79 (m, 4H), 6.76 (s, 2H), 6.54 (dd, J = 8.3, 1.3 Hz, 1H), 6.29 (ddd, J = 7.8, 1.6, 0.6 Hz, 6H), 3.53 – 3.39 (m, 2H), 3.35 (s, 3H), 3.19 – 3.07 (m, 2H), 2.23 (s, 6H), 2.05 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 156.05, 147.93, 142.73, 137.56, 137.34, 134.81, 130.89, 129.67, 129.57, 129.15, 128.39, 126.66, 121.44, 121.00, 111.83, 60.56, 54.98, 46.26, 44.73, 20.58, 17.60.



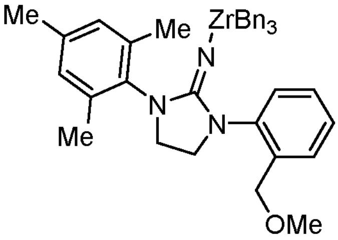
[0103] **Synthesis of Tribenzyl((1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)hafnium:** In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-imine (0.300 g, 0.970 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added dropwise to a stirring solution of $HfBn_4$ (0.527 g, 0.970 mmol, 1 equiv.) in benzene-d^6 (4 mL). The solution was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*, yielding a thick oil. The oil was dissolved in toluene (2 mL). Hexane (15 mL) was added to the stirring toluene solution dropwise, resulting in the precipitation of a solid. The suspension was cooled in a -30°C freezer for 16 h. The solid was filtered, washed with -30°C hexane, and dried *in vacuo* to afford the product as an off-white solid (0.626 g, 85% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.27 (dd, J = 7.7, 1.7 Hz, 1H), 7.07 – 6.96 (m, 7H), 6.89 – 6.78 (m, 4H), 6.77 – 6.73 (m, 2H), 6.54 (dd, J = 8.3, 1.3 Hz, 1H), 6.42 (ddd, J = 7.8, 1.6, 0.7 Hz, 6H), 3.53 – 3.40 (m, 2H), 3.34 (s, 3H), 3.19 – 3.08 (m, 2H), 2.21 (d, J = 0.6 Hz, 6H), 2.05 (s, 3H), 1.21 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 155.94, 151.11, 142.77, 137.53, 137.35, 134.76, 130.80, 129.48, 129.13, 129.10, 128.25, 127.39, 121.92, 121.02, 111.79, 70.76, 54.95, 45.98, 44.50, 20.58, 17.58.



[0104] **Synthesis of Tribenzyl((1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)zirconium:** In a nitrogen-filled glovebox, a solution of 1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-imine (0.300 g, 0.854 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added dropwise to a stirring solution of $ZrBn_4$ (0.389 g, 0.854 mmol, 1 equiv.) in benzene-d^6 (4 mL). The solution was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*, yielding a thick oil. The oil was dissolved in toluene (2 mL). Hexane (15 mL) was added to the stirring toluene solution dropwise, resulting in the precipitation of a solid. The suspension was cooled in a -30°C freezer for 16 h. The solid was filtered, washed with -30°C hexane, and dried *in vacuo* to afford the product as a yellow solid (0.509 g, 83% yield). Contains <10% of a dibenzyl derivative, presumably $LZrClBn_2$. ^1H NMR (400 MHz, Benzene-d_6) δ 7.30 (dd, J = 7.7, 1.7 Hz, 1H), 7.15 – 6.92 (m, 10H), 6.87 – 6.76 (m, 4H), 6.52 (dd, J = 8.3, 1.3 Hz, 1H), 6.35 – 6.27 (m, 6H), 3.49 – 3.42 (m, 2H), 3.36 (s, 3H), 3.35 – 3.31 (m, 2H), 3.25 (hept, J = 7.2, 6.8 Hz, 2H), 1.34 (d, J = 6.8 Hz, 6H), 1.31 (s, 6H), 1.15 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 156.10, 149.05, 148.21, 142.65, 134.84, 131.23, 129.64, 129.61, 128.84, 128.60, 126.85, 124.03, 121.52, 120.97, 111.70, 61.26, 54.95, 47.39, 46.31, 28.44, 24.96, 24.16.

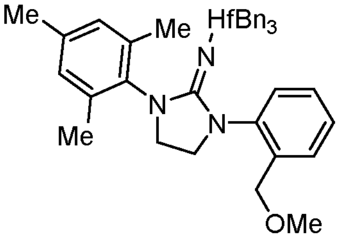


[0105] **Synthesis of Tribenzyl((1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)hafnium:** In a nitrogen-filled glovebox, a solution of 1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-imine (0.300 g, 0.854 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added dropwise to a stirring solution of $HfBn_4$ (0.464 g, 0.854 mmol, 1 equiv.) in benzene-d^6 (4 mL). The solution was stirred at room temperature for 1 h. All volatiles were removed *in vacuo*, yielding a thick oil. The oil was dissolved in toluene (2 mL). Hexane (15 mL) was added to the stirring toluene solution dropwise, resulting in the precipitation of a solid. The suspension was cooled in a -30°C freezer for 16 h. The solid was filtered, washed with -30°C hexane, and dried *in vacuo* to afford the product as a white solid (0.535 g, 78% yield). Contains <10% of a dibenzyl derivative, presumably $LZrClBn_2$. ^1H NMR (400 MHz, Benzene-d_6) δ 7.26 (dd, J = 7.7, 1.7 Hz, 1H), 7.18 – 6.96 (m, 10H), 6.89 – 6.83 (m, 3H), 6.79 (td, J = 7.6, 1.3 Hz, 1H), 6.52 (dd, J = 8.3, 1.3 Hz, 1H), 6.43 (ddd, J = 7.7, 1.5, 0.6 Hz, 6H), 3.51 – 3.43 (m, 2H), 3.35 (s, 3H), 3.39 – 3.30 (m, 2H), 3.23 (hept, J = 7.0 Hz, 2H), 1.32 (d, J = 6.8 Hz, 6H), 1.18 (s, 6H), 1.15 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 156.05, 152.33, 148.19, 142.79, 134.80, 131.21, 129.54, 129.08, 128.86, 128.52, 127.49, 124.04, 121.93, 121.00, 111.67, 71.82, 54.92, 47.18, 46.00, 28.43, 24.84, 24.26.

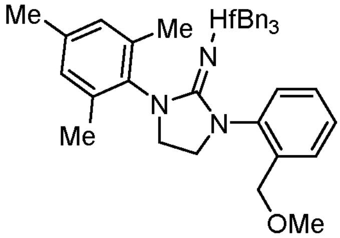


[0106] **Synthesis of Tribenzyl((1-mesityl-3-(2-**

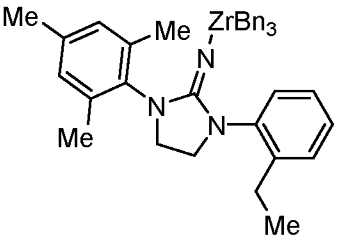
(methoxymethyl)phenyl)imidazolidin-2-ylidene)amino)zirconium: In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-imine (0.300 g, 0.928 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added to a solution of $ZrBn_4$ (0.423 g, 0.928 mmol, 1 equiv.) in benzene-d^6 (4 ml). The solution was stirred at room temperature for 1 hour. As a small amount of solid material had precipitated, the solution was filtered and concentrated *in vacuo* to yield a thick yellow oil. The material was dissolved in toluene (2 mL). While stirring, hexanes (17 mL) was added, producing a cloudy yellow solution. The solution was cooled in a -30°C freezer for 2 h, resulting in the separation of an oil. Vigorous shaking and stirring of the material resulted in the precipitation of a yellow solid, however some product still remained in the thick goo layer. The suspension was stored in a -30°C freezer for 1 h. The material was filtered, washed with cold hexanes, and dried *in vacuo* to yield the product as a yellow solid (0.364 g, 57% yield). The material remaining in the thick goo was dissolved in toluene (1 mL). Hexanes (10 mL) was added to the stirring toluene solution, resulting in the formation of a hazy yellow solution. The vial was stored in a -30°C freezer for 18 h, resulting in the precipitation of a yellow solid. The solid was filtered, washed with cold (-30°C) hexanes, and dried *in vacuo* to afford an additional crop of product (0.108 g, 17% yield), which was spectroscopically identical to the first crop. Combined: 0.472 g, 74% yield. ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.46 – 7.41 (m, 1H), 7.10 (ddd, J = 8.6, 6.2, 1.7 Hz, 1H), 7.06 – 7.01 (m, 2H), 7.00 – 6.94 (m, 6H), 6.87 – 6.81 (m, 3H), 6.75 (s, 2H), 6.26 – 6.21 (m, 6H), 4.60 (s, 2H), 3.36 – 3.27 (m, 2H), 3.22 (s, 3H), 3.13 – 3.02 (m, 2H), 2.23 (s, 6H), 2.05 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 147.43, 142.44, 139.31, 137.69, 137.43, 137.14, 134.64, 129.70, 129.64, 129.26, 128.74, 128.27, 127.60, 126.68, 121.60, 71.54, 60.65, 57.95, 47.63, 44.77, 20.59, 17.63.



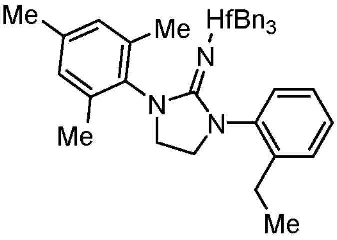
[0107] **Synthesis of Tribenzyl((1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-ylidene)amino)hafnium**: In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-imine (0.300 g, 0.928 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added to a solution of $HfBn_4$ (0.504 g, 0.928 mmol, 1 equiv.) in benzene-d^6 (4 ml). The solution was stirred at room temperature for 1 hour. As a small amount of solid material had precipitated, the solution was filtered and concentrated *in vacuo* to yield a thick yellow oil. The material was mostly dissolved in toluene (2 mL). While stirring, hexanes (17 mL) was added, producing a cloudy off-white solution. The suspension was cooled in a -30°C freezer for 1 h. The material was filtered, washed with cold hexanes, and dried *in vacuo* to yield the product as an off-white solid (0.677 g, 94% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.43 – 7.38 (m, 1H), 7.13 – 6.93 (m, 9H), 6.89 – 6.79 (m, 3H), 6.76 (s, 2H), 6.40 – 6.34 (m, 6H), 4.55 (s, 2H), 3.37 – 3.26 (m, 2H), 3.20 (s, 3H), 3.13 – 3.01 (m, 2H), 2.21 (s, 6H), 2.06 (s, 3H), 1.17 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 150.68, 142.67, 139.38, 137.66, 137.14, 137.11, 134.58, 129.78, 129.24, 129.09, 128.83, 128.09, 127.45, 127.40, 122.00, 71.64, 71.03, 58.06, 47.38, 44.55, 20.58, 17.60.



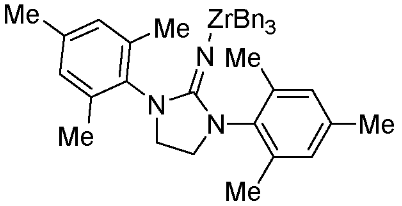
[0108] **Synthesis of Tribenzyl((1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-ylidene)amino)hafnium**: In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-imine (0.300 g, 0.928 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added to a solution of HfBn$_4$ (0.504 g, 0.928 mmol, 1 equiv.) in benzene-d^6 (4 ml). The solution was stirred at room temperature for 1 hour. As a small amount of solid material had precipitated, the solution was filtered and concentrated *in vacuo* to yield a thick yellow oil. The material was mostly dissolved in toluene (2 mL). While stirring, hexanes (17 mL) was added, producing a cloudy off-white solution. The suspension was cooled in a -30°C freezer for 1 h. The material was filtered, washed with cold hexanes, and dried *in vacuo* to yield the product as an off-white solid (0.677 g, 94% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.43 – 7.38 (m, 1H), 7.13 – 6.93 (m, 9H), 6.89 – 6.79 (m, 3H), 6.76 (s, 2H), 6.40 – 6.34 (m, 6H), 4.55 (s, 2H), 3.37 – 3.26 (m, 2H), 3.20 (s, 3H), 3.13 – 3.01 (m, 2H), 2.21 (s, 6H), 2.06 (s, 3H), 1.17 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 150.68, 142.67, 139.38, 137.66, 137.14, 137.11, 134.58, 129.78, 129.24, 129.09, 128.83, 128.09, 127.45, 127.40, 122.00, 71.64, 71.03, 58.06, 47.38, 44.55, 20.58, 17.60.



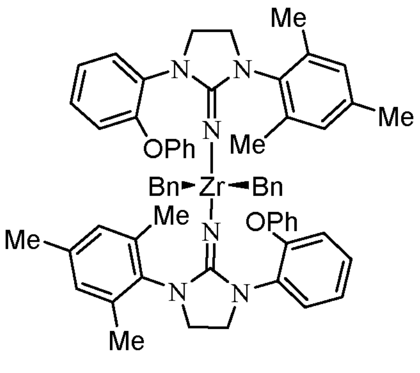
[0109] **Synthesis of Tribenzyl((1-(2-ethylphenyl)-3-mesitylimidazolidin-2-ylidene)amino)zirconium:** In a nitrogen-filled glovebox, a solution of 1-(2-ethylphenyl)-3-mesitylimidazolidin-2-imine (0.300 g, 0.976 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added to a solution of $ZrBn_4$ (0.445 g, 0.976 mmol, 1 equiv.) in benzene-d^6 (4 ml). The solution was stirred at room temperature for 1 hour. The solution was passed through a syringe filter and concentrated *in vacuo* to yield a yellow oil. The oil was dissolved in toluene (2 mL). Hexane (17 mL) was added to the stirring toluene solution dropwise, producing a solution with some precipitate. The mixture was stored in a -30°C freezer for 17 h, resulting in the precipitation of fine yellow crystals. The cold solution was stirred briefly to aid in the precipitation of additional material, then stored in a -30°C freezer for 2 h. The mixture was filtered, washed with cold hexane, and dried *in vacuo* to yield the product as a yellow solid (0.552 g, 84% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.11 – 6.94 (m, 10H), 6.87 – 6.81 (m, 3H), 6.77 – 6.73 (m, 2H), 6.27 – 6.20 (m, 6H), 3.24 – 3.12 (m, 2H), 3.04 (dd, J = 9.5, 6.8 Hz, 2H), 2.69 (q, J = 7.6 Hz, 2H), 2.22 (s, 6H), 2.06 (s, 3H), 1.28 (s, 6H), 1.22 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 147.74, 142.79, 142.52, 139.21, 137.66, 137.14, 134.67, 129.68, 129.25, 129.09, 128.54, 127.95, 127.08, 126.67, 121.54, 60.61, 47.53, 44.66, 24.66, 20.59, 17.60, 14.81.



