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(54) Title: PROCESS FOR CONTROLLING MOLECULAR WEIGHT OF POLYOLEFINS PREPARED USING PYRIDYL DI-AMIDE CATALYST SYSTEMS

(57) Abstract: Pyridyldiamido transition metal complexes are disclosed for use in alkene polymerization to produce polyolefins.

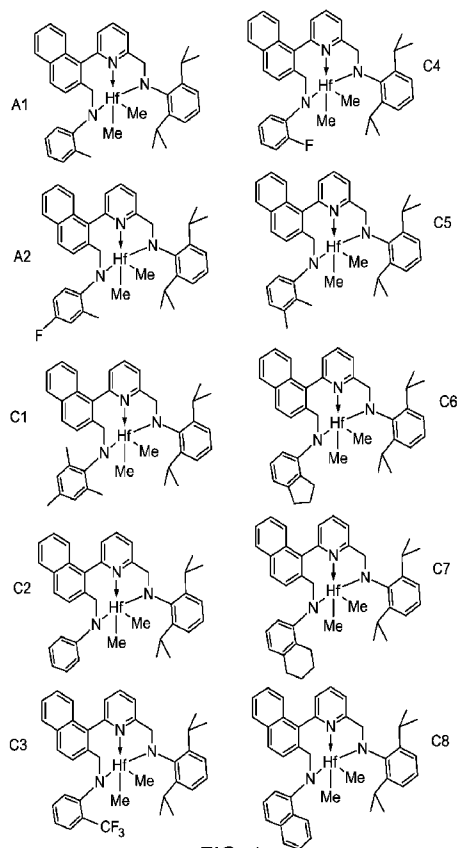


FIG. 1



DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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**PROCESS FOR CONTROLLING MOLECULAR WEIGHT OF POLYOLEFINS
PREPARED USING PYRIDYL DIAMIDE CATALYST SYSTEMS**

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PRIORITY CLAIM

5 This application claims priority to and the benefit of US Provisional Application No. 61/761,307, filed February 6, 2013 and EP 13167624.9 filed May 14, 2013.

FIELD OF INVENTION

 The invention relates to pyridyldiamido transition metal complexes and intermediates and processes for use in making such pyridyldiamido complexes. The transition metal
10 complexes may be used as catalysts for alkene polymerization processes.

BACKGROUND OF INVENTION

 Pyridyl amines have been used to prepare Group 4 complexes which are useful transition metal components in the polymerization of alkenes, see for example US 2002/0142912, US 6,900,321, and US 6,103,657, where the ligands have been used in
15 complexes in which the ligands are coordinated in a bidentate fashion to the transition metal atom.

 WO 2005/095469 shows catalyst compounds that use tridentate ligands through two nitrogen atoms (one amido and one pyridyl) and one oxygen atom.

 US 2004/0220050A1 and WO 2007/067965 disclose complexes in which the ligand is
20 coordinated in a tridentate fashion through two nitrogen (one amido and one pyridyl) and one carbon (aryl anion) donors.

 A key step in the activation of these complexes is the insertion of an alkene into the metal-aryl bond of the catalyst precursor (Froese, R. D. J. et al., J. Am. Chem. Soc. 2007, 129, pp. 7831-7840) to form an active catalyst that has both a five-membered and a seven-
25 membered chelate ring.

 WO 2010/037059 discloses pyridine containing amines for use in pharmaceutical applications.

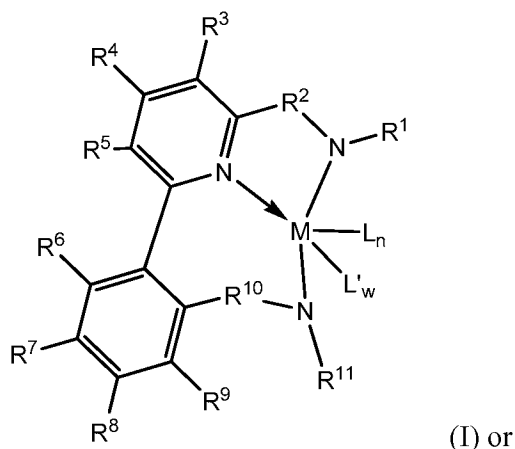
 US Patent 7,973,116, USSN 13/071,738, filed March 25, 2011 (now allowed); USSN 13/114,307, filed May 24, 2011, and USSN 13/207,847, filed August 11, 2011, which are
30 incorporated by reference herein, disclose pyridyldiamido transition metal complexes as polymerization catalysts.

 There still is need for adding synthetic routes to widen the range of catalysts complexes that may be prepared and broaden their performance in alkene polymerization. The performance may be varied with respect to the amount of polymer produced per amount

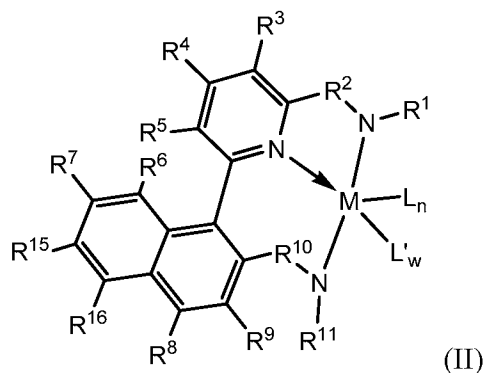
of catalyst (generally referred to as the “activity”) under the prevailing polymerization conditions; the molecular weight and molecular weight distribution achieved at a given temperature; and the placement of higher alpha-olefins in terms of the degree of stereoregular placement.

5 SUMMARY OF INVENTION

This invention relates to pyridyldiamido and related transition metal complexes represented by the formula (I), or (II)



10



wherein:

M is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal;

15 R^1 is selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups (preferably a phenyl group substituted at the 2 and 6 positions, preferably with the same or different C1-C20 alkyl groups);

R^{11} is selected from the group consisting of hydrocarbyls substituted, hydrocarbyls, and silyl groups, preferably R^{11} is a phenyl group substituted at the 2 position, preferably with a C1-C20 alkyl group and which is not substituted at the 3, 5, and/or 6 positions, optionally, the 4
20 position can be substituted with a group 17 element or a C1-C20 alkyl group;

- R^2 and R^{10} are each, independently, $-E(R^{12})(R^{13})-$ with E being carbon, silicon, or germanium, and each R^{12} and R^{13} being independently selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R^{12} and R^{13} may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R^{12} and R^{13} may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings;
- R^3 , R^4 , and R^5 are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R^3 & R^4 and/or R^4 & R^5) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;
- R^6 , R^7 , R^8 , R^9 , R^{15} , and R^{16} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R^6 & R^7 , and/or R^7 & R^{15} , and/or R^{16} & R^{15} , and/or R^8 & R^9) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;
- L is an anionic leaving group, wherein the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;
- n is 0, 1, 2, 3, or 4;
- L' is neutral Lewis base;
- w is 0, 1, 2, 3, or 4; and
- wherein $n + w$ is no greater than 4.

This invention further relates to process to make the above complex, process to make intermediates for the above complex and methods to polymerize olefins using the above complex.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 provides some of the formulae for pyridyldiamido transition metal catalyst described herein.

Figure 2 is a plot showing the effect of scavenger concentration on weight-average molecular weight of polypropylene produced at 85°C using complex **B** (Table 1 in examples) and [PhNHMe₂]B(C₆F₅)₄ catalyst system.

DETAILED DESCRIPTION

5 The specification describes transition metal complexes. The term complex is used to describe molecules in which an ancillary ligand is coordinated to a central transition metal atom. The ligand is bulky and stably bonded to the transition metal so as to maintain its influence during use of the catalyst, such as polymerization. The ligand may be coordinated to the transition metal by covalent bond and/or electron donation coordination or intermediate
10 bonds. The transition metal complexes are generally subjected to activation to perform their polymerization function using an activator which is believed to create a cation as a result of the removal of an anionic group, often referred to as a leaving group, from the transition metal.

As used herein, the numbering scheme for the Periodic Table groups is the new
15 notation as set out in Chemical and Engineering News, 63(5), p. 27 (1985).

As used herein, Me is methyl, Et is ethyl, Bu is butyl, t-Bu and ^tBu are tertiary butyl, Pr is propyl, iPr and ⁱPr are isopropyl, Cy is cyclohexyl, THF (also referred to as thf) is tetrahydrofuran, Bn is benzyl, and Ph is phenyl.

The term "substituted" generally means that a hydrogen of the substituted species has
20 been replaced with a different atom or group of atoms. For example, methyl-cyclopentadiene is cyclopentadiene that has been substituted with a methyl group. Likewise, picric acid can be described as phenol that has been substituted with three nitro groups, or, alternatively, as benzene that has been substituted with one hydroxyl and three nitro groups.

The terms "hydrocarbyl radical," "hydrocarbyl," and "hydrocarbyl group" are used
25 interchangeably throughout this document. Likewise, the terms "group," "radical," and "substituent" are also used interchangeably in this document. For purposes of this disclosure, "hydrocarbyl radical" is defined to be C₁-C₁₀₀ radicals, that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic.

A substituted hydrocarbyl radical is a hydrocarbyl radical in which at least one
30 hydrogen atom of the hydrocarbyl radical has been substituted with at least one functional group such as NR*₂, OR*, SeR*, TeR*, PR*₂, AsR*₂, SbR*₂, SR*, BR*₂, SiR*₃, GeR*₃, SnR*₃, PbR*₃, and the like, or where at least one heteroatom has been inserted within a

hydrocarbyl ring, where R* is, independently, hydrogen or a hydrocarbyl radical, or any combination thereof.

The term "catalyst system" is defined to mean a complex/activator pair. When "catalyst system" is used to describe such a pair before activation, it means the unactivated catalyst complex (precatalyst) together with an activator and, optionally, a co-activator. When it is used to describe such a pair after activation, it means the activated complex and the activator or other charge-balancing moiety. The transition metal compound may be neutral as in a precatalyst, or a charged species with a counter ion as in an activated catalyst system.

Complex, as used herein, is also often referred to as catalyst precursor, precatalyst, catalyst, catalyst compound, transition metal compound, or transition metal complex. These words are used interchangeably. Activator and cocatalyst are also used interchangeably.

A scavenger is a compound that is typically added to facilitate polymerization by scavenging impurities. Some scavengers may also act as activators and may be referred to as co-activators. A co-activator, that is not a scavenger, may also be used in conjunction with an activator in order to form an active catalyst. In some embodiments, a co-activator can be pre-mixed with the transition metal compound to form an alkylated transition metal compound.

Noncoordinating anion (NCA) is defined to mean an anion either that does not coordinate to the catalyst metal cation or that does coordinate to the metal cation, but only weakly. The term NCA is also defined to include multicomponent NCA-containing activators, such as N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, that contain an acidic cationic group and the non-coordinating anion. The term NCA is also defined to include neutral Lewis acids, such as tris(pentafluorophenyl)boron, that can react with a catalyst to form an activated species by abstraction of an anionic group. An NCA coordinates weakly enough that a neutral Lewis base, such as an olefinically or acetylenically unsaturated monomer can displace it from the catalyst center. Any metal or metalloid that can form a compatible, weakly coordinating complex may be used or contained in the noncoordinating anion. Suitable metals include, but are not limited to, aluminum, gold, and platinum. Suitable metalloids include, but are not limited to, boron, aluminum, phosphorus, and silicon. A stoichiometric activator can be either neutral or ionic. The terms ionic activator and stoichiometric ionic activator can be used interchangeably. Likewise, the terms neutral stoichiometric activator, and Lewis acid activator can be used interchangeably. The term

non-coordinating anion includes neutral stoichiometric activators, ionic stoichiometric activators, ionic activators, and Lewis acid activators.

An "olefin," alternatively referred to as "alkene," is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, including, but not limited to, ethylene, propylene, and butene, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an "ethylene" content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer. A "polymer" has two or more of the same or different mer units. A "homopolymer" is a polymer having mer units that are the same. A "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three mer units that are different from each other. "Different" as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. An oligomer is a polymer having a low molecular weight. In some embodiments, an oligomer has an Mn of 21,000 g/mol or less (e.g., 2,500 g/mol or less); in other embodiments, an oligomer has a low number of mer units (such as 50 mer units or less).

An "alpha-olefin" is an olefin having a double bond at the alpha (or 1-) position. A higher α -olefin is defined to be an α -olefin having 4 or more carbon atoms.

Unless otherwise noted, all molecular weights units (e.g., Mw, Mn, Mz) are g/mol.

Unless otherwise noted all melting points (T_m) are DSC second melt.

A "ring carbon atom" is a carbon atom that is part of a cyclic ring structure. By this definition, a benzyl group has six ring carbon atoms and para-methylstyrene also has six ring carbon atoms.

The term "aryl" or "aryl group" means a six carbon aromatic ring and the substituted variants thereof, including but not limited to, phenyl, 2-methyl-phenyl, xylyl, 4-bromo-xylyl. Likewise, heteroaryl means an aryl group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, preferably N, O, or S.

The term "ring atom" means an atom that is part of a cyclic ring structure. By this definition, a benzyl group has six ring atoms and tetrahydrofuran has 5 ring atoms.

A heterocyclic ring is a ring having a heteroatom in the ring structure as opposed to a heteroatom substituted ring where a hydrogen on a ring atom is replaced with a heteroatom.

For example, tetrahydrofuran is a heterocyclic ring and 4-N,N-dimethylamino-phenyl is a heteroatom substituted ring.

As used herein the term "aromatic" also refers to pseudoaromatic heterocycles which are heterocyclic substituents that have similar properties and structures (nearly planar) to aromatic heterocyclic ligands, but are not by definition aromatic; likewise, the term aromatic also refers to substituted aromatics.

The term "continuous" means a system that operates without interruption or cessation. For example, a continuous process to produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually withdrawn.

A solution polymerization means a polymerization process in which the polymer is dissolved in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Such systems are preferably not turbid as described in J. Vladimir Oliveira, C. Dariva and J. C. Pinto, Ind. Eng. Chem. Res. 29, 2000, p. 4627.

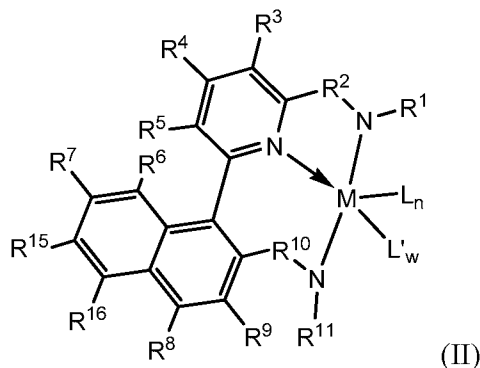
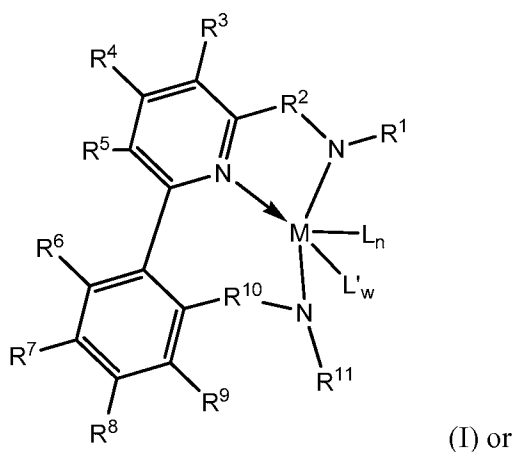
A bulk polymerization means a polymerization process in which the monomers and/or comonomers being polymerized are used as a solvent or diluent using little or no inert solvent as a solvent or diluent. A small fraction of inert solvent might be used as a carrier for catalyst and scavenger. A bulk polymerization system typically contains less than 25 wt% of inert solvent or diluent, preferably less than 10 wt%, preferably less than 1 wt%, preferably 0 wt%.

The term "multimodal," when used to describe a polymer or polymer composition, means "multimodal molecular weight distribution," which is understood to mean that the Gel Permeation Chromatography (GPC) trace, plotted as Absorbance versus Retention Time (seconds), has more than one peak or inflection point(s). An "inflection point" is that point where the second derivative of the curve changes in sign (e.g., from negative to positive or vice versa). For example, a polyolefin composition that includes a first lower molecular weight polymer component (such as a polymer having an Mw of 100,000 g/mol) and a second higher molecular weight polymer component (such as a polymer having an Mw of 300,000 g/mol) is considered to be a "bimodal" polyolefin composition. Preferably the Mw's of the polymer or polymer composition differ by at least 10%, relative to each other, preferably by at least 20%, preferably at least 50%, preferably by at least 100%, preferably by at least 200%. Likewise, in a preferred embodiment, the Mw's of the polymer or polymer

composition differ by 10% to 10,000%, relative to each other, preferably by 20% to 1000%, preferably 50% to 500%, preferably by at least 100% to 400%, preferably 200% to 300%.

"Catalyst activity" is a measure of how many grams of polymer (P) are produced using a polymerization catalyst comprising W mmol of transition metal (M), over a period of
 5 time of T hours; and may be expressed by the following formula: $P/(T \times W)$.

In a first aspect of the invention there is provided a pyridyldiamido transition metal complex (optionally for use in alkene polymerization) represented by the formula



wherein:

M is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal;

R¹ and R¹¹ are each independently selected from the group consisting of hydrocarbyls substituted hydrocarbyls, and silyl groups (preferably a phenyl group substituted at the 2 and
 15 6 positions, preferably with the same or different C1-C20 alkyl groups), more preferably R¹¹ is a phenyl group substituted at the 2 position, preferably with a C1-C20 alkyl group and which is not substituted at the 3, 5, and/or 6 positions, optionally, the 4 position can be substituted with a group 17 element or a C1-C20 alkyl group;

R² and R¹⁰ are each, independently, -E(R¹²)(R¹³)- with E being carbon, silicon, or
 20 germanium, and each R¹² and R¹³ being independently selected from the group consisting of

hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R^{12} and R^{13} may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R^{12} and R^{13} may be joined to form a
 5 saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings;

R^3 , R^4 , and R^5 are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R^3 & R^4 and/or R^4 & R^5) may be joined to form a substituted or
 10 unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

R^6 , R^7 , R^8 , R^9 , R^{15} , and R^{16} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R^6 & R^7 , and/or R^7 & R^{15} , and/or R^{16} & R^{15} , and/or R^8 & R^9)
 15 may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

20 n is 0, 1, 2, 3, or 4;

L' is neutral Lewis base;

w is 0, 1, 2, 3, or 4;

wherein $n + w$ is no greater than 4.

Preferably, the R groups above and other R groups mentioned hereafter, contain from 1 to 30,
 25 preferably 2 to 20 carbon atoms, especially from 6 to 20 carbon atoms.

Preferably, M is Ti, Zr, or Hf, and/or E is carbon, with Zr or Hf based complexes being especially preferred.

In a preferred embodiment, R^{11} may be selected from phenyl groups that are variously substituted with between zero to five substituents that include F, Cl, Br, I, CF_3 ,
 30 NO_2 , alkoxy, dialkylamino, aryl, and alkyl groups having 1 to 10 carbons, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and isomers thereof.

In one aspect, when R^{11} is a phenyl group, it is substituted at the ortho position, the 2 position, adjacent to the point of attachment to the nitrogen (N) group of the organic ligand as

shown in formulae (I) and (II). Preferably, the substituent is an alkyl group, such as C1-C20 alkyl groups, including methyl, ethyl, iso-propyl, propyl, butyl, sec-butyl, t-butyl, octyl, nonyl, dodecyl, etc. R¹¹ can be further substituted particularly at the 4 position by group 17 elements (preferably F, Cl, Br or I) or C1-C20 alkyl groups as described above. Preferably,
 5 the substituent at the ortho position is a C1-C5 group, including methyl, ethyl, iso-propyl, propyl, butyl, sec-butyl, t-butyl.

In another aspect, R¹¹ is not substituted at the 2 position with F, a fluoro group or a trifluoromethyl group.

In still another aspect, R¹¹ is substituted at the 2 and, optionally, the 4 positions as
 10 described above, but is not substituted at the 3, 5 and/or 6 positions.

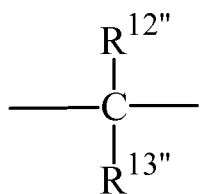
In a preferred embodiment, L may be selected from halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, and alkynyl. The selection of the leaving groups depends on the synthesis route adopted for arriving at the complex and may be changed by additional reactions to suit the later activation method in polymerization. For
 15 example, a preferred L is alkyl when using non-coordinating anions such as N,N-dimethylanilinium tetrakis(pentafluorophenyl)-borate or tris(pentafluorophenyl)borane. In another embodiment, two L groups may be linked to form a dianionic leaving group, for example oxalate.

In another embodiment, each L' is independently selected from the group consisting
 20 of ethers, thio-ethers, amines, nitriles, imines, pyridines, and phosphines, preferably ethers.

Preferred R² groups and preferred R¹⁰ groups include CH₂, CMe₂, SiMe₂, SiEt₂, SiPr₂, SiBu₂, SiPh₂, Si(aryl)₂, Si(alkyl)₂, CH(aryl), CH(Ph), CH(alkyl), and CH(2-isopropylphenyl), preferably where alkyl is a C₁ to C₄₀ alkyl group, aryl is a C₅ to C₄₀ aryl
 group.

25 In any embodiment described herein, E is preferably carbon.

In any embodiment described herein, R² is represented by the formula:



In any embodiment described herein, R^{12''} is hydrogen, alkyl, aryl, or halogen; and R^{13''} is hydrogen, alkyl, aryl, or halogen, preferably R^{12''} and R^{13''} are the same.

In any embodiment described herein, R⁶, R⁷, R⁸, R⁹, R¹⁵, and R¹⁶ may be, independently, selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl.

In any embodiment described herein, R³, R⁴, R⁵, and R¹¹ may each contain from 1 to 30 carbon atoms, preferably R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁵, and R¹⁶ each contain from 1 to than 30 carbon atoms.