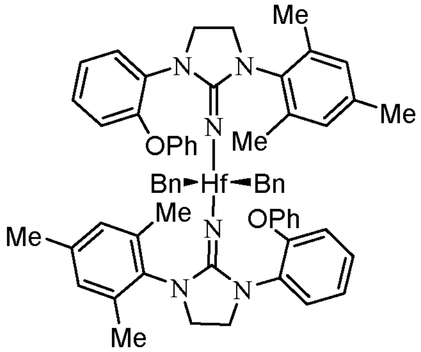
[0110] **Synthesis of Tribenzyl((1-(2-ethylphenyl)-3-mesitylimidazolidin-2-ylidene)amino)hafnium:** In a nitrogen-filled glovebox, a solution of 1-(2-ethylphenyl)-3-mesitylimidazolidin-2-imine (0.300 g, 0.976 mmol, 1 equiv.) in benzene-d^6 (4 mL) was added to a solution of $HfBn_4$ (0.530 g, 0.976 mmol, 1 equiv.) in benzene-d^6 (4 ml). The solution was stirred at room temperature for 1 hour. The solution was passed through a syringe filter and concentrated *in vacuo* to yield a pale yellow oil. The oil was dissolved in toluene (2 mL). Hexane (17 mL) was added to the stirring toluene solution dropwise, producing a solution with some precipitate. The mixture was stored in a -30°C freezer for 17 h, resulting in the precipitation of a white powder. The cold solution was stirred briefly to aid in the precipitation of additional material, then stored in a -30°C freezer for 2 h. The mixture was filtered, washed with cold hexane, and dried *in vacuo* to yield the product as a white powder (0.561 g, 76% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.12 – 6.92 (m, 10H), 6.89 – 6.82 (m, 3H), 6.76 (s, 2H), 6.43 – 6.28 (m, 6H), 3.21 – 3.14 (m, 2H), 3.09 – 2.99 (m, 2H), 2.67 (q, J = 7.6 Hz, 2H), 2.20 (s, 6H), 2.06 (s, 3H), 1.21 (t, J = 7.6 Hz, 3H), 1.15 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 151.03, 142.75, 142.58, 139.16, 137.63, 137.14, 134.61, 129.22, 129.11, 129.06, 128.55, 127.91, 127.40, 127.12, 122.01, 70.78, 47.33, 44.45, 24.65, 20.58, 17.56, 14.87.



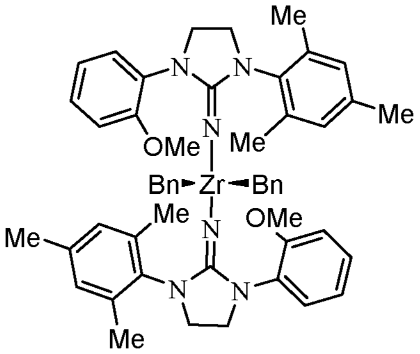
[0111] **Synthesis of Tribenzyl((1,3-dimesitylimidazolidin-2-ylidene)amino)zirconium:** In a nitrogen-filled glovebox, a solution of 1,3-dimesitylimidazolidin-2-imine (0.120 g, 0.373 mmol, 1 equiv.) in benzene-d^6 (1.5 mL) was added to a solution of $ZrBn_4$ (0.170 g, 0.373 mmol, 1 equiv.) in benzene-d^6 (1.5 ml). The solution was stirred at room temperature for 1 hour. The solution was concentrated *in vacuo* to yield a thick yellow oil. The oil was dissolved in toluene (0.75 mL), layered with hexane (6 mL), and stored in a -30°C freezer, resulting in the precipitation of a solid. The material was filtered, washed with cold hexanes, and dried *in vacuo* to yield the product as a yellow solid (0.187 g, 73% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 6.97 (dd, J = 8.1, 7.0 Hz, 6H), 6.87 – 6.80 (m, 3H), 6.77 (s, 4H), 6.27 – 6.15 (m, 6H), 3.09 (s, 4H), 2.24 (s, 12H), 2.05 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 146.75, 142.47, 137.64, 137.21, 134.53, 129.70, 129.25, 126.58, 121.49, 59.62, 44.50, 20.60, 17.62.



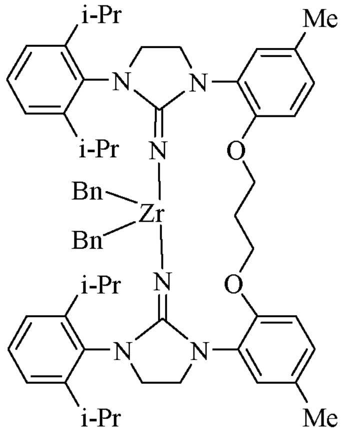
[0112] **Synthesis of Dibenzyl[bis-((1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-ylidene)amino)]zirconium:** In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-imine (50 mg, 0.135 mmol, 1 equiv.) in toluene-d^8 (2 mL) was added dropwise to a stirring solution of tribenzyl((1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-ylidene)amino)zirconium (99 mg, 0.135 mmol, 1 equiv.) in toluene-d^8 (2 mL). The reaction was allowed to stir 50°C for 15 hours. The yellow solution was concentrated *in vacuo*, yielding a thick yellow oil. The material was redissolved in toluene (0.5 mL), layered with hexane (10 mL), and stored in a -30°C freezer for 3 days. The material was filtered, washed with minimal -30°C hexanes, and dried *in vacuo* to afford the product as an off-white solid (70 mg, 51% yield). NMR spectra were complex and showed evidence of multiple isomers, oligomers, or loss of molecular symmetry as apparent from the multiple mesityl methyl peaks.



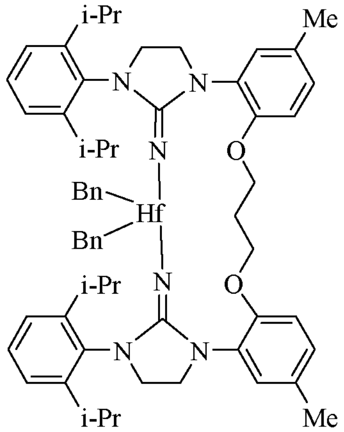
[0113] **Synthesis of Dibenzyl[bis-((1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-ylidene)amino)]hafnium:** In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-imine (50 mg, 0.135 mmol, 1 equiv.) in toluene-d^8 (2 mL) was added dropwise to a stirring solution of tribenzyl((1-mesityl-3-(2-phenoxyphenyl)imidazolidin-2-ylidene)amino)hafnium (111 mg, 0.135 mmol, 1 equiv.) in toluene-d^8 (2 mL). The reaction was allowed to stir 50°C for 15 hours. The yellow solution was concentrated *in vacuo*, yielding a thick yellow oil. The material was redissolved in toluene (0.5 mL), layered with hexane (10 mL), and stored in a -30°C freezer for 3 days. The material was filtered, washed with minimal -30°C hexanes, and dried *in vacuo* to afford the product as an off-white solid. Yield was low so another crop was obtained by concentrating the filtrate *in vacuo*, layering with hexane (5 mL), and storing in a -30°C for 16 h. The material was filtered, washed with minimal -30°C hexanes, and dried *in vacuo* to afford the product as an off-white solid. Combined yield 55 mg, 37%. NMR spectra were complex and showed evidence of multiple isomers, oligomers, or loss of molecular symmetry as apparent from the multiple mesityl methyl peaks.



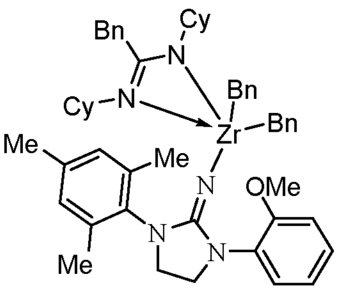
[0114] **Synthesis of Dibenzyl(bis(1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)zirconium:** In a nitrogen-filled glovebox, a solution of 1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-imine (46 mg, 0.149 mmol, 1 equiv.) in toluene-d^8 (0.5 mL) was added dropwise to a stirring solution of tribenzyl((1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)zirconium (100 mg, 0.149 mmol, 1 equiv.) in toluene-d^8 (0.5 mL) at 100°C. The ligand solution vial was rinsed with toluene-d^8 (0.5 mL), and this was also added to the stirring reaction The reaction was allowed to stir 100°C for 62 hours. The solution was allowed to cool to room temperature and concentrated *in vacuo*, yielding a thick oil. The material was dissolved in toluene (0.3 mL), layered with hexane (3 mL), and stored in a -30°C freezer for 2 days, resulting in the precipitation of a powder. The material was filtered, washed with minimal -30°C hexanes, and dried *in vacuo* to afford the product as an orange solid (63 mg, 48% yield). NMR spectra were complex and showed evidence of multiple isomers, oligomers, or loss of molecular symmetry as apparent from the multiple mesityl methyl peaks.



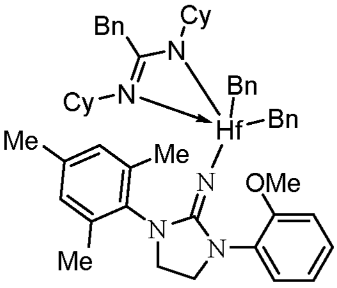
[0115] **Synthesis of Dibenzyl(3,3'-((propane-1,3-diylbis(oxy))bis(5-methyl-2,1-phenylene))bis(1-(2,6-diisopropylphenyl)imidazolidin-2-amino)zirconium:** In a nitrogen-filled glovebox, a solution of $ZrBn_4$ (55 mg, 0.121 mmol, 1 equiv.) in toluene-d^8 (2 mL) was added dropwise over several minutes to a stirring solution of 3,3'-((propane-1,3-diylbis(oxy))bis(5-methyl-2,1-phenylene))bis(1-(2,6-diisopropylphenyl)imidazolidin-2-imine) (100 mg, 0.121 mmol, 1 equiv.) in toluene-d^8 (2 mL) at 100°C. The solution was allowed to stir at 100°C for 18 h. The reaction was stirred at 100°C for an additional 18 h, however little change was observed from the previous spectrum. The solution was passed through a syringe filter, and all volatiles were removed *in vacuo* to yield a thick oil. The oil was dissolved in toluene (0.3 mL), layered with hexane (3 mL), and stored in a -30 C freezer for 2 days. The precipitated solid was filtered, washed with cold hexane, and dried *in vacuo* to yield the product as a beige solid (65 mg, 53% yield). NMR spectra were complex and showed evidence of multiple isomers, oligomers, or loss of molecular symmetry.



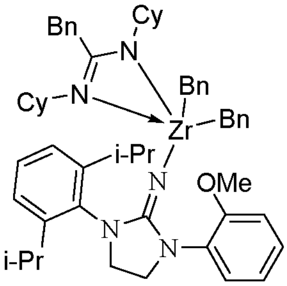
[0116] **Synthesis of Dibenzyl(3,3'-((propane-1,3-diylbis(oxy))bis(5-methyl-2,1-phenylene))bis(1-(2,6-diisopropylphenyl)imidazolidin-2-amino)hafnium:** In a nitrogen-filled glovebox, a solution of 3,3'-((propane-1,3-diylbis(oxy))bis(5-methyl-2,1-phenylene))bis(1-(2,6-diisopropylphenyl)imidazolidin-2-imine) (0.500 g, 0.603 mmol, 1 equiv.) in toluene (2.5 mL) was added to a solution of $HfBn_4$ (0.327 g, 0.603 mmol, 1 equiv.) in toluene (2.5 mL). Soon after addition, a powder precipitated from solution. The reaction was stirred at room temperature for 90 h. The suspension was filtered, washed with toluene (4x5 mL), and concentrated *in vacuo* to yield a thick brown oil. The oil was dissolved in toluene (2 mL), layered with hexanes (18 mL), and stored in a -30°C freezer for 18 h, resulting in the precipitation of a solid. The material was filtered, washed with cold hexanes, and dried *in vacuo* to yield the product as a white solid (0.386 g, 58% yield). NMR spectra were complex and showed evidence of multiple isomers, oligomers, or loss of molecular symmetry.