In any embodiment described herein, E is carbon and R¹¹ is selected from phenyl groups that are substituted with 0, 1, 2, 3, 4, or 5 substituents selected from the group consisting of F, Cl, Br, I, CF₃, NO₂, alkoxy, dialkylamino, hydrocarbyl, and substituted hydrocarbyls groups with from one to ten carbons.

In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the Formula (I) or (II) above, and M is a Group 4 metal preferably Zr or Hf, preferably Hf.

In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the Formula (I) or (II) above, the R² and R¹⁰ groups are -CH₂-, M is a Group 4 metal (preferably Zr or Hf, preferably Hf) and R¹¹ is a phenyl group with substitution at the 2 position, but not further substituted at either the 3, 5 and/or 6 position, with the substituents preferably being C1-C5 alkyl groups, such as methyl, ethyl, propyl, butyl or pentyl.

In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the Formula (I) or (II) above, wherein the R² and R¹⁰ groups are -CH₂-, M is a Group 4 metal (preferably Zr or Hf, preferably Hf), R¹ is 2,6-diisopropylphenyl, and R¹¹ is a phenyl group with a substituent at the 2 position, preferably a C1-C5 alkyl group, such as methyl, ethyl, propyl, isopropyl, butyl or pentyl. In particular, the 3, 5 and 6 positions of the phenyl group are not substituted. It should be understood where a substituent is not denoted that the position is a hydrogen atom and/or a carbon bond that forms a ring.

In another embodiment, the 2 and 4 positions of the R¹¹ phenyl group are substituted with, each independently, C1-C20 alkyl groups and more particularly, C1-C5 alkyl groups.

In a second aspect of the invention, there are provided various processes for synthesizing the complexes described herein.

Ligand Synthesis

The pyridyl diamine ligands described herein are generally prepared in multiple steps. One step involves the preparation of an amine-containing "linker" group where the linker is typically a boronic acid ester of an aryl methyl amine or substituted amine. This amine-

containing linker may be prepared from an aryl-methyl boronic ester in two steps, the first of which involves the conversion of the methyl group to a halo-methyl group by free radical halogenation in unreactive solvents (e.g., CCl₄, benzene). The second step then involves reaction of this halo-methyl group containing species with an amine or protected amine or deprotonated protected amine to yield an amine-containing linker. This amine-containing linker is then coupled with a suitable pyridine containing species, such as 6-bromo-2-pyridinecarboxaldehyde. This coupling step typically uses a metal catalyst (e.g., Pd(PPh₃)₄) in less than 5 mol% loading. Following this coupling step, the new derivative, which can be described as amine-linker-pyridine-aldehyde, is then reacted with a second amine to produce the imine derivative amine-linker-pyridine-imine in a condensation reaction. This can then be reduced to the pyridyl diamine ligand by reaction with a suitable aryl anion, alkyl anion, or hydride source. This reaction is generally performed in etherial solvents at temperatures between -100°C and 50°C when aryllithium or alkylolithium reagents are employed. This reaction is generally performed in methanol at reflux when sodium cyanoborohydride is employed.

The preparation of pyridyl diamide metal complexes from pyridyl diamines may be accomplished using typical protonolysis and methylation reactions. In the protonolysis reaction, the pyridyl diamine is reacted with a suitable metal reactant to produce a pyridyldiamide metal complex. A suitable metal reactant will feature a basic leaving group that will accept a proton from the pyridyl diamine and then generally depart and be removed from the product. Suitable metal reactants include, but are not limited to, HfBn₄ (Bn = CH₂Ph), ZrBn₄, TiBn₄, Hf(NMe₂)₄, Hf(NEt₂)₄, ZrBn₂Cl₂(OEt₂), HfBn₂Cl₂(OEt₂)₂, Zr(NMe₂)₂Cl₂(dimethoxyethane), and Hf(NMe₂)₂Cl₂(dimethoxyethane). Pyridyldiamide (PDA) metal complexes that contain metal-chloride groups, such as the PDA dichloride complex, can be alkylated by reaction with an appropriate organometallic reagent. Suitable reagents include organolithium and organomagnesium, and Grignard reagents. The alkylations are generally performed in etherial or hydrocarbon solvents or solvent mixtures at temperatures typically ranging from -100°C to 50°C.

Activators

After the complexes have been synthesized, catalyst systems may be formed by combining them with activators in any manner known from the literature including by supporting them for use in slurry or gas phase polymerization. The catalyst systems may also be added to or generated in solution polymerization or bulk polymerization (in the monomer).

The catalyst system typically comprises a complex as described above and an activator such as alumoxane or a non-coordinating anion. Activation may be performed using alumoxane solution including methyl alumoxane, referred to as MAO, as well as modified MAO, referred to herein as MMAO, containing some higher alkyl groups to improve the solubility. Particularly useful MAO can be purchased from Albemarle in a 10 wt% solution in toluene. The catalyst system employed in the present invention preferably uses an activator selected from alumoxanes, such as methyl alumoxane, modified methyl alumoxane, ethyl alumoxane, *iso*-butyl alumoxane, and the like.

When an alumoxane or modified alumoxane is used, the complex-to-activator molar ratio is from about 1:3000 to 10:1; alternatively 1:2000 to 10:1; alternatively 1:1000 to 10:1; alternatively 1:500 to 1:1; alternatively 1:300 to 1:1; alternatively 1:200 to 1:1; alternatively 1:100 to 1:1; alternatively 1:50 to 1:1; and alternatively 1:10 to 1:1. When the activator is an alumoxane (modified or unmodified), some embodiments select the maximum amount of activator at a 5000-fold molar excess over the catalyst precursor (per metal catalytic site). The preferred minimum activator-to-complex ratio is 1:1 molar ratio.

Activation may also be performed using non-coordinating anions, referred to as NCA's, of the type described in EP 277 003 A1 and EP 277 004 A1. NCA may be added in the form of an ion pair using, for example, $[\text{DMAH}]^+ [\text{NCA}]^-$ in which the N,N-dimethylanilinium (DMAH) cation reacts with a basic leaving group on the transition metal complex to form a transition metal complex cation and $[\text{NCA}]^-$. The cation in the precursor may, alternatively, be trityl. Alternatively, the transition metal complex may be reacted with a neutral NCA precursor, such as $\text{B}(\text{C}_6\text{F}_5)_3$, which abstracts an anionic group from the complex to form an activated species. Useful activators include N,N-dimethylanilinium tetrakis (pentafluorophenyl)borate (i.e., $[\text{PhNMe}_2\text{H}]\text{B}(\text{C}_6\text{F}_5)_4$) and N,N-dimethylanilinium tetrakis (heptafluoronaphthyl)borate, where Ph is phenyl, and Me is methyl.

Additionally, preferred activators useful herein include those described in US 7,247,687 at column 169, line 50 to column 174, line 43, particularly column 172, line 24 to column 173, line 53.

Particularly preferred activators include: trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(*n*-butyl)ammonium tetraphenylborate, tri(*t*-butyl)ammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate, tropillium tetraphenylborate, triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate

triethylsilylium tetraphenylborate, benzene(diazonium)tetraphenylborate,
 trimethylammonium tetrakis(pentafluorophenyl)borate, triethylammonium
 tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(pentafluorophenyl)borate,
 tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, tri(sec-butyl)ammonium
 5 tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
 N,N-diethylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-
 trimethylanilinium) tetrakis(pentafluorophenyl)borate, tropillium
 tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(pentafluorophenyl)borate,
 triphenylphosphonium tetrakis(pentafluorophenyl)borate, triethylsilylium
 10 tetrakis(pentafluorophenyl)borate, benzene(diazonium) tetrakis(pentafluorophenyl)borate,
 trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, triethylammonium tetrakis-
 (2,3,4,6-tetrafluorophenyl)borate, tripropylammonium tetrakis-(2,3,4,6-
 tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate,
 dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-
 15 dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-diethylanilinium tetrakis-
 (2,3,4,6-tetrafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-
 tetrafluorophenyl)borate, tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylphosphonium
 tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylsilylium tetrakis-(2,3,4,6-
 20 tetrafluorophenyl)borate, benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
 trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium
 tetrakis(perfluoronaphthyl)borate, tripropylammonium tetrakis(perfluoronaphthyl)borate,
 tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate, tri(t-butyl)ammonium
 tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
 25 N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-
 trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium
 tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
 triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium
 tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
 30 trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium
 tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate,
 tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(t-butyl)ammonium
 tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
 N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-

trimethylanilinium) tetrakis(perfluorobiphenyl)borate, tropillium
 tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
 triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium
 tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate,
 5 trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylammonium
 tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tripropylammonium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, tri(n-butyl)ammonium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, tri(t-butyl)ammonium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, N,N-dimethylanilinium tetrakis(3,5-
 10 bis(trifluoromethyl)phenyl)borate, N,N-diethylanilinium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylphosphonium
 tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylsilylium tetrakis(3,5-
 15 bis(trifluoromethyl)phenyl)borate, benzene(diazonium) tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
 dicyclohexylammonium tetrakis(pentafluorophenyl)borate; tri(o-tolyl)phosphonium
 tetrakis(pentafluorophenyl)borate, tri(2,6-dimethylphenyl)phosphonium
 tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate,
 20 triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium
 tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
 tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium
 tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
 N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium
 25 tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
 triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium
 tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
 trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium
 tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate,
 30 tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(t-butyl)ammonium
 tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
 N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-
 trimethylanilinium) tetrakis(perfluorobiphenyl)borate, tropillium
 tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate,

triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, [4-t-butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B], (where Ph is phenyl and Me is methyl), and the NCA's disclosed in U.S. Patent No. 7,297,653.

5 Most preferably, the ionic stoichiometric activator is N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, or triphenylcarbenium
10 tetrakis(perfluorophenyl)borate.

When an NCA (such as an ionic or neutral stoichiometric activator) is used, the complex-to-activator molar ratio is typically from 1:10 to 1:1; 1:10 to 10:1; 1:10 to 2:1; 1:10 to 3:1; 1:10 to 5:1; 1:2 to 1.2:1; 1:2 to 10:1; 1:2 to 2:1; 1:2 to 3:1; 1:2 to 5:1; 1:3 to 1.2:1; 1:3 to 10:1; 1:3 to 2:1; 1:3 to 3:1; 1:3 to 5:1; 1:5 to 1:1; 1:5 to 10:1; 1:5 to 2:1; 1:5 to 3:1; 1:5 to 5:1; and 1:1 to 1:1.2.

Alternately, a co-activator may also be used in the catalyst system herein. The complex-to-co-activator molar ratio is from 1:100 to 100:1; 1:75 to 75:1; 1:50 to 50:1; 1:25 to 25:1; 1:15 to 15:1; 1:10 to 10:1; 1:5 to 5:1; 1:2 to 2:1; 1:100 to 1:1; 1:75 to 1:1; 1:50 to 1:1; 1:25 to 1:1; 1:15 to 1:1; 1:10 to 1:1; 1:5 to 1:1; 1:2 to 1:1; and 1:10 to 2:1.

20 Supports

In some embodiments, the complexes described herein may be supported (with or without an activator) by any method effective to support other coordination catalyst systems, effective meaning that the catalyst so prepared can be used for oligomerizing or polymerizing olefin in a heterogeneous process. The catalyst precursor, activator, co-activator if needed, suitable solvent, and support may be added in any order or simultaneously. Typically, the complex and activator may be combined in solvent to form a solution. Then the support is added, and the mixture is stirred for 1 minute to 10 hours. The total solution volume may be greater than the pore volume of the support, but some embodiments limit the total solution volume below that needed to form a gel or slurry (about 90% to 400%, preferably about 100-200% of the pore volume). After stirring, the residual solvent is removed under vacuum, typically at ambient temperature and over 10-16 hours. But greater or lesser times and temperatures are possible.

The complex may also be supported absent the activator; in that case, the activator (and co-activator if needed) is added to a polymerization process's liquid phase.

Additionally, two or more different complexes may be placed on the same support. Likewise, two or more activators or an activator and co-activator may be placed on the same support.

Suitable solid particle supports are typically comprised of polymeric or refractory
5 oxide materials, each being preferably porous. Preferably any support material that has an average particle size greater than 10 μm is suitable for use in this invention. Various embodiments select a porous support material, such as for example, talc, inorganic oxides, inorganic chlorides, for example magnesium chloride and resinous support materials such as polystyrene polyolefin or polymeric compounds or any other organic support material and the
10 like. Some embodiments select inorganic oxide materials as the support material including Group-2, -3, -4, -5, -13, or -14 metal or metalloid oxides. Some embodiments select the catalyst support materials to include silica, alumina, silica-alumina, and their mixtures. Other inorganic oxides may serve either alone or in combination with the silica, alumina, or silica-alumina. These are magnesia, titania, zirconia, and the like. Lewis acidic materials such as
15 montmorillonite and similar clays may also serve as a support. In this case, the support can optionally double as the activator component; however, an additional activator may also be used.

The support material may be pretreated by any number of methods. For example, inorganic oxides may be calcined, chemically treated with dehydroxylating agents such as
20 aluminum alkyls and the like, or both.

As stated above, polymeric carriers will also be suitable in accordance with the invention, see for example the descriptions in WO 95/15815 and US 5,427,991. The methods disclosed may be used with the catalyst complexes, activators or catalyst systems of this invention to adsorb or absorb them on the polymeric supports, particularly if made up of
25 porous particles, or may be chemically bound through functional groups bound to or in the polymer chains.

Useful supports typically have a surface area of from 10-700 m^2/g , a pore volume of 0.1-4.0 cc/g and an average particle size of 10-500 μm . Some embodiments select a surface area of 50-500 m^2/g , a pore volume of 0.5-3.5 cc/g , or an average particle size of 20-200 μm .
30 Other embodiments select a surface area of 100-400 m^2/g , a pore volume of 0.8-3.0 cc/g , and an average particle size of 30-100 μm . Useful supports typically have a pore size of 10-1000 Angstroms, alternatively 50-500 Angstroms, or 75-350 Angstroms.

The catalyst complexes described herein are generally deposited on the support at a loading level of 10-100 micromoles of complex per gram of solid support; alternately 20-80

micromoles of complex per gram of solid support; or 40-60 micromoles of complex per gram of support. But greater or lesser values may be used provided that the total amount of solid complex does not exceed the support's pore volume.

Polymerization

5 Inventive catalyst complexes are useful in polymerizing unsaturated monomers conventionally known to undergo metallocene-catalyzed polymerization such as solution, slurry, gas-phase, and high-pressure polymerization. Typically one or more of the complexes described herein, one or more activators, and one or more monomers are contacted to produce polymer. In certain embodiments, the complexes may be supported and as such will be
10 particularly useful in the known, fixed-bed, moving-bed, fluid-bed, slurry, solution, or bulk operating modes conducted in single, series, or parallel reactors.

One or more reactors in series or in parallel may be used in the present invention. The complexes, activator and when required, co-activator, may be delivered as a solution or slurry, either separately to the reactor, activated in-line just prior to the reactor, or
15 preactivated and pumped as an activated solution or slurry to the reactor. Polymerizations are carried out in either single reactor operation, in which monomer, comonomers, catalyst/activator/co-activator, optional scavenger, and optional modifiers are added continuously to a single reactor or in series reactor operation, in which the above components are added to each of two or more reactors connected in series. The catalyst components can
20 be added to the first reactor in the series. The catalyst component may also be added to both reactors, with one component being added to first reaction and another component to other reactors. In one preferred embodiment, the complex is activated in the reactor in the presence of olefin.

In a particularly preferred embodiment, the polymerization process is a continuous
25 process.

Polymerization processes used herein typically comprise contacting one or more alkene monomers with the complexes (and, optionally, activator) described herein. For purpose of this invention, alkenes are defined to include multi-alkenes (such as dialkenes) and alkenes having just one double bond. Polymerization may be homogeneous (solution or
30 bulk polymerization) or heterogeneous (slurry -in a liquid diluent, or gas phase -in a gaseous diluent). In the case of heterogeneous slurry or gas phase polymerization, the complex and activator may be supported. Silica is useful as a support herein. Chain transfer agents (such as hydrogen or diethyl zinc) may be used in the practice of this invention.

The present polymerization processes may be conducted under conditions preferably including a temperature of about 30°C to about 200°C, preferably from 60°C to 195°C, preferably from 75°C to 190°C. The process may be conducted at a pressure of from 0.05 MPa to 1500 MPa. In a preferred embodiment, the pressure is between 1.7 MPa and 30 MPa, or in another embodiment, especially under supercritical conditions, the pressure is between 15 MPa and 1500 MPa.

Monomers

Monomers useful herein include olefins having from 2 to 20 carbon atoms, alternately 2 to 12 carbon atoms (preferably ethylene, propylene, butylene, pentene, hexene, heptene, octene, nonene, decene, and dodecene) and optionally also polyenes (such as dienes). Particularly preferred monomers include ethylene, and mixtures of C₂ to C₁₀ alpha olefins, such as ethylene-propylene, ethylene-hexene, ethylene-octene, propylene-hexene, and the like.

The complexes described herein are also particularly effective for the polymerization of ethylene, either alone or in combination with at least one other olefinically unsaturated monomer, such as a C₃ to C₂₀ α-olefin, and particularly a C₃ to C₁₂ α-olefin. Likewise, the present complexes are also particularly effective for the polymerization of propylene, either alone or in combination with at least one other olefinically unsaturated monomer, such as ethylene or a C₄ to C₂₀ α-olefin, and particularly a C₄ to C₂₀ α-olefin. Examples of preferred α-olefins include ethylene, propylene, butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, dodecene-1, 4-methylpentene-1, 3-methylpentene-1, 3, 5, 5-trimethylhexene-1, and 5-ethylnonene-1.

In some embodiments, the monomer mixture may also comprise one or more dienes at up to 10 wt%, such as from 0.00001 to 1.0 wt%, for example from 0.002 to 0.5 wt%, such as from 0.003 to 0.2 wt%, based upon the monomer mixture. Non-limiting examples of useful dienes include, cyclopentadiene, norbornadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, 1,4-hexadiene, 1,5-hexadiene, 1,5-heptadiene, 1,6-heptadiene, 6-methyl-1,6-heptadiene, 1,7-octadiene, 7-methyl-1,7-octadiene, 1,9-decadiene, 1 and 9-methyl-1,9-decadiene.

Where olefins are used that give rise to short chain branching, such as propylene, the catalyst systems may, under appropriate conditions, generate stereoregular polymers or polymers having stereoregular sequences in the polymer chains.

Scavengers

In some embodiments, when using the complexes described herein, particularly when they are immobilized on a support, the catalyst system will additionally comprise one or more scavenging compounds. Here, the term scavenging compound means a compound that removes polar impurities from the reaction environment. These impurities adversely affect catalyst activity and stability. Typically, the scavenging compound will be an organometallic compound such as the Group-13 organometallic compounds of US Patents 5,153,157, 5,241,025 and WO-A-91/09882, WO-A-94/03506, WO-A-93/14132, and that of WO 95/07941. Exemplary compounds include triethyl aluminum, triethyl borane, tri-*iso*-butyl aluminum, methyl alumoxane, *iso*-butyl alumoxane, and tri-*n*-octyl aluminum. Those scavenging compounds having bulky or C₆-C₂₀ linear hydrocarbyl substituents connected to the metal or metalloid center usually minimize adverse interaction with the active catalyst. Examples include triethylaluminum, but more preferably, bulky compounds such as tri-*iso*-butyl aluminum, tri-*iso*-prenyl aluminum, and long-chain linear alkyl-substituted aluminum compounds, such as tri-*n*-hexyl aluminum, tri-*n*-octyl aluminum, or tri-*n*-dodecyl aluminum. When alumoxane is used as the activator, any excess over that needed for activation will scavenge impurities and additional scavenging compounds may be unnecessary. Alumoxanes also may be added in scavenging quantities with other activators, e.g., methylalumoxane, [Me₂HNPh]⁺[B(pfp)₄]⁻ or B(pfp)₃ (perfluorophenyl = pfp = C₆F₅).

Preferred aluminum scavengers useful in the invention include those where there is an oxygen present. That is, the material per se or the aluminum mixture used as a scavenger, includes an aluminum/oxygen species, such as an alumoxane or alkylaluminum oxides, e.g., dialkylaluminum oxides, such as bis(diisobutylaluminum) oxide. In one aspect, aluminum containing scavengers can be represented by the formula ((R_z-Al)_yO)_x, wherein z is 1-2, y is 1-2, x is 1-100, and R is a C₁-C₁₂ hydrocarbyl group. In another aspect, the scavenger has an oxygen to aluminum (O/Al) molar ratio of from about 0.25 to about 1.5, more particularly from about 0.5 to about 1.

In a preferred embodiment, two or more complexes are combined with diethyl zinc in the same reactor with monomer. Alternately, one or more complexes are combined with another catalyst (such as a metallocene) and diethyl zinc in the same reactor with monomer.

Polymer Products

While the molecular weight of the polymers produced herein is influenced by reactor conditions including temperature, monomer concentration and pressure, the presence of chain

terminating agents and the like, the homopolymer and copolymer products produced by the present process may have an Mw of about 1,000 to about 2,000,000 g/mol, alternately of about 30,000 to about 600,000 g/mol, or alternately of about 100,000 to about 500,000 g/mol, as determined by GPC. Preferred polymers produced here may be homopolymers or
5 copolymers. In a preferred embodiment, the comonomer(s) are present at up to 50 mol%, preferably from 0.01 to 40 mol%, preferably 1 to 30 mol%, preferably from 5 to 20 mol%.

In some embodiments herein, a multimodal polyolefin composition is produced, comprising a first polyolefin component and at least another polyolefin component, different from the first polyolefin component by molecular weight, preferably such that the GPC trace
10 has more than one peak or inflection point.