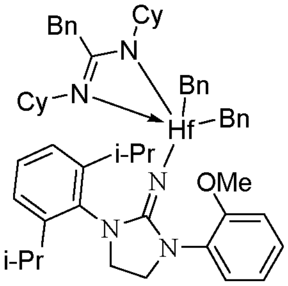
[0117] **Synthesis of Dibenyl(1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino))(cyclohexyl(1-(cyclohexylimino)-2-phenylethyl)amido)zirconium :** In a nitrogen-filled glovebox, a solution of DCC (31 mg, 0.149 mmol, 1 equiv.) in benzene-d[6] (0.7 mL) was added to a solution of tribenzyl((1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)zirconium (100 mg, 0.147 mmol, 1 equiv.) in benzene-d[6] (0.7 mL). The reaction was stirred at room temperature for 2 h. Multiple isomers appear to be present, however there is a clear major isomer (>80%). All volatiles were removed *in vacuo*, yielding a thick oil. The material was dissolved in toluene (0.5 mL), layered with hexanes (4 mL) and stored in a -30°C freezer for 64 hours, yielding a crystalline solid. The material was filtered, washed with cold (-30°C) hexanes, and dried *in vacuo* to yield the product as a pale yellow solid (84.5 mg, 65% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.84 (dd, J = 7.8, 1.8 Hz, 1H), 7.25 – 6.83 (m, 17H), 6.75 (s, 2H), 6.55 (dd, J = 8.2, 1.4 Hz, 1H), 3.67 – 3.59 (m, 2H), 3.45 (s, 2H), 3.37 (s, 3H), 3.24 – 3.16 (m, 2H), 2.90 (tt, J = 10.8, 4.4 Hz, 2H), 2.25 (s, 6H), 2.25 (d, J = 10.3 Hz, 2H), 2.06 (s, 3H), 1.80 (d, J = 10.3 Hz, 2H), 1.61 – 0.92 (m, 20H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 176.37, 154.93, 147.80, 145.71, 137.04, 136.86, 136.21, 135.06, 130.24, 129.06, 128.87, 128.62, 127.99, 127.86, 127.28, 126.80, 126.30, 120.71, 119.95, 111.52, 66.28, 56.73, 54.63, 45.96, 44.73, 34.83, 31.17, 25.96, 25.37, 20.62, 18.23.



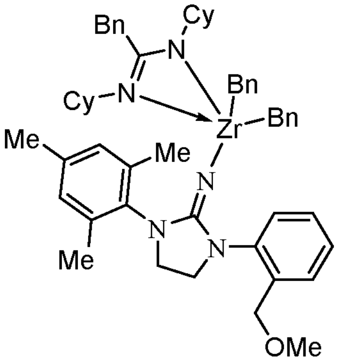
[0118] **Synthesis of Dibenzyl(1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino))(cyclohexyl(1-(cyclohexylimino)-2-phenylethyl)amido)hafnium:** In a nitrogen-filled glovebox, a solution of DCC (27 mg, 0.132 mmol, 1 equiv.) in benzene-d[6] (0.7 mL) was added to a solution of tribenzyl((1-mesityl-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)hafnium (100 mg, 0.132 mmol, 1 equiv.) in benzene-d[6] (0.7 mL). The reaction was stirred at room temperature for 17 h. All volatiles were removed *in vacuo*, yielding a thick oil. The material was dissolved in toluene (0.4 mL), layered with hexanes (4 mL) and stored in a -30°C freezer for 17 hours, resulting in the precipitation of a solid. The material was filtered, washed with cold (-30°C) hexanes, and dried *in vacuo* to yield the product as a white solid (65 mg, 51% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.79 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.28 – 7.22 (m, 4H), 7.18 – 7.05 (m, 6H), 7.03 – 6.94 (m, 4H), 6.93 – 6.86 (m, 3H), 6.75 (s, 2H), 6.55 (dd, *J* = 8.2, 1.4 Hz, 1H), 3.68 – 3.59 (m, 2H), 3.41 (s, 2H), 3.36 (s, 3H), 3.24 – 3.15 (m, 2H), 3.05 (ddd, *J* = 10.9, 6.6, 4.3 Hz, 2H), 2.23 (s, 6H), 2.07 (s, 3H), 1.96 (d, *J* = 11.2 Hz, 2H), 1.58 (d, *J* = 11.2 Hz, 2H), 1.56 – 0.88 (m, 20H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 176.26, 154.91, 149.02, 148.43, 137.09, 136.69, 135.91, 135.08, 130.24, 129.02, 128.98, 128.67, 127.93, 127.75, 127.54, 126.66, 126.40, 120.77, 120.16, 111.43, 74.07, 56.52, 54.61, 45.71, 44.48, 34.66, 31.39, 25.93, 25.28, 20.65, 18.22.



[0119] **Synthesis of Dibenzyl((1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)(cyclohexyl(1-(cyclohexylimino)-2-phenylethyl)amido)zirconium:** In a nitrogen-filled glovebox, a solution of DCC (29 mg, 0.140 mmol, 1 equiv.) in benzene-d^6 (0.7 mL) was added to a solution of tribenzyl((1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)zirconium (100 mg, 0.140 mmol, 1 equiv.) in benzene-d^6 (0.7 mL). The reaction was stirred at room temperature for 17 h. All volatiles were removed *in vacuo*, yielding a thick oil. The material was dissolved in toluene (0.4 mL), layered with hexanes (4 mL) and stored in a -30°C freezer for 15 hours, resulting in the precipitation of a solid. The material was filtered, washed with cold (-30°C) hexanes, and dried *in vacuo* to yield the product as a white solid (88 mg, 68% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.73 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.27 – 6.78 (m, 20H), 6.51 (dd, *J* = 8.2, 1.4 Hz, 1H), 3.65 – 3.58 (m, 2H), 3.53 – 3.42 (m, 4H), 3.41 (s, 2H), 3.36 (s, 3H), 2.83 (tt, *J* = 11.1, 4.0 Hz, 2H), 2.16 (d, *J* = 10.4 Hz, 2H), 1.94 (d, *J* = 10.4 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 6H), 1.14 (d, *J* = 6.8 Hz, 6H), 1.55 – 0.88 (m, 20H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 175.85, 155.03, 148.07, 147.84, 147.00, 136.18, 135.36, 130.33, 130.04, 128.91, 128.57, 128.47, 128.05, 127.40, 127.28, 126.28, 124.02, 121.00, 120.20, 111.30, 65.67, 56.68, 54.67, 47.86, 46.33, 34.53, 31.53, 28.37, 25.95, 25.69, 25.36, 23.80.

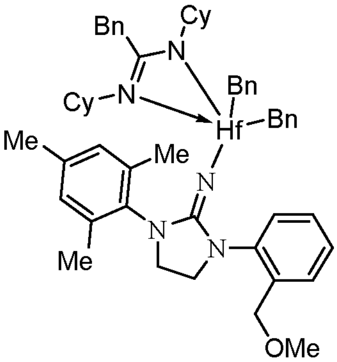


[0120] **Synthesis of Dibenzyl((1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)(cyclohexyl(1-(cyclohexylimino)-2-phenylethyl)amido)hafnium:** In a nitrogen-filled glovebox, a solution of DCC (26 mg, 0.125 mmol, 1 equiv.) in benzene-d^6 (0.7 mL) was added to a solution of tribenzyl((1-(2,6-diisopropylphenyl)-3-(2-methoxyphenyl)imidazolidin-2-ylidene)amino)hafnium (100 mg, 0.125 mmol, 1 equiv.) in benzene-d^6 (0.7 mL). The reaction was stirred at room temperature for 17 h. All volatiles were removed *in vacuo*, yielding a thick oil. The material was dissolved in toluene (0.4 mL), layered with hexanes (4 mL) and stored in a -30°C freezer for 17 hours, resulting in the precipitation of a solid. The material was filtered, washed with cold (-30°C) hexanes, and dried *in vacuo* to yield the product as a white solid (87 mg, 69% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.63 (dd, J = 7.7, 1.8 Hz, 1H), 7.26 (dd, J = 8.1, 7.1 Hz, 4H), 7.21 – 7.04 (m, 10H), 7.02 – 6.88 (m, 5H), 6.84 (td, J = 7.6, 1.4 Hz, 1H), 6.51 (dd, J = 8.2, 1.3 Hz, 1H), 3.72 – 3.57 (m, 2H), 3.51 – 3.41 (m, 4H), 3.39 (s, 2H), 3.36 (s, 3H), 2.97 (tt, J = 11.1, 4.1 Hz, 2H), 1.84 (d, J = 11.4 Hz, 2H), 1.71 (d, J = 11.4 Hz, 2H), 1.36 (d, J = 6.8 Hz, 6H), 1.15 (d, J = 6.8 Hz, 6H), 1.53 – 0.89 (m, 20H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 175.45, 155.23, 150.50, 148.61, 148.17, 135.90, 135.42, 130.54, 130.18, 128.91, 128.59, 128.31, 128.06, 127.76, 127.72, 126.36, 123.95, 121.15, 120.37, 111.23, 73.80, 56.47, 54.71, 47.70, 45.99, 34.33, 31.70, 28.33, 25.92, 25.63, 25.32, 23.80.



[0121] **Synthesis of Dibenzyl((1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-ylidene)amino)(cyclohexyl(1-(cyclohexylimino)-**

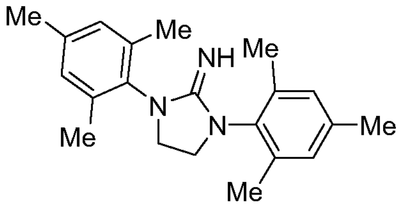
2-phenylethyl)amido)zirconium: In a nitrogen-filled glovebox, a solution of DCC (30 mg, 0.146 mmol, 1 equiv.) in benzene-d^6 (0.7 mL) was added to a solution of tribenzyl((1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-ylidene)amino)zirconium (100 mg, 0.146 mmol, 1 equiv.) in benzene-d^6 (0.7 mL). The reaction was stirred at room temperature for 18 h. All volatiles were removed *in vacuo*, yielding a thick oil. Hexamethyldisiloxane (4 mL) was added, and the mixture was vigorously stirred for 3 h. The resulting suspension was stored in a -30°C freezer for 16 h, resulting in the precipitation of a yellow solid. The material was filtered, washed with cold (-30°C) hexanes, and dried *in vacuo* to yield the product as a yellow solid (42 mg, 32% yield). Material contained approximately 0.3 equiv. of hexamethyldisiloxane. ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.38 (d, J = 6.9 Hz, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.24 – 7.06 (m, 11H), 7.03 – 6.96 (m, 4H), 6.89 (t, J = 7.2 Hz, 2H), 6.77 (s, 2H), 4.62 (s, 2H), 3.46 – 3.40 (m, 4H), 3.25 (s, 3H), 3.19 – 3.12 (m, 2H), 2.94 – 2.82 (m, 2H), 2.28 (s, 6H), 2.13 (d, J = 10.4 Hz, 2H), 2.08 (s, 3H), 1.83 (d, J = 10.5 Hz, 2H), 1.63 – 0.87 (m, 20H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 176.30, 148.64, 145.46, 140.25, 137.01, 136.85, 136.27, 135.58, 134.96, 130.23, 129.22, 128.61, 128.56, 127.92 (2 carbons), 127.09, 126.72, 126.29, 126.12, 119.85, 72.22, 66.14, 58.30, 56.77, 47.84, 44.75, 34.76, 31.40, 25.90, 25.33, 20.62, 18.31.



[0122] **Synthesis of Dibenzyl((1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-ylidene)amino)(cyclohexyl(1-(cyclohexylimino)-2-phenylethyl)amido)hafnium:** In a nitrogen-filled glovebox, a solution of DCC (27 mg, 0.129 mmol, 1 equiv.) in benzene-d^6 (0.7 mL) was added to a solution of tribenzyl((1-mesityl-3-(2-(methoxymethyl)phenyl)imidazolidin-2-ylidene)amino)hafnium (**CS-255**) (100 mg, 0.129 mmol, 1 equiv.) in benzene-d^6 (0.7 mL). The reaction was stirred at room temperature for 18 h. All volatiles were removed *in vacuo*, yielding a thick oil. The material was dissolved in toluene (0.2 mL) and hexanes (4 mL) was added dropwise. The vial was stored in a -30°C freezer for 6 days, resulting in the precipitation of a white powder. The material was filtered, washed with cold (-30°C) hexanes, and dried *in vacuo* to yield the product as a white solid (63 mg, 50% yield). ^{1}H NMR (400 MHz, Benzene-d_6) δ 7.36 (dd, J = 7.7, 1.6 Hz, 1H), 7.28 – 7.20 (m, 5H), 7.17 – 7.06 (m, 8H), 7.01 – 6.94 (m, 3H), 6.88 (t, J = 7.3 Hz, 2H), 6.78 (s, 2H), 4.59 (s, 2H), 3.50 – 3.38 (m, 4H), 3.27 (s, 3H), 3.16 (t, J = 7.9 Hz, 2H), 3.09 – 2.95 (m, 2H), 2.27 (s, 6H), 2.09 (s, 3H), 1.84 (d, J = 11.3 Hz, 2H), 1.61 (d, J = 11.3 Hz, 2H), 1.56 – 0.84 (m, 20H). ^{13}C NMR (101 MHz, Benzene-d_6) δ 175.98, 149.51, 148.55, 140.36, 136.92 (2 carbons), 136.05, 135.22, 135.07, 130.27, 129.19, 128.62 (2 carbons), 127.92, 127.60, 127.33, 126.38, 126.35, 125.83, 119.98, 73.06, 72.49, 58.46, 56.58, 47.51, 44.52, 34.66, 31.69, 25.88, 25.28, 20.63, 18.28.