Measurements of weight average molecular weight (Mw), number average molecular weight (Mn), and z average molecular weight (Mz) are determined by Gel Permeation Chromatography (GPC) as described in *Macromolecules*, 2001, Vol. 34, No. 19, pg. 6812, which is fully incorporated herein by reference, including that, a High Temperature Size
15 Exclusion Chromatograph (SEC, Waters Alliance 2000), equipped with a differential refractive index detector (DRI) equipped with three Polymer Laboratories PLgel 10 mm Mixed-B columns is used. The instrument is operated with a flow rate of 1.0 cm³ /min, and an injection volume of 300 µL. The various transfer lines, columns and differential refractometer (the DRI detector) are housed in an oven maintained at 145°C. Polymer
20 solutions are prepared by heating 0.75 to 1.5 mg/mL of polymer in filtered 1,2,4-(TCB) containing ~1000 ppm of butylated hydroxy toluene (BHT) at 160°C for 2 hours with continuous agitation. A sample of the polymer containing solution is injected into the GPC and eluted using filtered 1,2,4-trichlorobenzene (TCB) containing ~1000 ppm of BHT. The separation efficiency of the column set is calibrated using a series of narrow MWD
25 polystyrene standards reflecting the expected Mw range of the sample being analyzed and the exclusion limits of the column set. Seventeen individual polystyrene standards, obtained from Polymer Laboratories (Amherst, MA) and ranging from Peak Molecular Weight (Mp) ~580 to 10,000,000, were used to generate the calibration curve. The flow rate is calibrated for each run to give a common peak position for a flow rate marker (taken to be the positive
30 inject peak) before determining the retention volume for each polystyrene standard. The flow marker peak position is used to correct the flow rate when analyzing samples. A calibration curve (log(Mp) vs. retention volume) is generated by recording the retention volume at the peak in the DRI signal for each PS standard, and fitting this data set to a 2nd-order

polynomial. The equivalent polyethylene molecular weights are determined by using the Mark-Houwink coefficients shown in Table B.

Table B

Mark-Houwink coefficients		
Material	K (dL/g)	α
PS	1.75×10^{-4}	0.67
PE	5.79×10^{-4}	0.695

5 In a preferred embodiment, the homopolymer and copolymer products produced by the present process may have an Mw of about 1,000 to about 2,000,000 g/mol, alternately of about 30,000 to about 600,000 g/mol, or alternately of about 100,000 to about 500,000 g/mol, as determined by GPC and have a multi-modal, preferably bimodal, Mw/Mn.

Blending and Processing

10 The polymers described herein may be formed into articles using conventional equipment and methods, such as by dry blending the individual components and subsequently melt mixing in a mixer, or by mixing the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which may include a compounding extruder and a side-arm extruder used
15 directly downstream of a polymerization process. Additionally, additives may be included in the blend, in one or more components of the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives are well known in the art, and can include, for example: fillers; antioxidants (e.g., hindered phenolics such as IRGANOX™ 1010 or IRGANOX™ 1076 available from Ciba-Geigy); phosphites (e.g., IRGAFOS™ 168 available
20 from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins, alkali metal and glycerol stearates and hydrogenated rosins; UV stabilizers; heat stabilizers; antiblocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; talc; and the like.

Applications

25 Articles made using polymers produced herein may include, for example, molded articles (such as containers and bottles, e.g., household containers, industrial chemical containers, personal care bottles, medical containers, fuel tanks, and storageware, toys, sheets, pipes, tubing) films, non-wovens, and the like. It should be appreciated that the list of applications above is merely exemplary, and is not intended to be limiting.

30 The polymer compositions described herein are useful in a wide variety of

applications, including transparent articles such as cook and storage ware, and in other articles such as furniture, automotive components, toys, sportswear, medical devices, sterilizable medical devices and sterilization containers, nonwoven fibers and fabrics and articles therefrom such as drapes, gowns, filters, hygiene products, diapers, and films, oriented films, sheets, tubes, pipes and other items where softness, high impact strength, and impact strength below freezing are important.

Additional examples of desirable articles of manufacture made from compositions of the invention include films, sheets, fibers, woven and nonwoven fabrics, automotive components, furniture, sporting equipment, food storage containers, transparent and semi-transparent articles, toys, tubing and pipes, sheets, packaging, bags, sacks, coatings, caps, closures, crates, pallets, cups, non-food containers, pails, insulation, and medical devices. Further examples include automotive components, wire and cable jacketing, pipes, agricultural films, geomembranes, toys, sporting equipment, medical devices, casting and blowing of packaging films, extrusion of tubing, pipes and profiles, sporting equipment, outdoor furniture (*e.g.*, garden furniture) and playground equipment, boat and water craft components, and other such articles.

Films

The compositions described above and the blends thereof may be formed into monolayer or multilayer films. These films may be formed by any of the conventional techniques known in the art including extrusion, co-extrusion, extrusion coating, lamination, blowing and casting. The film may be obtained by the flat film or tubular process which may be followed by orientation in a uniaxial direction or in two mutually perpendicular directions in the plane of the film. One or more of the layers of the film may be oriented in the transverse and/or longitudinal directions to the same or different extents. This orientation may occur before or after the individual layers are brought together. For example, a polyethylene layer can be extrusion coated or laminated onto an oriented polypropylene layer or the polyethylene and polypropylene can be coextruded together into a film then oriented. Likewise, oriented polypropylene could be laminated to oriented polyethylene or oriented polyethylene could be coated onto polypropylene, then optionally the combination could be oriented even further. Typically the films are oriented in the Machine Direction (MD) at a ratio of up to 15, preferably between 5 and 7, and in the Transverse Direction (TD) at a ratio of up to 15 preferably 7 to 9. However, in another embodiment, the film is oriented to the same extent in both the MD and TD directions.

In multilayer constructions, the other layer(s) may be any layer typically included in

multilayer film structures. For example, the other layer or layers may be:

1. Polyolefins. Preferred polyolefins include homopolymers or copolymers of C₂ to C₄₀ olefins, preferably C₂ to C₂₀ olefins, preferably a copolymer of an alpha-olefin and another olefin or alpha-olefin (ethylene is defined to be an alpha-olefin for purposes of this invention). Preferably homopolyethylene, homopolypropylene, propylene copolymerized with ethylene and or butene, ethylene copolymerized with one or more of propylene, butene or hexene, and optional dienes. Preferred examples include thermoplastic polymers such as ultra-low density polyethylene, very low density polyethylene, linear low density polyethylene, low density polyethylene, medium density polyethylene, high density polyethylene, polypropylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene and/or butene and/or hexene, elastomers such as ethylene propylene rubber, ethylene propylene diene monomer rubber, neoprene, and blends of thermoplastic polymers and elastomers, such as, for example, thermoplastic elastomers and rubber toughened plastics.
2. Polar polymers. Preferred polar polymers include homopolymers and copolymers of esters, amides, acetates, anhydrides, copolymers of a C₂ to C₂₀ olefin, such as ethylene and/or propylene and/or butene with one or more polar monomers such as acetates, anhydrides, esters, alcohol, and or acrylics. Preferred examples include polyesters, polyamides, ethylene vinyl acetate copolymers, and polyvinyl chloride.
3. Cationic polymers. Preferred cationic polymers include polymers or copolymers of geminally disubstituted olefins, alpha-heteroatom olefins and/or styrenic monomers. Preferred geminally disubstituted olefins include isobutylene, isopentene, isoheptene, isohexane, isooctene, isodecene, and isododecene. Preferred alpha-heteroatom olefins include vinyl ether and vinyl carbazole, preferred styrenic monomers include styrene, alkyl styrene, para-alkyl styrene, alpha-methyl styrene, chloro-styrene, and bromo-para-methyl styrene. Preferred examples of cationic polymers include butyl rubber, isobutylene copolymerized with para methyl styrene, polystyrene, and poly-alpha-methyl styrene.
4. Miscellaneous. Other preferred layers can be paper, wood, cardboard, metal, metal foils (such as aluminum foil and tin foil), metallized surfaces, glass (including silicon oxide (SiO_x) coatings applied by evaporating silicon oxide onto a film surface), fabric,

spunbonded fibers, and non-wovens (particularly polypropylene spun bonded fibers or non-wovens), and substrates coated with inks, dyes, pigments, and the like.

The films may vary in thickness depending on the intended application; however, films of a thickness from 1 μm to 250 μm are usually suitable. Films intended for packaging
5 are usually from 10 to 60 micron thick. The thickness of the sealing layer is typically 0.2 μm to 50 μm . There may be a sealing layer on both the inner and outer surfaces of the film or the sealing layer may be present on only the inner or the outer surface.

Additives such as block, antiblock, antioxidants, pigments, fillers, processing aids, UV stabilizers, neutralizers, lubricants, surfactants and/or nucleating agents may also be
10 present in one or more than one layer in the films. Preferred additives include silicon dioxide, titanium dioxide, polydimethylsiloxane, talc, dyes, wax, calcium stearate, carbon black, low molecular weight resins and glass beads, preferably these additives are present at from 0.1 ppm to 1000 ppm.

In another embodiment, one more layers may be modified by corona treatment,
15 electron beam irradiation, gamma irradiation, or microwave irradiation. In a preferred embodiment, one or both of the surface layers is modified by corona treatment.

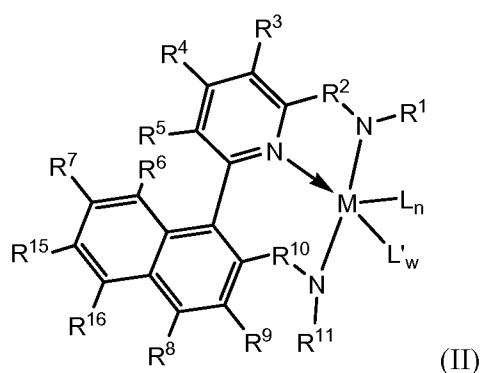
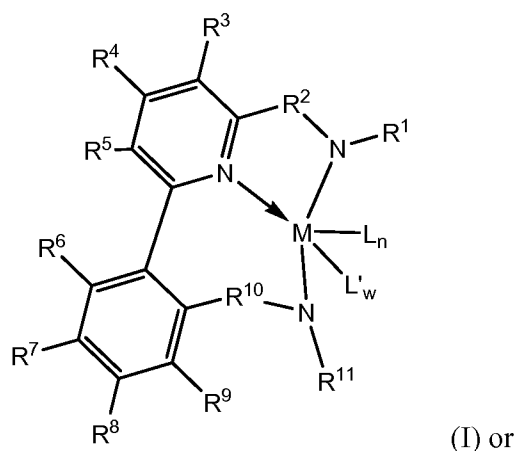
The films described herein may also comprise from 5 wt% to 60 wt%, based upon the weight of the polymer and the resin, of a hydrocarbon resin. The resin may be combined with the polymer of the seal layer(s) or may be combined with the polymer in the core
20 layer(s). The resin preferably has a softening point above 100°C, even more preferably from 130°C to 180°C. Preferred hydrocarbon resins include those described above. The films comprising a hydrocarbon resin may be oriented in uniaxial or biaxial directions to the same or different degrees. For more information on blends of tackifiers and modifiers useful herein, see USSN 60/617,594, filed October 8, 2004.

25 The films described above may be used as stretch and/or cling films. Stretch/cling films are used in various bundling, packaging and palletizing operations. To impart cling properties to, or improve the cling properties of, a particular film, a number of well-known tackifying additives have been utilized. Common tackifying additives include polybutenes, terpene resins, alkali metal stearates and hydrogenated rosins and rosin esters. The cling
30 properties of a film can also be modified by the well-known physical process referred to as corona discharge. Some polymers (such as ethylene methyl acrylate copolymers) do not need cling additives and can be used as cling layers without tackifiers. Stretch/clings films may comprise a slip layer comprising any suitable polyolefin or combination of polyolefins such as polyethylene, polypropylene, copolymers of ethylene and propylene, and polymers

obtained from ethylene and/or propylene copolymerized with minor amounts of other olefins, particularly C₄ to C₁₂ olefins. Particularly, preferred is linear low density polyethylene (LLDPE). Additionally, the slip layer may include one or more anticling (slip and/or antiblock) additives which may be added during the production of the polyolefin or subsequently blended in to improve the slip properties of this layer. Such additives are well-known in the art and include, for example, silicas, silicates, diatomaceous earths, talcs, and various lubricants. These additives are preferably utilized in amounts ranging from about 100 ppm to about 20,000 ppm, more preferably between about 500 ppm to about 10,000 ppm, by weight based upon the weight of the slip layer. The slip layer may, if desired, also include one or more other additives as described above.

In another embodiment, this invention relates to:

1. A method to prepare a polyolefin comprising the step:
contacting an olefinic monomer or olefinic monomers with a pyridyldiamido transition metal catalyst, optionally an activator, and an aluminum containing scavenger that has an oxygen to aluminum (O/Al) molar ratio from about 0.25 and about 1.5.
2. The method of paragraph 1, wherein the olefinic monomers are one or more of ethylene, a propylene, a butylene, a hexane or an octene.
3. The method of paragraph 1, wherein the olefinic monomer is ethylene or propylene.
4. The method of paragraph 1, wherein the olefinic monomers are propylene and ethylene.
5. The method of paragraph 1, further comprising a trialkyl aluminum compound present in a concentration of from about 1 micromolar to about 50 micromolar.
6. The method of any of paragraphs 1 through 5, wherein the activator is a non-coordinating anion activator.
7. The method of paragraph 6, wherein the non-coordinating activator is N,N'-dimethylanilinium tetrakis(pentafluorophenyl)borate.
8. The method of any of paragraphs 1 through 7, wherein the concentration activator is present from about 0.1 molar equivalents to about 10 molar equivalents, based on the transition metal catalyst.
9. The method of paragraph 8, wherein the concentration of activator present is about 1 molar equivalent.
10. The method of any of paragraphs 1 through 9, wherein the pyridyldiamido transition metal catalyst is represented by the formula (I) or (II):



wherein:

5 M is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal;

R¹ and R¹¹ are each independently selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups;

R² and R¹⁰ are each, independently, -E(R¹²)(R¹³)- with E being carbon, silicon, or germanium, and each R¹² and R¹³ being independently selected from the group consisting of
 10 hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R¹² and R¹³ may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R¹² and R¹³ may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on
 15 the ring can join to form additional rings;

R³, R⁴, and R⁵ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R³ & R⁴ and/or R⁴ & R⁵) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and
 20 where substitutions on the ring can join to form additional rings;

R⁶, R⁷, R⁸, R⁹, R¹⁵, and R¹⁶ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R⁶ & R⁷, and/or R⁷ & R¹⁵, and/or R¹⁶ & R¹⁵, and/or R⁸ & R⁹) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic
5 ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

n is 0, 1, 2, 3, or 4;

10 L' is neutral Lewis base;

w is 0, 1, 2, 3, or 4; and

wherein n + w is no greater than 4.

11. The method of paragraph 10, wherein M is Ti, Zr, or Hf.

12. The method of either of paragraphs 10 or 11, wherein R⁶, R⁷, R⁸, R⁹, R¹⁵, and R¹⁶,
15 are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl.

13. The method of any of paragraphs 10 through 12, wherein each L is independently selected from the group consisting of halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, and alkynyl.

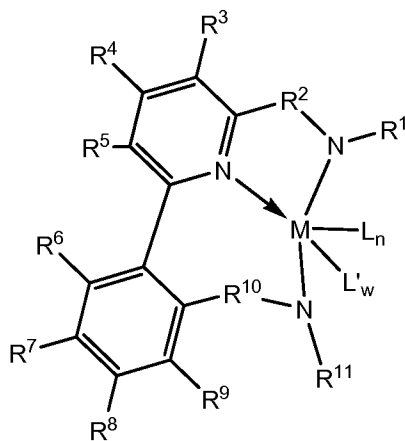
20 14. The method of any of paragraphs 10 through 13, wherein each L' is independently selected from the group consisting of ethers, thio-ethers, amines, nitriles, imines, pyridines, and phosphines.

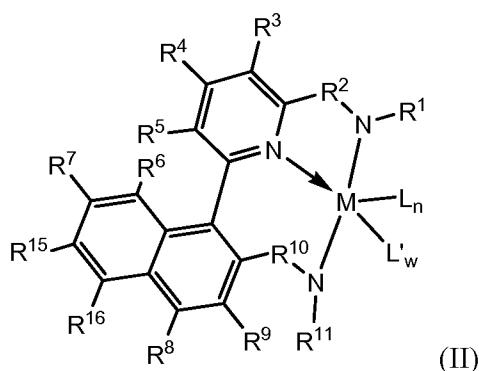
15. The method of any of paragraphs 10 through 14, wherein the R² group(s) are selected from the group consisting of CH₂, CMe₂, SiMe₂, SiEt₂, SiPr₂, SiBu₂, SiPh₂, Si(aryl)₂, and
25 Si(alkyl)₂, CH(aryl), CH(Ph), CH(alkyl), CH(2-isopropylphenyl), where alkyl is a C₁ to C₄₀ alkyl group, aryl is a C₅ to C₄₀ aryl group.

16. The method of any of paragraphs 10 through 15, wherein the R¹⁰ group(s) are selected from the group consisting of CH₂, CMe₂, SiMe₂, SiEt₂, SiPr₂, SiBu₂, SiPh₂, Si(aryl)₂, and Si(alkyl)₂, CH(aryl), CH(Ph), CH(alkyl), CH(2-isopropylphenyl), where alkyl is a C₁ to C₄₀
30 alkyl group, aryl is a C₅ to C₄₀ aryl group, and Ph is phenyl.

17. The method of any of paragraphs 10 through 16, wherein R¹¹ is an ortho alkyl substituted phenyl group.

18. The method of paragraph 17, wherein the ortho alkyl substituent is a methyl, ethyl, iso-propyl, propyl, butyl, or isobutyl group.
19. The method of either of paragraphs 17 or 18, wherein the remaining positions of the phenyl group are hydrogen atoms or the 4 and 6 positions are substituted by an alkyl group.
20. The method of any of paragraphs 1 through 19, wherein the aluminum containing scavenger is represented by the formula $((R_z-Al)_yO)_x$, wherein z is 1-2, y is 1-2, x is 1-100 and R is a C1-C12 hydrocarbyl group.
21. The method of paragraph 20, wherein R is a C4-C10 hydrocarbyl group.
22. The method of paragraph 21, wherein R is a methyl group.
23. The method of paragraph 20, wherein R is t-butyl, z is 2, y is 2 and x is 1 or alumoxane.
24. The method of any of paragraphs 1 through 23, wherein the aluminum containing scavenger is present from about 1 to about 5000 equivalents to 1 pyridyldiamido transition metal catalyst equivalent.
25. The method of paragraph 24, wherein the aluminum containing scavenger is present from about 500 to 1000 equivalents to 1 pyridyldiamido transition metal catalyst equivalent.
26. The method of any of paragraphs 1 through 25, wherein the polyolefin has a molecular weight of from about 1000 Da to about 3,000,000 Da.
27. A pyridyldiamido transition metal catalyst represented by the formula (I) or (II):





wherein:

M is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal;

5 R¹ is selected from the group consisting of hydrocarbyls, substituted hydrocarbyls, and silyl groups (preferably a phenyl group substituted at the 2 and 6 positions, preferably with the same or different C1-C20 alkyl groups);

R¹¹ is a phenyl group substituted at the 2 position, preferably with a C1-C20 alkyl group and which is not substituted at the 3, 5, and/or 6 positions provided that the 4 position can be substituted with a group 17 (preferably Cl, Br, F or I) element or a C1-C20 alkyl group;

R² and R¹⁰ are each, independently, -E(R¹²)(R¹³)- with E being carbon, silicon, or germanium, and each R¹² and R¹³ being independently selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R¹² and R¹³ may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R¹² and R¹³ may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings;

R³, R⁴, and R⁵ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R³ & R⁴ and/or R⁴ & R⁵) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

R⁶, R⁷, R⁸, R⁹, R¹⁵, and R¹⁶ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R⁶ & R⁷, and/or R⁷ & R¹⁵, and/or R¹⁶ & R¹⁵, and/or R⁸ & R⁹) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic

ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

5 n is 0, 1, 2, 3, or 4;

L' is neutral Lewis base;

w is 0, 1, 2, 3, or 4; and

wherein $n + w$ is no greater than 4.

28. The pyridyldiamido transition metal catalyst of paragraph 27, wherein M is Ti, Zr, or
10 Hf.

29. The pyridyldiamido transition metal catalyst of either of paragraphs 27 or 28, wherein R^6 , R^7 , R^8 , R^9 , R^{15} , and R^{16} , are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl.

30. The pyridyldiamido transition metal catalyst of any of paragraphs 27 through 29,
15 wherein each L is independently selected from the group consisting of halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, and alkynyl.

31. The pyridyldiamido transition metal catalyst of any of paragraphs 27 through 30, wherein each L' is independently selected from the group consisting of ethers, thio-ethers, amines, nitriles, imines, pyridines, and phosphines.

20 32. The pyridyldiamido transition metal catalyst of any of paragraphs 27 through 31, wherein the R^2 group(s) are selected from the group consisting of CH_2 , CMe_2 , $SiMe_2$, $SiEt_2$, $SiPr_2$, $SiBu_2$, $SiPh_2$, $Si(aryl)_2$, and $Si(alkyl)_2$, $CH(aryl)$, $CH(Ph)$, $CH(alkyl)$, $CH(2-isopropylphenyl)$, where alkyl is a C_1 to C_{40} alkyl group, aryl is a C_5 to C_{40} aryl group.