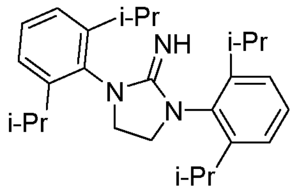
[0123] Polymerization results are presented in Tables 2-24, below. In these tables, “Metal” refers to the metal-containing precursor that reacts with the ligand to form the metal-ligand complex; “Metal (µmol)” refers to the amount of the metal-containing precursor in micromoles; “Co-catalyst” refers to the identity of the co-catalyst, which is either tetrakis(pentafluorophenyl)borate(1-) amine (“RIBS-2”) or tris(pentafluorophenyl)borane (FAB); “Co-Catalyst (µmol)” refers to the amount of the co-catalyst in micromoles; “Ligand (µmol)” refers to the amount of ligand in micromoles; “L:M” is the molar ratio of ligand to metal; “MMAO (µmol)” refers to the amount of modified methylalumoxane in micromoles; “octene (mol %)” refers to the amount of octene expressed in mole percent based to the total moles of ethylene and octene; “Mn” refers to the number average molecular weight in grams/mole; “Mw” refers to the weight average molecular weight in grams/mole; “MWD” is the molecular weight dispersity (ratio of weight average molecular weight to number average molecular weight).

Table 2, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	7.9	287	27469	95.71
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	7.7	240	16043	66.85
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	8.3	223	9821	44.04
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	9.9	239	2311	9.67
$Hf(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	10.0	4085	251255	61.51
$Hf(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	12.3	3429	105746	30.84
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.2	2:1	0.5	7.7	213	47859	224.69
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.2	2:1	0.5	7.7	211	44240	209.67
Controls										
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5	5.0	4408	277379	62.93
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5	5.0	4162	298918	71.82

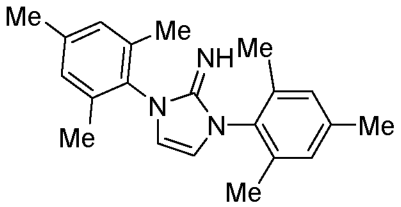
Table 3, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
$Hf(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	15.3	2339	50399	21.55

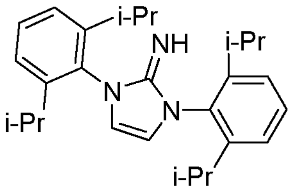
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	14.9	2495	71116	28.50
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	7.1	1570	10407	6.63
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	6.9	14.81	8209	5.54
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.5	5.4	3152	25721	8.16
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.5	5.5	2853	14477	5.07
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.5	6.7	1569	7821	4.98
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.5	6.1	1668	7751	4.65
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.4	6851	253328	36.98
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.8	3980	267407	67.19

Table 4, Ligand =



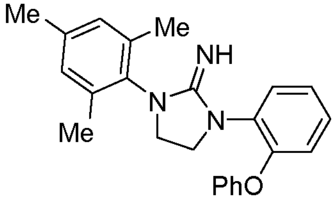
Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5		3685	186766	50.68
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5		5972	306225	51.28
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	7.8	835	52180	62.49
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	7.3	860	33942	39.47
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.5	5.9	692	57701	83.38
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.5	6.5	704	62612	88.94
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.4	6851	253328	36.98
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.8	3980	267407	67.19

Table 5, Ligand =



Metal	Metal (μmol)	Co-catalyst	Co-catalyst (μmol)	Ligand (μmol)	L:M	MMAO (μmol)	Octene (mol %)	Mn	Mw	MWD
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.503	7.9	1789	4650	2.6
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.503	10.2	1702	4587	2.7
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	13.5	1735	22732	13.1
Hf(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	17.4	2106	25935	12.31
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	7.4	1213	7865	6.48
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	8.8	1160	6778	5.84
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.503	16.8	1127	2715	2.41
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.2	2:1	0.503	22.9	1088	2443	2.25
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.503	4.5	4323	288214	66.67
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.503	4.1	6348	315797	49.75

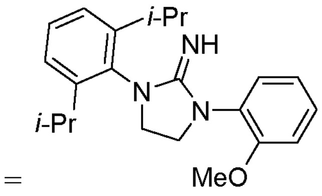
Table 6, Ligand =



Metal	Metal (μmol)	Co-catalyst	Co-catalyst (μmol)	Ligand (μmol)	L:M	MMAO (μmol)	Octene (mol %)	Mn	Mw	MWD
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	6.0	1263	54011	42.76

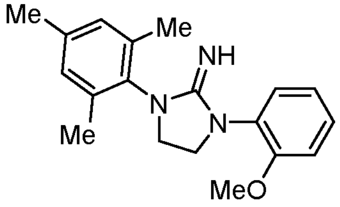
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	6.6	1290	72808	56.44
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.503	4.5	4323	288214	66.67
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.503	4.1	6348	315797	49.75

Table 7, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.5	3810	226248	59.38
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.4	3565	234785	65.86
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	5.0	4886	280795	57.47
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.6	6980	286837	41.09

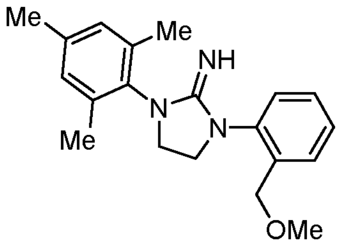
Table 8, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	3.8	7357	354560	48.19

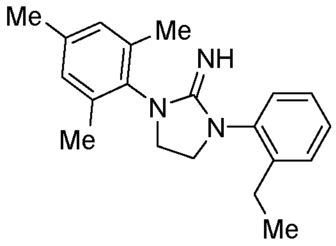
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.8	4522	407757	90.17
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	5.0	4886	280795	57.47
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.6	6980	286837	41.09

Table 9, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	5.1	1556	107204	69.90
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	4.9	1554	90890	58.55
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.503	6.3	2424	208984	86.21
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.503	5.2	3784	349977	92.49

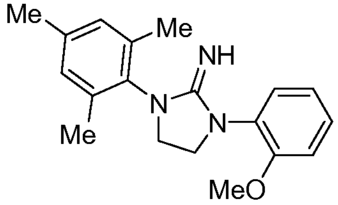
Table 10, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD

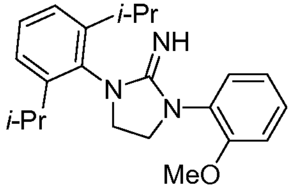
			(µmol)							
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	6.9	824	34664	42.07
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	6.9	908	28262	31.13
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.503	4.2	4803	348156	72.49
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.503	4.2	4071	351160	86.26

Table 11, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
Ti(Bn)$_4$	0.1	FAB	0.5	0.1	1:1	0.5	6.8	17220	164371	9.55
Ti(Bn)$_4$	0.1	FAB	0.5	0.1	1:1	0.5	5.5	16017	185601	11.59
Ti(Bn)$_4$	0.1	FAB	0.5	0.1	1:1	0.5	5.5	18717	184411	9.85
Ti(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	8.2	6246	271385	43.45
Ti(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	7.7	6484	296060	45.66
Ti(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	8.0	6277	260791	41.55

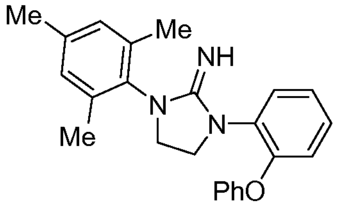
Table 12, Ligand =



Metal	Metal	Co-	Co-	Ligand	L:M	MMAO	Octene	Mn	Mw	MWD

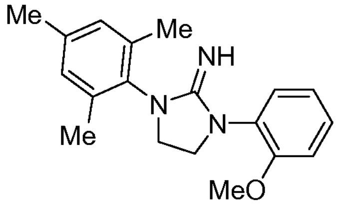
	(µmol)	catalyst	catalyst (µmol)	(µmol)		(µmol)	(mol %)			
Ti(Bn)$_4$	0.1	FAB	0.5	0.1	1:1	0.5	5.6	16455	134161	8.15
Ti(Bn)$_4$	0.1	FAB	0.5	0.1	1:1	0.5	5.5	14540	140411	9.66
Ti(Bn)$_4$	0.1	FAB	0.5	0.1	1:1	0.5	5.6	24904	148376	5.96
Ti(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	5.9	10136	314116	30.99
Ti(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	5.2	15281	362714	23.74
Ti(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	7.5	6629	312771	47.18

Table 13, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	5.5	2009	139890	69.63
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	6.3	2071	151688	73.24

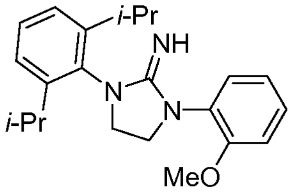
Table 14, Ligand =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD

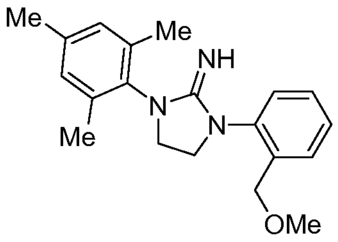
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.6	4770	330464	69.28
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.7	4550	307832	67.66
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.7	4553	338179	74.28
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.1	4666	317379	68.02
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.4	4855	306114	63.05
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	3.5	9812	342470	34.90
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.3	6466	292247	45.2
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	3.3	10238	324267	31.67
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.0	5831	317540	54.46

Table 15, Ligand =



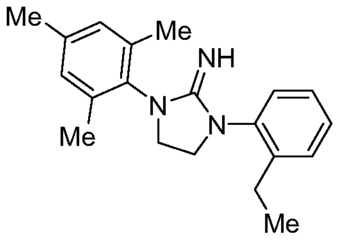
Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.7	3071	172521	56.18
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.6	3155	167132	52.97
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.6	3174	189859	59.82
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.3	3168	157421	49.69
Zr(Bn)$_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	4.3	3099	155668	50.23
Controls										
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	3.5	9812	342470	34.90
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.3	6466	292247	45.20
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	3.3	10238	324267	31.67
Zr(Bn)$_4$	0.1	RIBS-II	0.15			0.5	4.0	5831	317540	54.46

Table 16, Ligand =



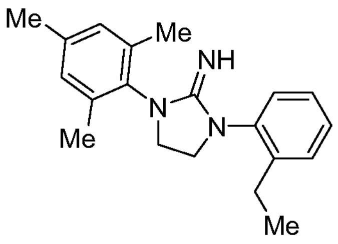
Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	4.6	1908	120613	63.21
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.503	5.2	1576	110406	70.05
Controls										
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.503	6.3	2424	208984	86.21
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.503	5.2	3784	349977	92.49

Table 17, Ligand =



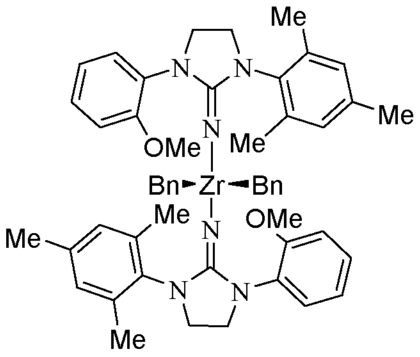
Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	8.1	904	29330	32.44
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	6.9	981	31533	32.14
$Zr(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	8.8	782	8299	10.61

Table 18, Ligand =



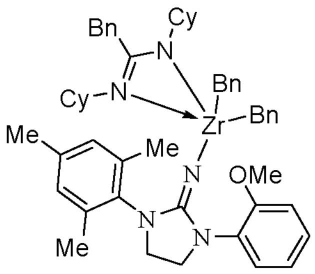
Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
$Hf(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	14.4	2950	91585	31.05
$Hf(Bn)_4$	0.1	RIBS-II	0.15	0.1	1:1	0.5	14.9	2814	56648	20.13

Table 19, Metal-Ligand Complex =



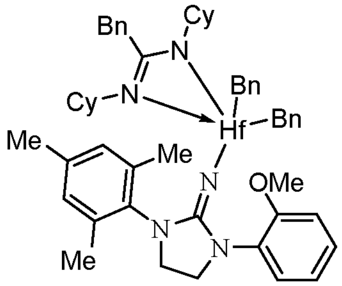
Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
--	0.1	RIBS-II	0.15	--	--	0.5	14.4	2950	91585	31.05
--	0.1	RIBS-II	0.15	--	--	0.5	14.9	2814	56648	20.13

Table 20, Metal-Ligand Complex =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
--	0.1	RIBS-II	0.15	--	--	0.5	1.5	41534	396801	9.55
--	0.1	RIBS-II	0.15	--	--	0.5	1.2	17700	309752	17.50
--	0.1	RIBS-II	0.15	--	--	0.5	1.0	43240	430695	9.96
Controls										
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5	3.7	9108	295644	32.46
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5	3.8	10039	276226	27.52

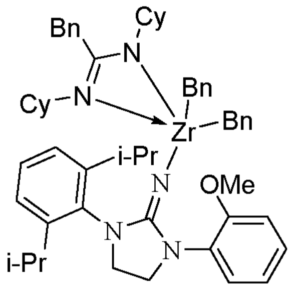
Table 21, Metal-Ligand Complex =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
--	0.1	RIBS-II	0.15	--	--	0.5		75931	239754	3.16

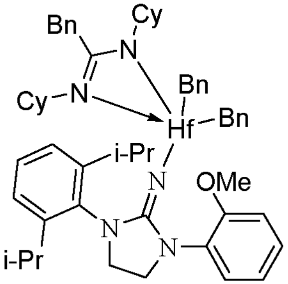
--	0.1	RIBS-II	0.15	--	--	0.5		65892	257734	3.91
--	0.1	RIBS-II	0.15	--	--	0.5		55711	228602	4.10
Controls										
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5		5139	367603	71.53
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5		4854	353604	72.85

Table 22, Metal-Ligand Complex =



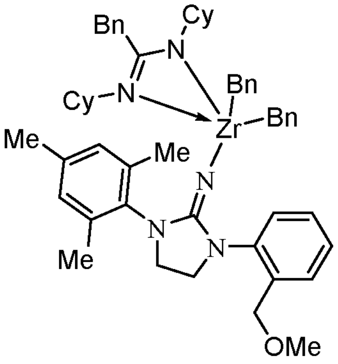
Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
--	0.1	RIBS-II	0.15	--	--	0.5		7644	241494	31.59
--	0.1	RIBS-II	0.15	--	--	0.5		54563	254407	4.66
Controls										
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5		5139	367603	71.53
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5		4854	353604	72.85