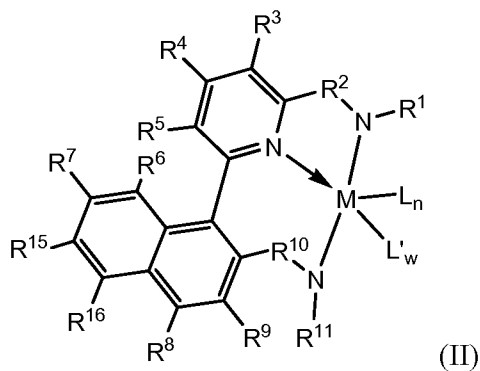
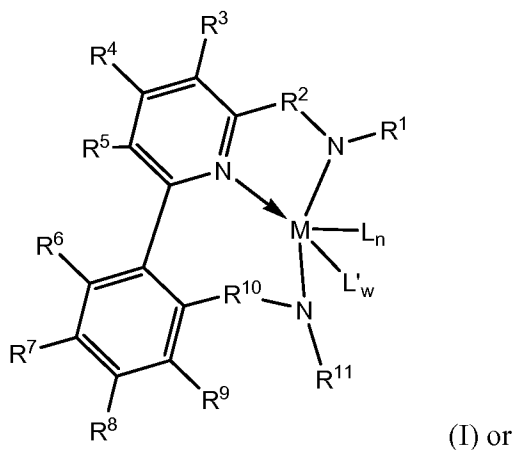
33. The pyridyldiamido transition metal catalyst of any of paragraphs 27 through 32,
25 wherein the R^{10} group(s) are selected from the group consisting of CH_2 , CMe_2 , $SiMe_2$, $SiEt_2$, $SiPr_2$, $SiBu_2$, $SiPh_2$, $Si(aryl)_2$, and $Si(alkyl)_2$, $CH(aryl)$, $CH(Ph)$, $CH(alkyl)$, $CH(2-isopropylphenyl)$, where alkyl is a C_1 to C_{40} alkyl group, aryl is a C_5 to C_{40} aryl group, and Ph is phenyl.

34. The pyridyldiamido transition metal catalyst of any of paragraphs 27 through 33,
30 wherein R^{11} is an ortho alkyl substituted phenyl group.

35. The pyridyldiamido transition metal catalyst of paragraph 34, wherein the ortho alkyl substituent is a methyl, ethyl, iso-propyl, propyl, butyl, or isobutyl group.

36. The pyridyldiamido transition metal catalyst of either of paragraphs 34 or 35, wherein the remaining positions of the phenyl group are hydrogen atoms or the 4 position is substituted by a halogen or a C1-C20 alkyl group.

37. A catalyst system comprising optionally an activator, an aluminum containing
5 scavenger that has an oxygen to aluminum (O/Al) molar ratio from about 0.25 to about 1.5 and a pyridyldiamido transition metal complex represented by the formula (I) or (II):



10 wherein:

M is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal;

R¹ and R¹¹ are each independently selected from the group consisting of hydrocarbyls, and substituted hydrocarbyls, or silyl groups;

15 R² and R¹⁰ are each, independently, -E(R¹²)(R¹³)- with E being carbon, silicon, or germanium, and each R¹² and R¹³ being independently selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R¹² and R¹³ may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R¹² and R¹³ may be joined to form a

saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings;

R³, R⁴, and R⁵ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and
5 wherein adjacent R groups (R³ & R⁴ and/or R⁴ & R⁵) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

R⁶, R⁷, R⁸, R⁹, R¹⁵, and R¹⁶ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and
10 wherein adjacent R groups (R⁶ & R⁷, and/or R⁷ & R¹⁵, and/or R¹⁶ & R¹⁵, and/or R⁸ & R⁹) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two

15 L groups may be linked to form a dianionic leaving group;

n is 0, 1, 2, 3, or 4;

L' is neutral Lewis base;

w is 0, 1, 2, 3, or 4; and

wherein n + w is no greater than 4.

20 38. The catalyst system of paragraph 37, wherein the optional activator is a non-coordinating anion.

39. The catalyst system of paragraph 37, wherein the optional activator is alumoxane.

40. The catalyst system of paragraph 37, wherein R¹¹ is a phenyl group substituted at the 2 position with a C1-C20 alkyl group.

25 41. The catalyst system of paragraph 38, wherein R¹ is a phenyl group substituted at the 2 and 6 position with the same or different C1-C20 alkyl groups.

42. The catalyst system of paragraph 38, where R¹¹ is a phenyl group substituted at the 2 position, preferably with a C1-C20 alkyl group and which is not substituted at the 3, 5, and/or 6 positions.

30 43. The catalyst system of paragraph 42, where the 4 position can be substituted with a group 17 element or a C1-C20 alkyl group.

EXAMPLES

¹H NMR spectroscopic data were acquired at 250, 400, or 500 MHz using solutions prepared by dissolving approximately 10 mg of a sample in either C₆D₆, CD₂Cl₂, CDCl₃, or D₈-toluene. The chemical shifts (δ) presented are relative to the residual protium in the deuterated solvent at 7.15, 5.32, 7.24, and 2.09 (methyl resonance) for C₆D₆, CD₂Cl₂, CDCl₃, and D₈-toluene, respectively. For purposes of the claims 500Mz and CD₂Cl₂ are used.

Gel Permeation Chromatography (GPC) - Multiple Angle Light Scattering (MALLS)

Mw, Mn and Mw/Mn are determined by using a High Temperature Size Exclusion Chromatograph (Polymer Laboratories), equipped with three in-line detectors, a differential refractive index detector (DRI), a light scattering (LS) detector, and a viscometer. Experimental details, including detector calibration, are described in T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001) and references therein. Three Polymer Laboratories PLgel 10μm Mixed-B LS columns are used. The nominal flow rate is 0.5 ml/min, and the nominal injection volume is 300 μL. The various transfer lines, columns, viscometer and differential refractometer (the DRI detector) are contained in an oven maintained at 145°C. Solvent for the experiment is prepared by dissolving 6 grams of butylated hydroxytoluene as an antioxidant in 4 liters of Aldrich reagent grade 1, 2, 4 trichlorobenzene (TCB). The TCB mixture is then filtered through a 0.1 μm Teflon filter. The TCB is then degassed with an online degasser before entering the Size Exclusion Chromatograph. Polymer solutions are prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160°C with continuous shaking for about 2 hours. All quantities are measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/ml at room temperature and 1.284 g/ml at 145°C. The injection concentration is from 0.5 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples. Prior to running each sample, the DRI detector and the injector are purged. Flow rate in the apparatus is then increased to 0.5 ml/minute, and the DRI is allowed to stabilize for 8 to 9 hours before injecting the first sample. The LS laser is turned on at least 1 to 1.5 hours before running the samples. The concentration, c, at each point in the chromatogram is calculated from the baseline-subtracted DRI signal, IDRI, using the following equation:

$$c = KDRI/DRI / (dn/dc)$$

where KDRI is a constant determined by calibrating the DRI, and (dn/dc) is the refractive index increment for the system. The refractive index, $n = 1.500$ for TCB at 145°C and $\lambda = 690$ nm. For purposes of this invention and the claims thereto (dn/dc) = 0.1048 for propylene polymers, 0.0916 for butene polymers. Units on parameters throughout this description of the SEC method are such that concentration is expressed in g/cm^3 , molecular weight is expressed in g/mole , and intrinsic viscosity is expressed in dL/g .

The LS detector is a Wyatt Technology High Temperature DAWN HELEOS. The molecular weight, M , at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M.B. Huglin, Light Scattering from Polymer Solutions, Academic Press, 1971):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c$$

Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ ; c is the polymer concentration determined from the DRI analysis; A_2 is the second virial coefficient; for purposes of this invention $A_2 = 0.0006$ for propylene polymers; 0.0015 for butene polymers; (dn/dc) = 0.1048 for propylene polymers; 0.0916 for butene polymers; $P(\theta)$ is the form factor for a monodisperse random coil; and K_o is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system. The refractive index, $n = 1.500$ for TCB at 145°C and $\lambda = 657$ nm.

A high temperature Viscotek Corporation viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

$$\eta_s = c[\eta] + 0.3(c[\eta])^2$$

where c is concentration and was determined from the DRI output.

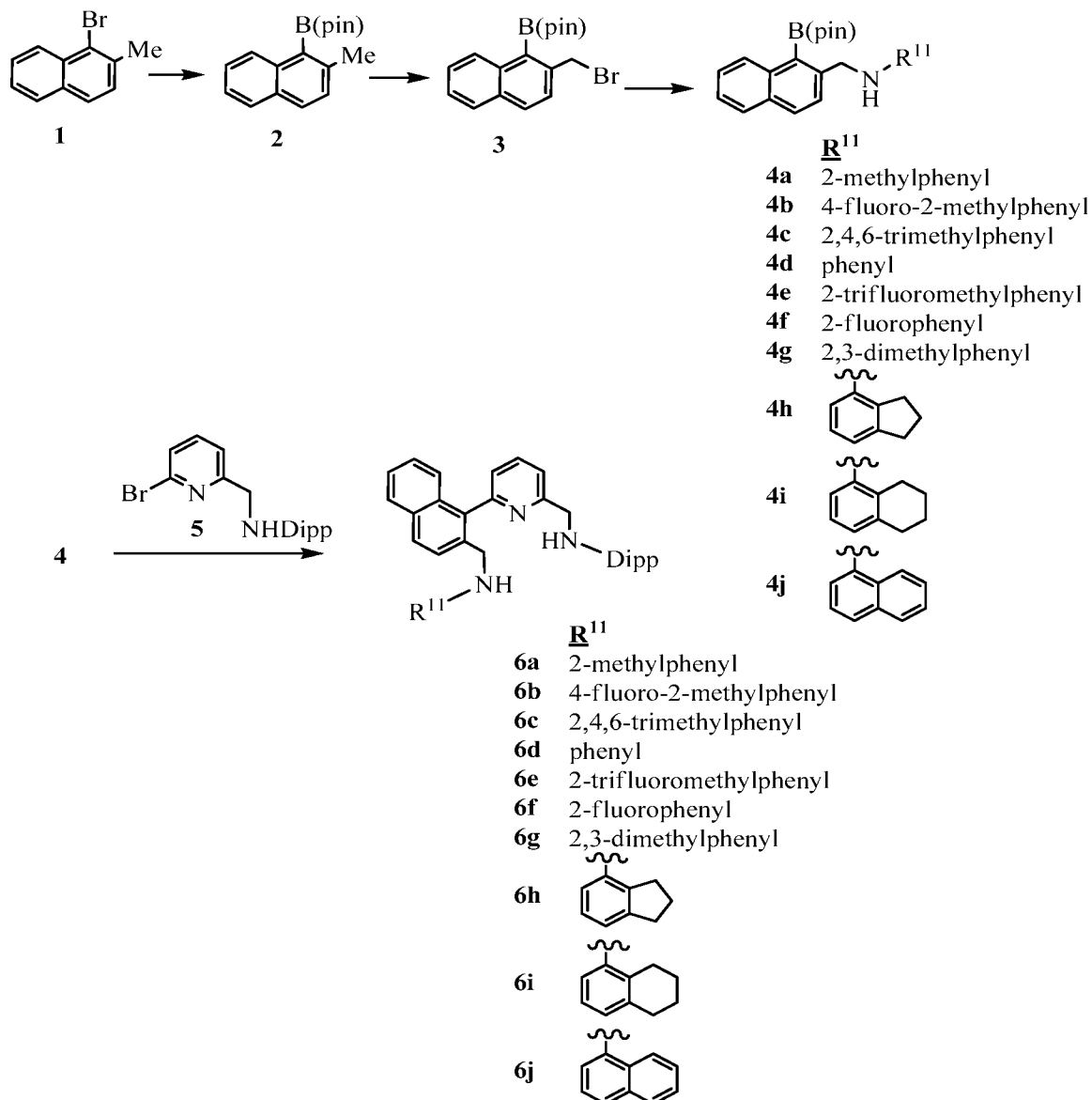
All molecular weights are weight average unless otherwise noted. All molecular weights are reported in g/mol unless otherwise noted.