Table 23, Metal-Ligand Complex =



Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
--	0.1	RIBS-II	0.15	--	--	0.5		82507	229368	2.78
Controls										
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5		5139	367603	71.53
$Zr(Bn)_4$	0.1	RIBS-II	0.15			0.5		4854	353604	72.85

Table 24, Metal-Ligand Complex =

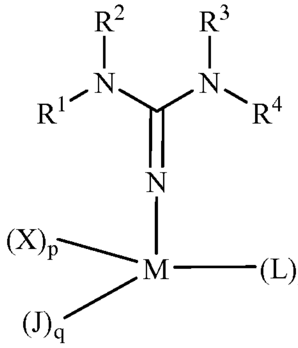


Metal	Metal (µmol)	Co-catalyst	Co-catalyst (µmol)	Ligand (µmol)	L:M	MMAO (µmol)	Octene (mol %)	Mn	Mw	MWD
--	0.1	RIBS-II	0.15	--	--	0.5	1.4	25355	468225	18.47

--	0.1	RIBS-II	0.15	--	--	0.5	1.4	57110	422197	7.39
--	0.1	RIBS-II	0.15	--	--	0.5	1.3	24212	379072	15.66
--	0.1	RIBS-II	0.15	--	--	0.5	2.1	16427	488105	29.71
--	0.1	RIBS-II	0.15	--	--	0.5	2.0	15796	529514	33.52
--	0.1	RIBS-II	0.15	--	--	0.5	1.9	19901	475700	23.90

CLAIMS

1. A metal-ligand complex of formula (I):



(I)

wherein

J is a monoanionic moiety selected from $(R^K)(R^L)(R^X)P{=}N$-, $(R^K)(R^L)C{=}N$-, $(R^K)((R^L)(R^X)N)C{=}N$-, $(R^K)(R^L)B$-O-, R^KO-, R^KS-, $R^KS(O)$-, $(R^K)(R^L)N$-, $(R^KN{=}C(R^L)$-$N(R^X))$-, $(R^K)(R^L)NO$-, $R^KC(O)O$-, $R^KC(O)NH$-, and $(R^K)(R^L)P$-, wherein each R^K, R^L, and R^X is independently is hydrogen, $(C_1$-$C_{40})$hydrocarbyl-, $((C_1$-$C_{15})$hydrocarbyl$)_3$Si-, $((C_1$-$C_{15})$hydrocarbyl$)_2$N-, or $(C_1$-$C_{40})$heterohydrocarbyl-;

L is independently at each occurrence halogen, hydrogen, $((C_1$-$C_{40})$hydrocarbyl)C(O)N(H)-, $((C_1$-$C_{40})$hydrocarbyl)C(O)N(H)$(C_1$-$C_{20})$hydrocarbyl-, $((C_1$-$C_{40})$hydrocarbyl)C(O)O-, $(C_1$-$C_{40})$hydrocarbyl-, $(C_1$-$C_{40})$heterohydrocarbyl-, $R^K(R^L)N$-, R^LO-, R^LS-, or $R^K(R^L)P$-, wherein each of R^K and R^L independently is as defined above; and each occurrence of L is a monoanionic moiety that is bonded to M;

M is a metal of any one of Groups 3, 4, 5, and 6 of a Periodic Table of the Elements, the metal being in a formal oxidation state of +2, +3, +4, +5, or +6;

R^1, R^2, R^3, and R^4 are independently at each occurrence hydrogen, $(C_1$-$C_{40})$hydrocarbyl-, $((C_1$-$C_{40})$hydrocarbyl)O-, $((C_1$-$C_{40})$hydrocarbyl)S-, $((C_1$-$C_{40})$hydrocarbyl$)_3$Si-, or $(C_1$-$C_{40})$heterohydrocarbyl-;

X is a neutral Lewis base group selected from $R^XN(R^K)(R^L)$, $R^X{=}N(R^K)$, $R^KO(R^L)$, $R^KS(R^L)$, and $R^XP(R^K)(R^L)$, wherein each of R^K , R^L, and R^X independently is as defined above;

p is 0, 1, 2, or 3, and q is 0 or 1, provided that the sum of p and q is at least 1;

r is 2 or 3;

two occurrences of L are optionally taken together to form a $(C_2$-$C_{40})$hydrocarbylene or (C_1-C_{40})heterohydrocarbylene, or $(R^D)_2C{=}C(R^D)-C(R^D){=}C(R^D)_2$, wherein each R^D independently is H, unsubstituted (C_1-C_6)alkyl, phenyl, or naphthyl;

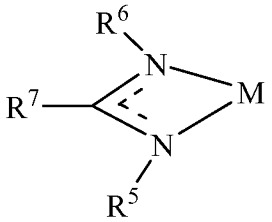
J and one of R^1, R^2, R^3, and R^4 are optionally taken together to form (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene;

one occurrence of L and one of R^1, R^2, R^3, and R^4 are optionally taken together to form (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene;

one occurrence of X and one of R^1, R^2, R^3, and R^4 are optionally taken together to form (C_1-C_{40})heterohydrocarbylene;

any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene;

X and J are optionally taken together to form a monoanionic bidentate moiety X-J, provided that when X-J is bound to M to form a fragment having the structure



,

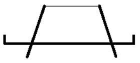
then R^5, R^6, and R^7 are each independently hydrogen, (C_1-C_{40})hydrocarbyl-, $((C_1-C_{40})$hydrocarbyl$)O$-, $((C_1-C_{40})$hydrocarbyl$)S$-, $((C_1-C_{40})$hydrocarbyl$)_3Si$-, or (C_1-C_{40})heterohydrocarbyl-; and provided that when X-J is bound to M via an anionic nitrogen and a Lewis base nitrogen, X-J and M form a four-membered metallocycle or a six-membered metallocycle; and

each of the above-mentioned (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, (C_2-C_{40})hydrocarbylene, and (C_1-C_{40})heterohydrocarbylene independently is the same or different and is unsubstituted or substituted with one or more substituents R^S selected from halogen, unsubstituted (C_1-C_{18})hydrocarbyl, F_3C-, FCH_2O-, F_2HCO-, F_3CO-, oxo, R_3Si-, RO-, RS-, RS(O)-, $RS(O)_2$-, R_2P-, R_2N-, $R_2C{=}N$-, NC-, RC(O)O-, ROC(O)-, RC(O)N(R)-, and $R_2NC(O)$-, wherein each R independently is an unsubstituted (C_1-C_{18})hydrocarbyl.

2. The metal-ligand complex of claim 1, wherein M is Ti, Zr, or Hf.

3. The metal-ligand complex of claim 1 or 2, wherein one of R^1 and R^2 and one of R^3

and R^4 are taken together to form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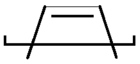
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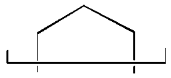
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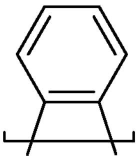
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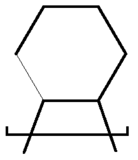
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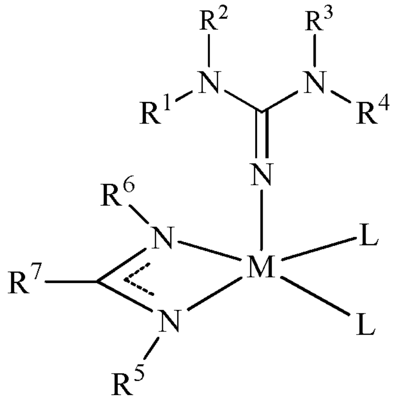
4. The metal-ligand complex of any of claims 1-3, having formula (II)



(II)

wherein

L, M, R^1, R^2, R^3, and R^4 are as defined in claim 1;

R^5, R^6, and R^7 are each independently hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})$hydrocarbyl)O-, $((C_1\text{-}C_{40})$hydrocarbyl)S-, $((C_1\text{-}C_{40})\text{hydrocarbyl})_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-;

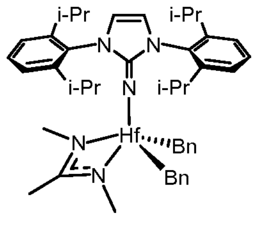
one occurrence of L and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene;

any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene;

one of R^5, R^6, and R^7 is optionally taken together with one of R^1, R^2, R^3, R^4, and L to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene; and

the two occurrences of L are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, or $(R^D)_2C{=}C(R^D)\text{-}C(R^D){=}C(R^D)_2$, wherein each R^D independently is H, unsubstituted $(C_1\text{-}C_6)$alkyl, phenyl, or naphthyl.

5. The metal-ligand complex of claim 4, comprising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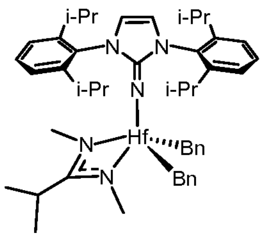
Bn
N
Bn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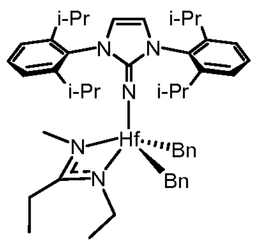
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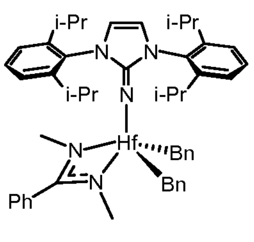
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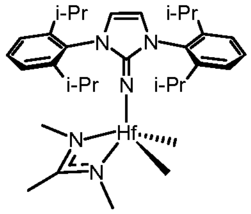
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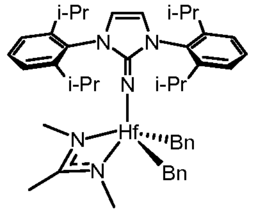
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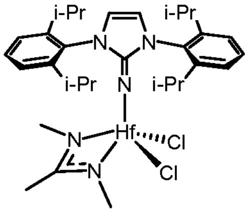
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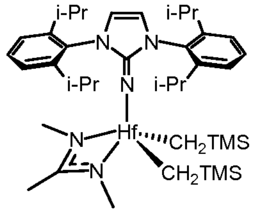
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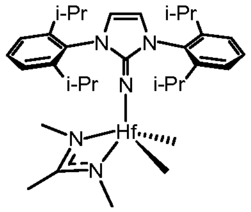
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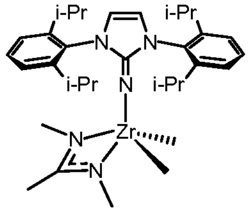
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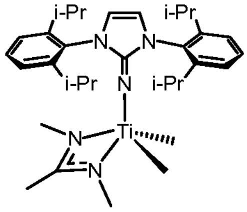
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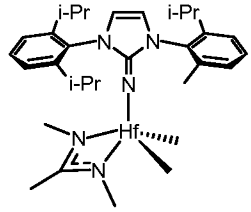
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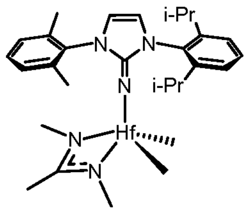
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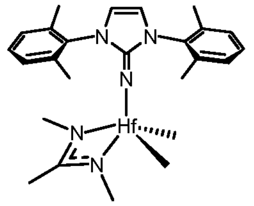
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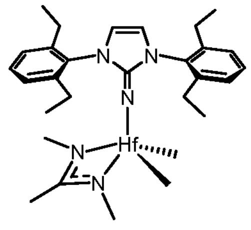
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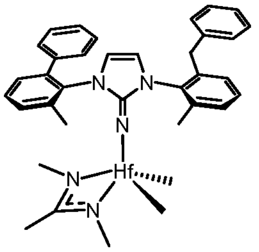
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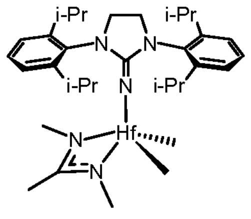
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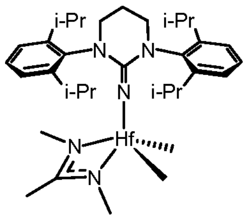
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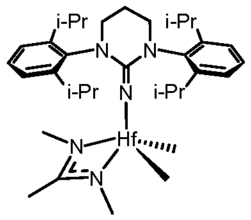
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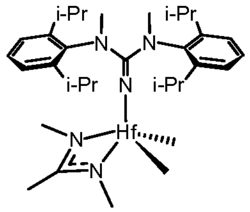
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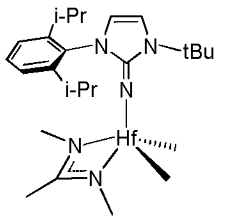
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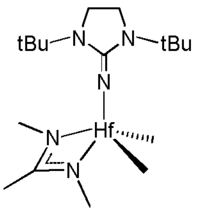
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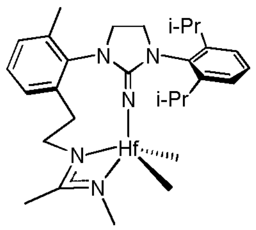
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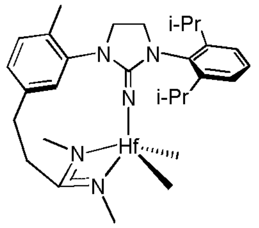
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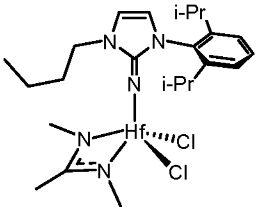
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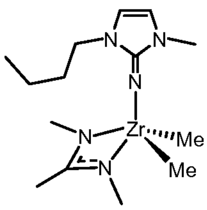
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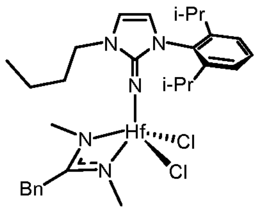
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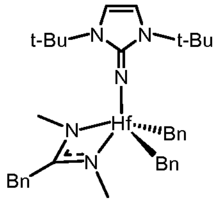
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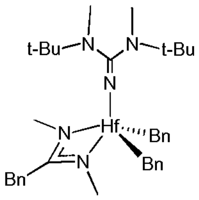
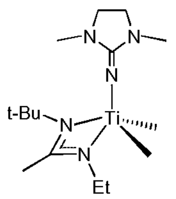
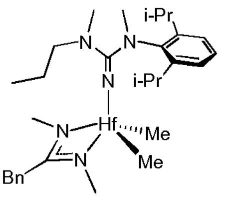
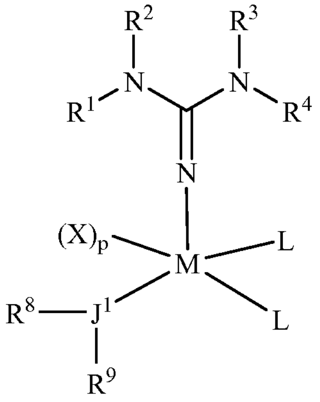






or a combination thereof.

6. The metal-ligand complex of any of claims 1-3, having formula (III)



(III)

wherein

L, M, p, R^1, R^2, R^3, R^4, and X are as defined in claim 1;

J^1 is N or P;

R^8 and R^9 are each independently hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})$hydrocarbyl)O-, $((C_1\text{-}C_{40})$hydrocarbyl)S-, $((C_1\text{-}C_{40})\text{hydrocarbyl})_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-;

one occurrence of L and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene;

the two occurrences of L are optionally taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene, or $(R^D)_2C=C(R^D)\text{-}C(R^D)=C(R^D)_2$, wherein each R^D independently is H, unsubstituted $(C_1\text{-}C_6)$alkyl, phenyl, or naphthyl;

any two of R^1, R^2, R^3, and R^4 optionally are taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene;

R^8 and R^9 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene;

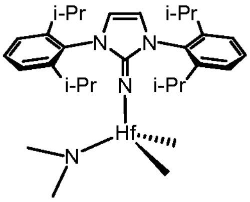
R^8 and R^9 are optionally taken together to form a group double bonded to J^1;

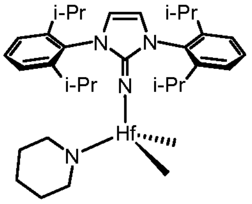
one of R^8 and R^9 is optionally taken together with one of R^1, R^2, R^3, R^4, and L to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene;

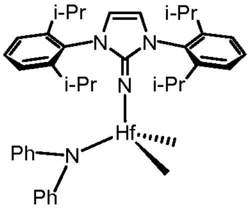
one of R^8 and R^9 is optionally covalently bonded to X; and

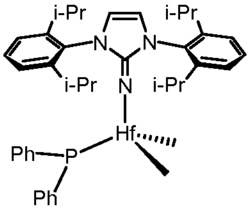
X and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_1\text{-}C_{40})$heterohydrocarbylene.

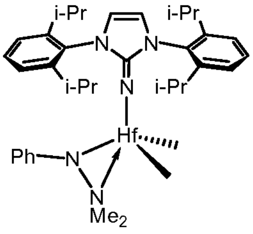
7. The metal-ligand complex of claim 6, comprising

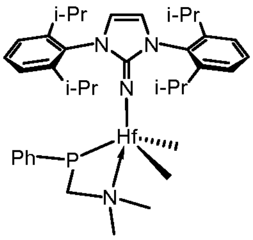


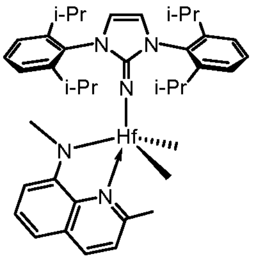


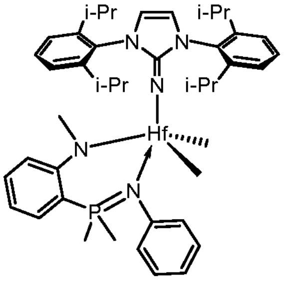


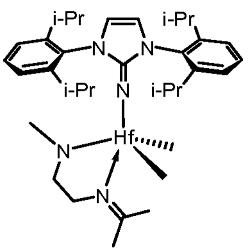


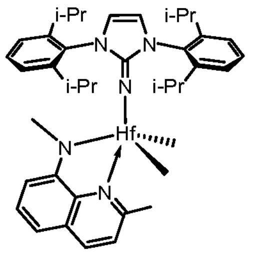


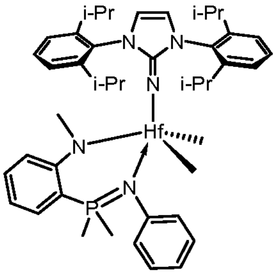


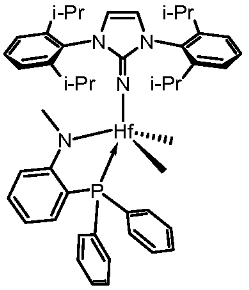


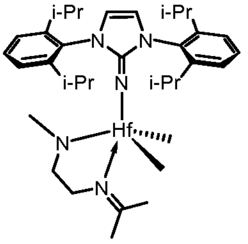


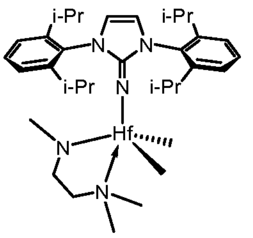


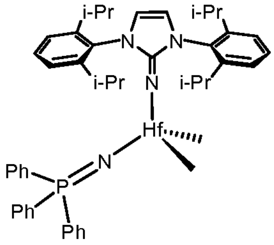


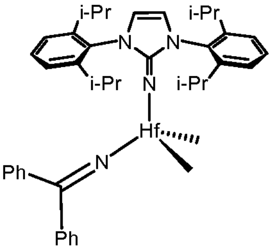


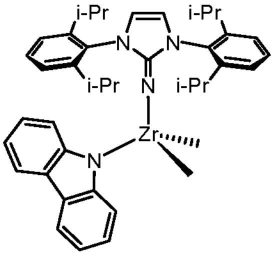


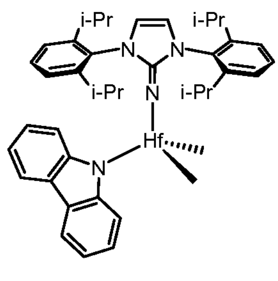


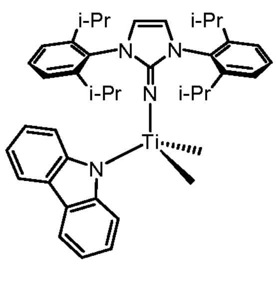


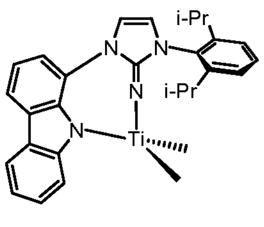


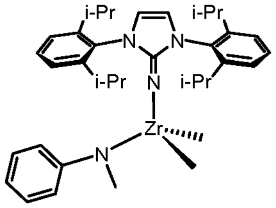


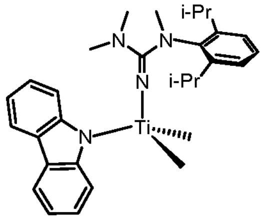


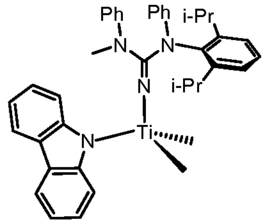


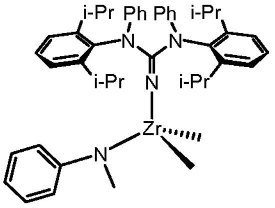






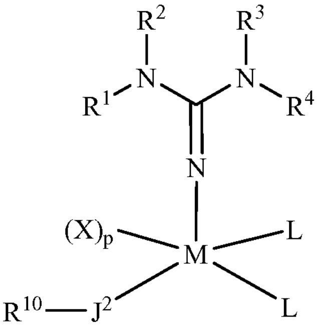






or a combination thereof.

8. The metal-ligand complex of any of claims 1-3, having formula (IV)



(IV)

wherein

L, M, p, R^1, R^2, R^3, R^4, and X are as defined in claim 1;

J^2 is O or S; and

R^{10} is $(C_1\text{-}C_{40})$hydrocarbyl-, $((C_1\text{-}C_{40})\text{hydrocarbyl})_3$Si-, or $(C_1\text{-}C_{40})$heterohydrocarbyl-;

one occurrence of L and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene;

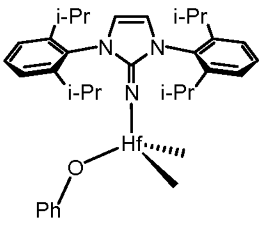
any two of R^1, R^2, R^3, and R^4 optionally are taken together to form a $(C_2\text{-}C_{40})$hydrocarbylene or $(C_1\text{-}C_{40})$heterohydrocarbylene;

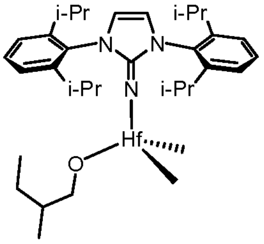
X and any one of R^1, R^2, R^3, and R^4 are optionally taken together to form $(C_1\text{-}C_{40})$heterohydrocarbylene; and

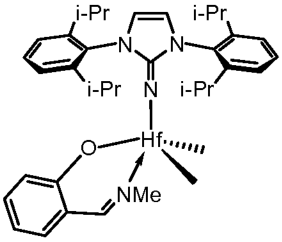
R^{10} is optionally taken together with one of R^1, R^2, R^3, R^4, and L to form a $(C_1\text{-}C_{40})$heterohydrocarbylene; and

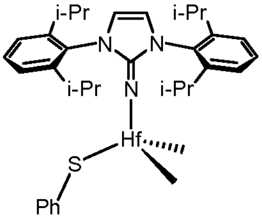
R^{10} is optionally covalently bonded to X.

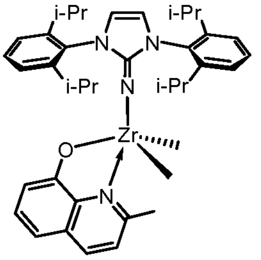
9. The metal-ligand complex of claim 8, comprising

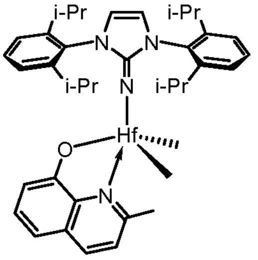


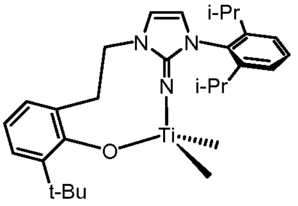


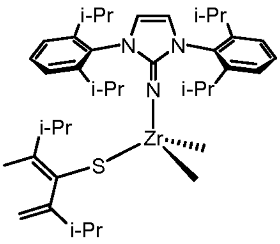


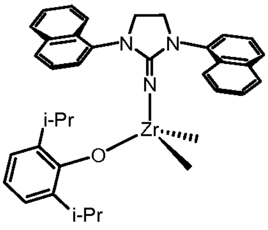


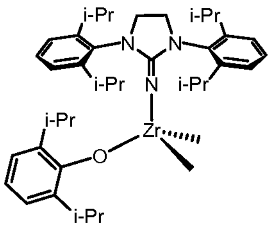


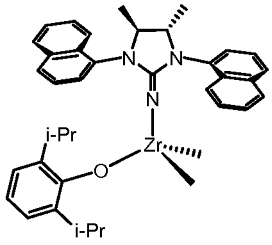


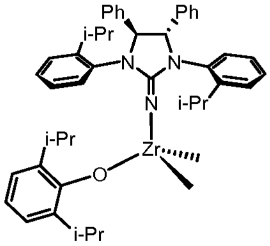


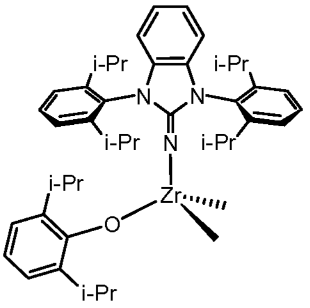






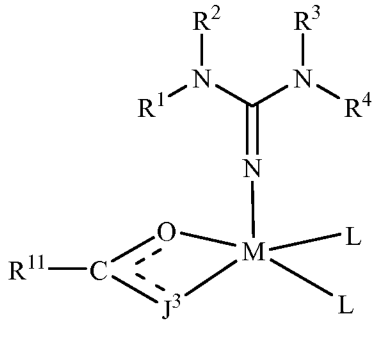






or a combination thereof.

10. The metal-ligand complex of any of claims 1-3, having formula (V)



(V)

wherein

L, M, R^1, R^2, R^3, and R^4 are as defined for formula (I);

J^3 is O or NR^{12};

R^{11} and R^{12} are each independently hydrogen, $(C_1\text{-}C_{40})$hydrocarbyl-, ((C$_1$-C$_{40}$)hydrocarbyl)O-, ((C$_1$-C$_{40}$)hydrocarbyl)S-, ((C$_1$-C$_{40}$)hydrocarbyl)$_3$Si-, or (C$_1$-C$_{40}$)heterohydrocarbyl-;

R^{11} and R^{12} are optionally taken together to form (C$_2$-C$_{40}$)hydrocarbylene or (C$_1$-C$_{40}$)heterohydrocarbylene;

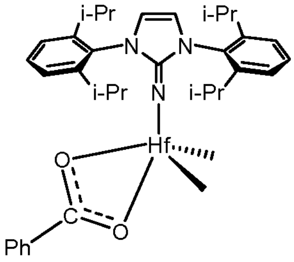
one of R^{11} and R^{12} is optionally taken together with one of R^1, R^2, R^3, R^4, and L to form a (C$_2$-C$_{40}$)hydrocarbylene or (C$_1$-C$_{40}$)heterohydrocarbylene;

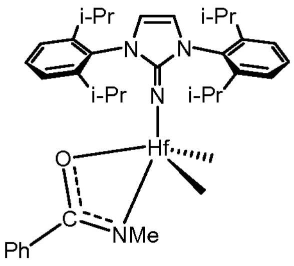
two occurrences of L are optionally taken together to form a (C$_2$-C$_{40}$)hydrocarbylene or (C$_1$-C$_{40}$)heterohydrocarbylene, or $(R^D)_2C=C(R^D)-C(R^D)=C(R^D)_2$, wherein each R^D independently is H, unsubstituted (C$_1$-C$_6$)alkyl, phenyl, or naphthyl;

one occurrence of L and one of R^1, R^2, R^3, and R^4 are optionally taken together to form (C$_2$-C$_{40}$)hydrocarbylene or (C$_1$-C$_{40}$)heterohydrocarbylene; and

any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a (C$_2$-C$_{40}$)hydrocarbylene or (C$_1$-C$_{40}$)heterohydrocarbylene.

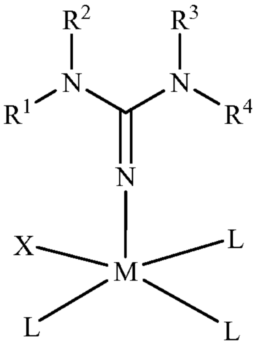
11. The metal-ligand complex of claim 10, comprising





or a combination thereof.

12. The metal-ligand complex of any of claims 1-3, having formula (VI)



(VI)

wherein

L, M, R^1, R^2, R^3, R^4, and X are as defined for formula (I);

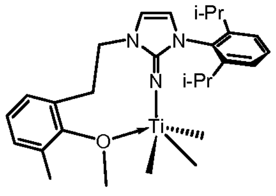
two occurrences of L are optionally taken together to form a (C$_2$-C$_{40}$)hydrocarbylene or (C_1-C_{40})heterohydrocarbylene, or $(R^D)_2C=C(R^D)-C(R^D)=C(R^D)_2$, wherein each R^D independently is H, unsubstituted (C_1-C_6)alkyl, phenyl, or naphthyl;

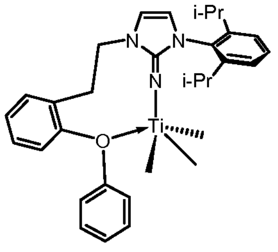
one occurrence of L and one of R^1, R^2, R^3, and R^4 are optionally taken together to form (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene;

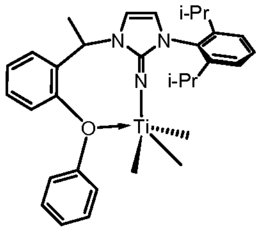
X and one of R^1, R^2, R^3, and R^4 are optionally taken together to form (C_1-C_{40})heterohydrocarbylene; and

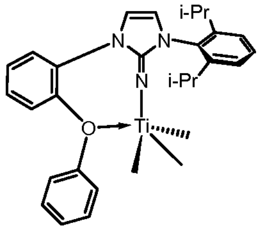
any two of R^1, R^2, R^3, and R^4 are optionally taken together to form a (C_2-C_{40})hydrocarbylene or (C_1-C_{40})heterohydrocarbylene.

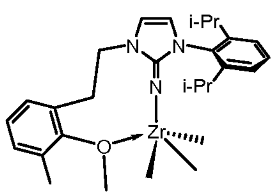
13. The metal ligand complex of claim 12, comprising

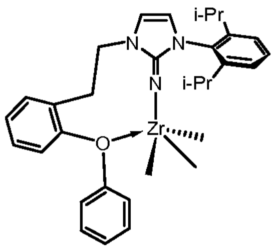


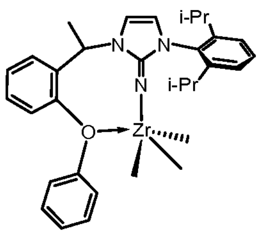


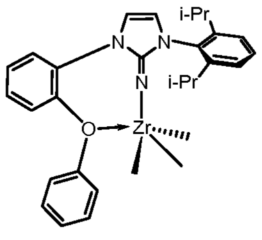


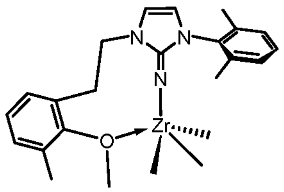


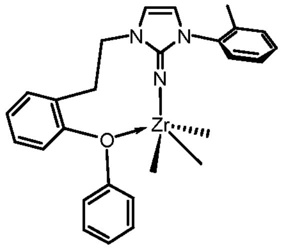


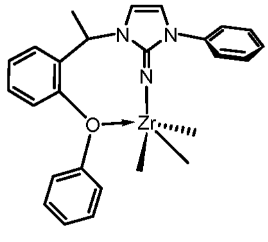


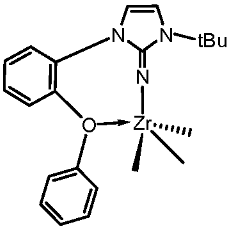


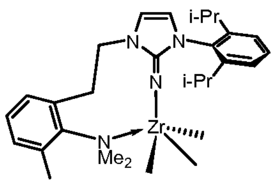


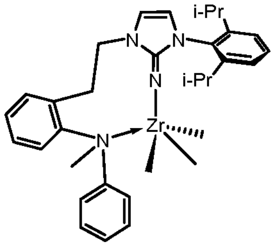


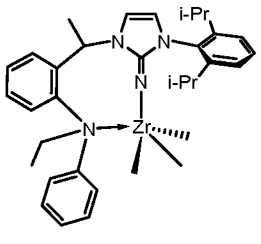


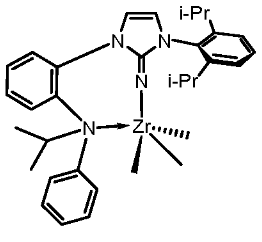


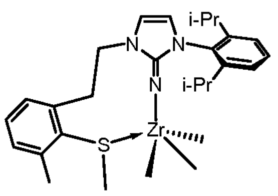


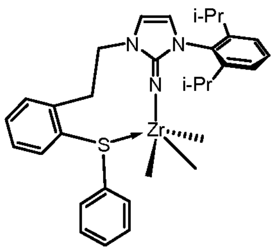


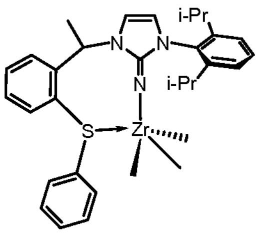


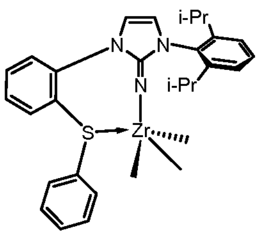


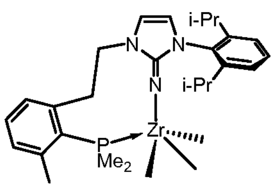


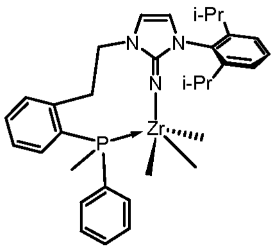


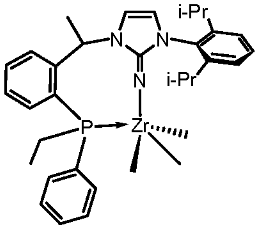


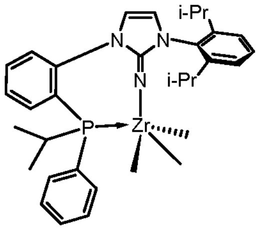


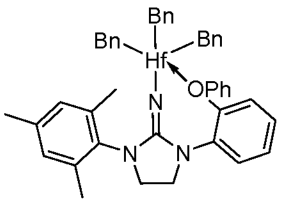






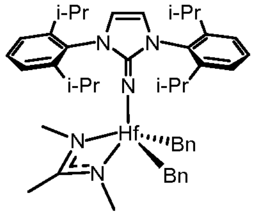


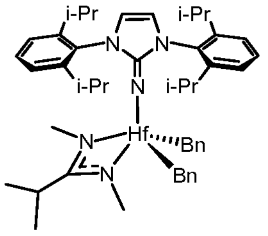


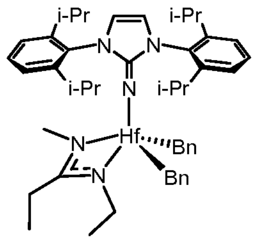


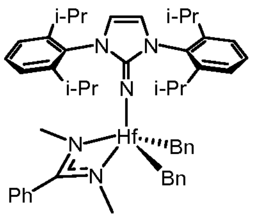
or a combination thereof.

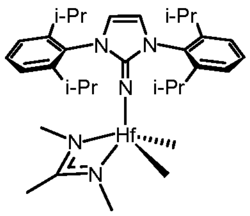
14. The metal-ligand complex of claim 1, comprising

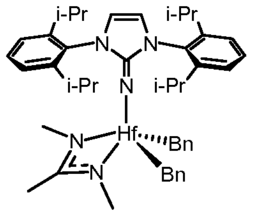


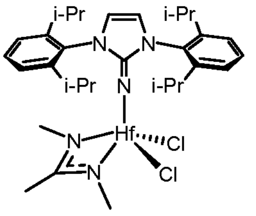


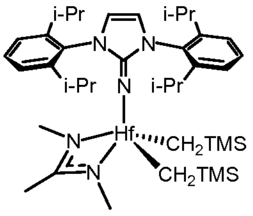


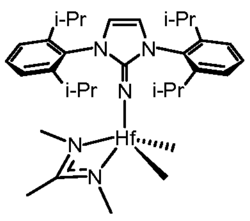


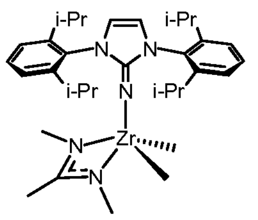


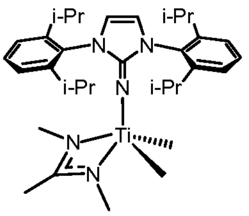


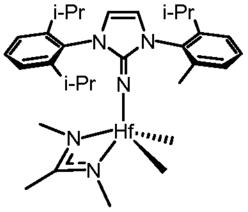


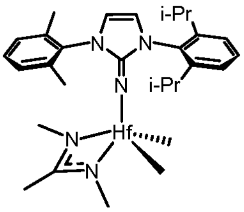








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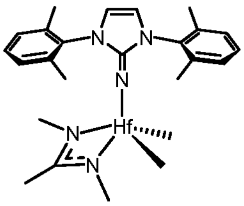
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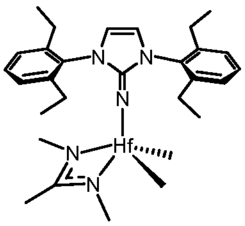
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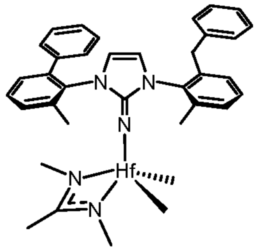
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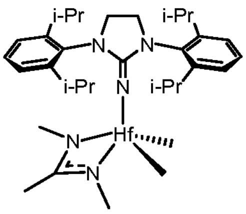
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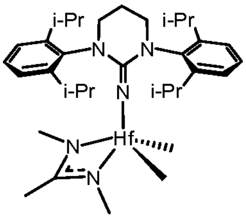
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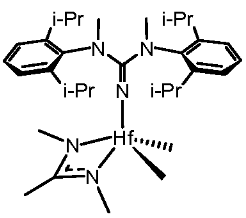
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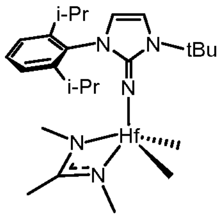
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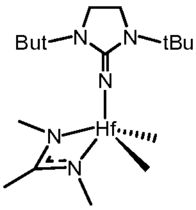
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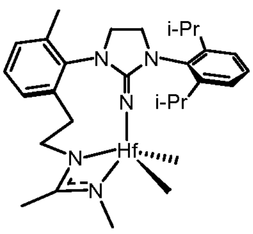
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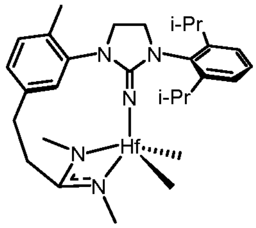
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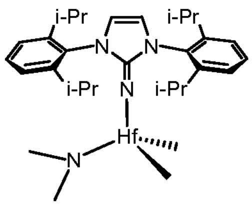
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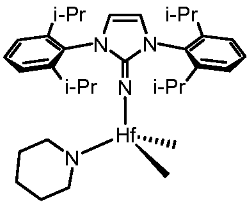
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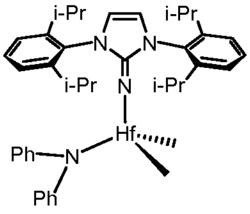
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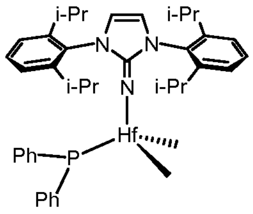
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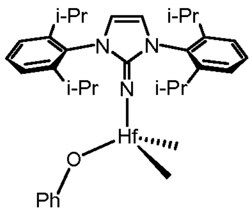
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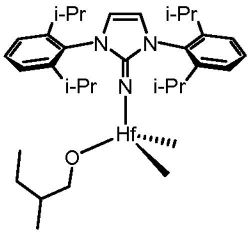
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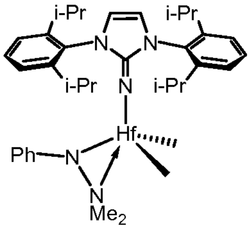
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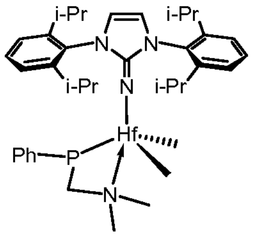
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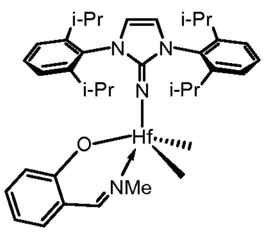
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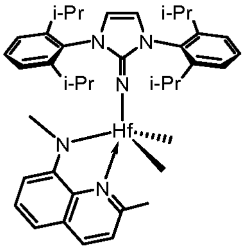
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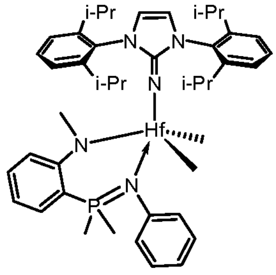
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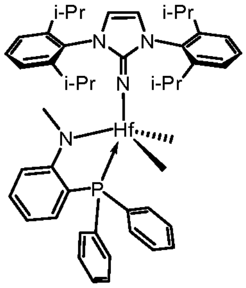
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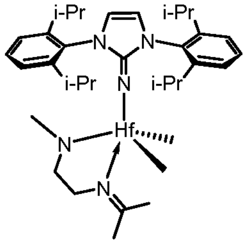
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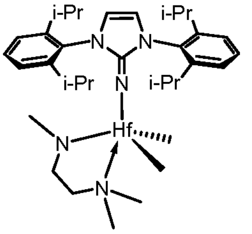
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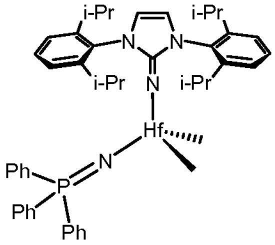
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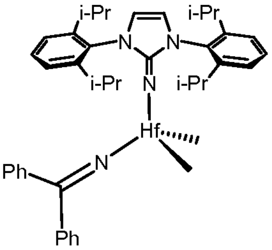
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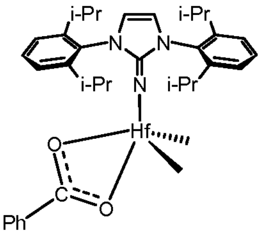
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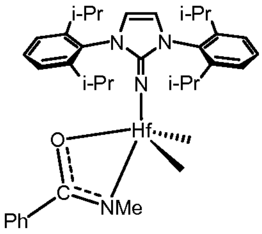
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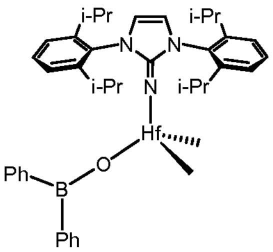
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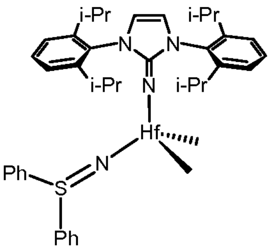
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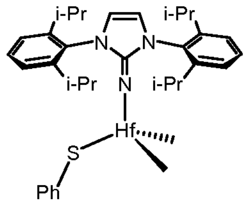
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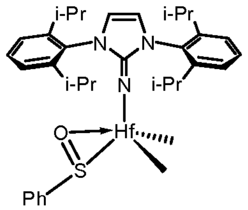
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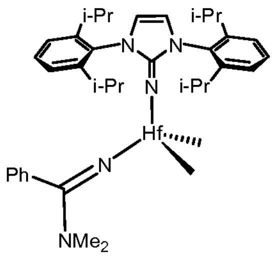
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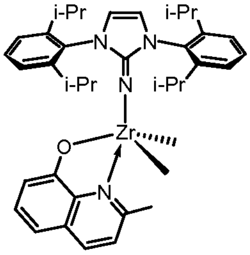
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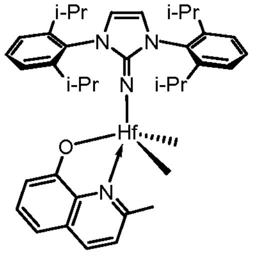
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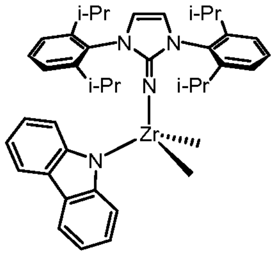
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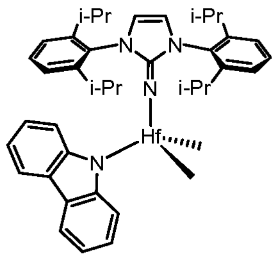
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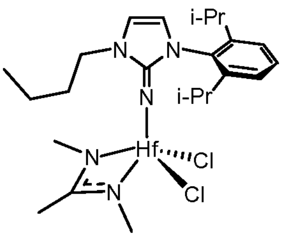
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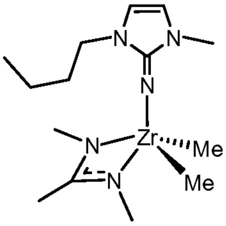
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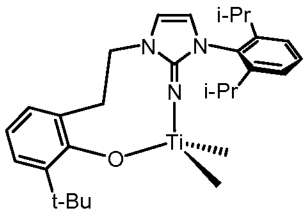
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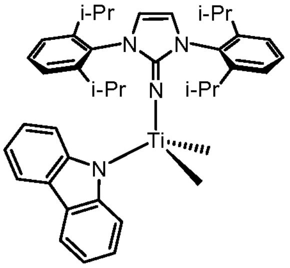
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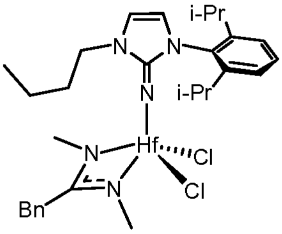
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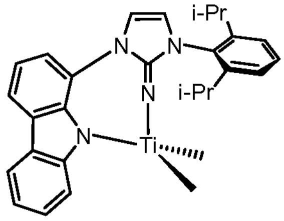
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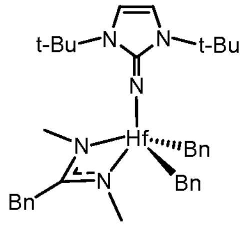
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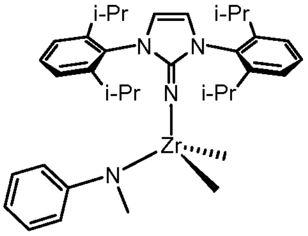
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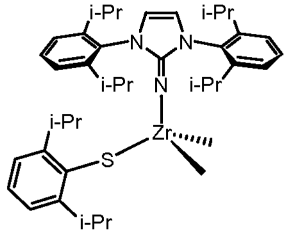
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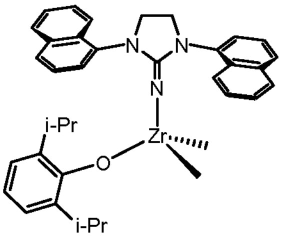
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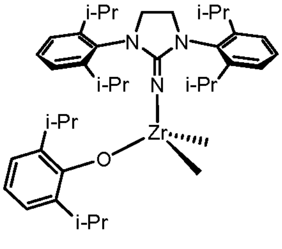
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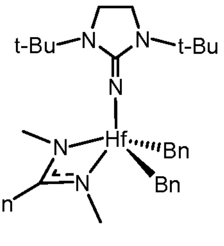
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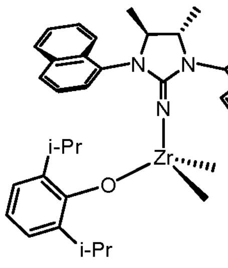

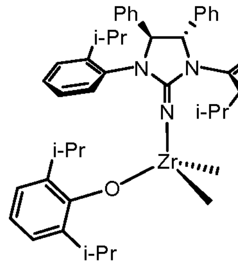

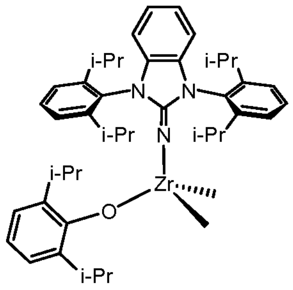

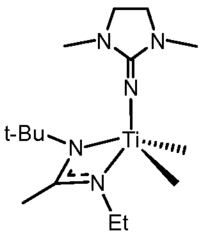

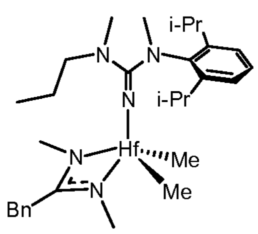

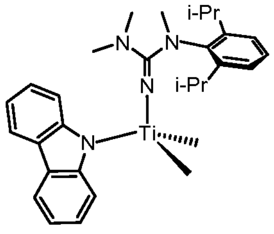

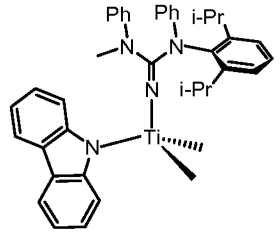

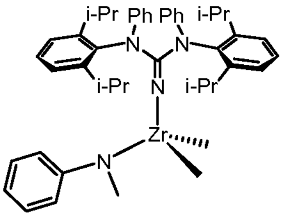

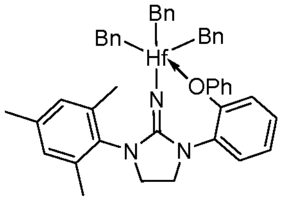

or a combination thereof.

15. A catalyst comprising, or comprising the reaction product of, one or more metal-ligand complexes of any of claims 1-14, and one or more activating cocatalysts, wherein a ratio of total number of moles of the one or more metal-ligand complexes to total number of moles of the one or more activating cocatalyst is 1:10,000 to 100:1.

16. A process for preparing a polyolefin, the process comprising contacting at least one polymerizable olefin with the catalyst of claim 15 under conditions sufficient to polymerize at least some of the at least one polymerizable olefin, thereby producing a polyolefin.

17. The process of claim 16, wherein the at least one polymerizable olefin comprises ethylene and octene.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/064931

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-17(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/064931

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J31/00 C07F7/00 C08F4/659 C08F210/16 C08F110/02
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2014/139861 A1 (UNIVERSITÄT BAYREUTH [DE]) 18 September 2014 (2014-09-18) table 1 examples 1,2,3,5 page 13, line 9 - page 14, line 19 claims 3,5,6 -----	1-4,6,8, 12,15-17
X	ISABELLE HAAS ET AL: "A Highly Efficient Titanium Catalyst for the Synthesis of Ultrahigh-Molecular-Weight Polyethylene (UHMWPE)", CHEMISTRY - A EUROPEAN JOURNAL, vol. 19, no. 28, 8 July 2013 (2013-07-08), pages 9132-9136, XP055169886, ISSN: 0947-6539, DOI: 10.1002/chem.201301176 Complexes 3,4 ----- -/--	1-4,6,8, 12,15-17

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 18 February 2015	Date of mailing of the international search report 12/03/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Thomas, Dominik

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MANAB SHARMA ET AL: "Bis(1,3-di- tert -butylimidazolin-2-iminato) Titanium Complexes as Effective Catalysts for the Monodisperse Polymerization of Propylene", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 134, no. 41, 17 October 2012 (2012-10-17), pages 17234-17244, XP055169973, ISSN: 0002-7863, DOI: 10.1021/ja3071545 cited in the application the whole document -----	1-4,6,8, 15,17
A	MATTHIAS TAMM ET AL: "Imidazolin-2-iminato titanium complexes: synthesis, structure and use in ethylene polymerization catalysis", DALTON TRANSACTIONS, no. 3, 1 January 2006 (2006-01-01), page 459, XP055169978, ISSN: 1477-9226, DOI: 10.1039/b511752f the whole document -----	1-4,6,8, 15,17

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/064931

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2014139861 A1	18-09-2014	NONE	

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-17(partially)

Present claims 1-15 and the related process claims 16,17 relates to an extremely large number of possible compounds. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds claimed. All complexes described in the experimental part have in common:
(i) the meals used are Ti, Zr, Hf
(ii) an 1,3-aryl- substituted imidazolin-2-iminato ligand; with R2, R3 = CH2-CH2 or R2, R3 = CH=CH)
The non-compliance with the substantive
provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of claims 1-17(PCT Guidelines 9.19 and 9.23).
The search of claim
was restricted to those claimed compounds having the above mentioned features (i) and (ii), (for example: compounds of present claim 7 with the exception of the last three formulas on page 92 of the application as filed; and compounds of present claim 14, except where R2, R3 is not CH2-CH2 or CH=CH).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.