The complexes used as catalyst components in polymerization examples are shown in Figure 1. Complexes C1 and C2 and the intermediates 4c, 4d, 6c, and 6d (Scheme 1) were prepared as described in US2011/0301310A1 and US2012/0071616A1. All other pyridyldiamines and pyridyldiamide complexes were prepared using the general procedures described below.

General synthesis of pyridyl diamines

Outlined in Scheme 1 is the general synthetic route that was used to prepare the pyridyldiamines used herein with the exception of those listed above. In the Scheme, pin is pinacolate (2,3-dimethylbutane-2,3-diolate), Me is methyl, Dipp is 2,6-diisopropylphenyl. A detailed procedure is presented for the preparation of pyridyldiamine 6a. The pyridyldiamines 6b, 6e, 6f, 6g, 6h, 6i, 6j were prepared and isolated analogously to 6a and only characterization data are presented.

15

Scheme 1. Overview of pyridyl diamine synthesis routes.**4,4,5,5-Tetramethyl-2-(2-methyl-1-naphthyl)-1,3,2-dioxaborolane (2).**

5 1,2-Dibromoethane (~0.3 ml) was added to 6.10 g (250 mmol) magnesium turnings in 1000 cm³ of THF. This mixture was stirred for 10 min, and then 55.3 g (250 mmol) of 1-bromo-2-methylnaphthalene was added for 1 h by vigorous stirring at room temperature for 3.5 h. Thereafter, 46.5 g (250 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added in one portion. The resulting mixture was stirred for 15 minutes

10 and then was poured into 1000 cm³ of cold water. The product was extracted with 3 x 300 ml of ethyl acetate. The organic layer was separated, washed by water, brine, then dried over MgSO₄, and, finally, evaporated to dryness. The resulting white solid was washed by 2 x 75

ml of pentane and dried in vacuum. Yield 47.3 g (70%). Anal. calc. for $C_{17}H_{21}BO_2$: C, 76.14; H, 7.89. Found: C, 76.31; H, 8.02. 1H NMR ($CDCl_3$): 8.12 (m, 1H, 8-H), 7.77 (m, 1H, 5-H), 7.75 (d, $J = 8.4$ Hz, 1H, 4-H), 7.44 (m, 1H, 7-H), 7.38 (m, 1H, 6-H), 7.28 (d, $J = 8.4$ Hz, 1H, 3-H), 2.63 (s, 3H, 2-Me), 1.48 (s, 12H, CMe_2CMe_2).

5 **2-[2-(Bromomethyl)-1-naphthyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3).**

A mixture of 47.3 g (176 mmol) of 4,4,5,5-tetramethyl-2-(2-methyl-1-naphthyl)-1,3,2-dioxaborolane, 33.0 g (185 mmol) of NBS (N-Bromosuccinimide) and 0.17 g of benzoyl peroxide in 340 ml of CCl_4 was stirred at $75^\circ C$ for 14 h. Thereafter the reaction mixture was cooled to room temperature, filtered through glass frit (G3), and the filtrate was
10 evaporated to dryness. This procedure gave 62.2 g (99%) of beige solid. Anal. calc. for $C_{17}H_{20}BBrO_2$: C, 58.83; H, 5.81. Found: C, 59.00; H, 5.95. 1H NMR ($CDCl_3$): 8.30 (m, 1H, 8-H), 7.84 (d, $J = 8.3$ Hz, 1H, 4-H), 7.79 (m, 1H, 5-H), 7.43-7.52 (m, 3H, 3,6,7-H), 4.96 (s, 2H, CH_2Br), 1.51 (s, 12H, CMe_2CMe_2).

15 **2-Methyl-N-((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-yl)methyl)aniline (4a).**

A mixture of 10.8 g (101 mmol) of 2-methylaniline, 23.3 g (67.0 mmol) of 2-[2-(bromomethyl)-1-naphthyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 3), and 10.2 g (74.0 mmol) of K_2CO_3 in 450 mL of DMF was stirred for 12 h at $80^\circ C$. The resulting mixture was poured into 1000 mL of water. The product was extracted with 3 x 200 ml of
20 ethyl acetate. The combined extract was dried over $MgSO_4$ and then evaporated to dryness. The residue was re-crystallized from a mixture of 200 ml of hexane and 10 ml of ethyl acetate. Yield 15.7 g (63%) of a brown crystalline powder. Anal. calc. for $C_{24}H_{28}BNO_2$: C, 77.22; H, 7.56; N, 3.75. Found: C, 77.33; H, 7.67; N, 3.59. 1H NMR ($CDCl_3$): δ 8.20 (m, 1H, 8-H in naphthyl), 7.84 (d, $J = 8.5$ Hz, 1H, 4-H in naphthyl), 7.82 (m, 1H, 5-H in naphthyl), 7.43-7.52 (m, 3H, 3,6,7-H in naphthyl), 7.14 (m, 1H, 5-H in o-tolyl), 7.06 (m, 1H, 3-H in o-tolyl), 6.79 (m, 1H, 6-H in o-tolyl), 6.68 (m, 1H, 4-H in o-tolyl), 4.53 (s, 2H, CH_2N), 3.95 (br.s, 1H, NH), 2.11 (s, 3H, 2-Me in o-tolyl), 1.36 (s, 12H, CMe_2CMe_2).

N-[(6-Bromopyridin-2-yl)methyl]-2,6-diisopropylaniline (5).

A mixture of 25.0 g (134 mmol) of 6-bromopyridine-2-carbaldehyde, 23.8 g (134
30 mmol) of 2,6-diisopropylaniline and 1.15 g (6.70 mmol) of TsOH in 600 ml of toluene was refluxed for 15 min using a Soxhlet apparatus filled with $CaCl_2$. The obtained solution was evaporated to dryness, and the residue was re-crystallized from 100 ml of methanol to give

the imine product *N*-[(1*E*)-(6-bromopyridin-2-yl)methylene]-2,6-diisopropylaniline as a yellow crystalline solid (23.9 g). In argon atmosphere, a mixture of 22.4 g (65.0 mmol) of *N*-[(1*E*)-(6-bromopyridin-2-yl)methylene]-2,6-diisopropylaniline, 6.53 g (104 mmol) of NaBH₃CN, 2 ml of AcOH and 430 ml of methanol was refluxed for 12 h. The obtained mixture was cooled, poured into 1000 ml of water, and then extracted with 3 x 200 ml of ethyl acetate. The combined extract was dried over MgSO₄ and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 19.8 g (43%) of a yellow oil. Anal. calc. for C₁₈H₂₃BrN₂: C, 62.25; H, 6.68; N, 8.07. Found: C, 62.40; H, 6.77; N, 7.96. ¹H NMR (CDCl₃): δ 7.50 (m, 1H, 4-H in 6-bromopyridyl), 7.38 (m, 1H, 5-H in 6-bromopyridyl), 7.28 (m, 1H, 3-H in 6-bromopyridyl), 7.01-7.11 (m, 3H, 3,4,5-H in 2,6-diisopropylphenyl), 4.16 (s, 2H, CH₂N), 3.93 (br.s, 1H, NH), 3.31 (sep, J = 6.9 Hz, 2H, CHMe₂), 1.22 (d, J = 6.9 Hz, 12H, CHMe₂).

2,6-Diisopropyl-*N*-{[6-(2-[(2-methylphenyl)amino]methyl]-1-naphthyl)pyridin-2-yl]methyl}aniline (6a).

A mixture of 27.2 g (95.0 mmol) of Na₂CO₃·10H₂O, 410 ml of water and 120 ml of methanol was purged with argon for 30 min. The obtained solution was added to a mixture of 14.2 g (38.0 mmol) of 2-methyl-*N*-{[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthyl]methyl}aniline (**4a**), 13.3 g (38.0 mmol) of *N*-[(6-bromopyridin-2-yl)methyl]-2,6-diisopropylaniline, and 2.19 g (1.90 mmol) of Pd(PPh₃)₄ in 500 ml of toluene. This mixture was stirred for 12 h at 70°C, then cooled to room temperature. The organic layer was separated; the aqueous layer was extracted with 3×200 ml of ethyl acetate. The combined organic extract was washed with brine, dried over Na₂SO₄ and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate-triethylamine = 100:20:1, vol.). Yield 10.1 g (52%) of a yellow powder. Anal. calc. for C₃₆H₃₉N₃: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.28; H, 7.73; N, 8.09. ¹H NMR (CDCl₃): δ 7.91 (d, J = 8.4 Hz, 1H, 4-H in naphthyl), 7.89 (m, 1H, 8-H in naphthyl), 7.79 (m, 1H, 4-H in Py), 7.66 (d, J = 8.4 Hz, 1H, 3-H in naphthyl), 7.47 (m, 1H, 7-H in naphthyl), 7.36-7.42 (m, 4H, 3,5-H in Py and 5,6-H in naphthyl), 7.04-7.10 (m, 3H, 3,5-H in *ortho*-tolyl and 4-H in 2,6-diisopropylphenyl), 7.01 (m, 2H, 3,5-H in 2,6-diisopropylphenyl), 6.61 (m, 1H, 4-H in *ortho*-tolyl), 6.52 (m, 1H, 6-H in *ortho*-tolyl), 4.22-4.35 (m, 4H, CH₂N), 4.02 (br.s, 1H, NH), 3.93 (br.s, 1H, NH), 3.28 (sept, J = 6.8 Hz, 2H, CHMe₂), 2.09 (s, 3H, Me in *ortho*-tolyl), 1.16 (d, J = 6.8 Hz, 6H, CHMeMe'), 1.14 (d, J = 6.8 Hz, 6H, CHMeMe').

***N*-{[1-(6-[(2,6-Diisopropylphenyl)amino]methyl]pyridin-2-yl)-2-naphthyl]methyl}-4-fluoro-2-methylaniline (6b)**

Anal. calc. for C₃₆H₃₈FN₃: C, 81.32; H, 7.20; N, 7.90. Found: C, 80.98; H, 7.14; N, 7.82.

5 ¹H NMR (CDCl₃): δ 7.91 (d, J = 8.5 Hz, 1H), 7.89 (m, 1H), 7.80 (m, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.35-7.50 (m, 5H), 7.03-7.11 (m, 3H), 6.75 (m, 1H), 6.71 (m, 1H), 6.42 (dd, J = 8.7 Hz, J = 4.6 Hz, 1H), 4.28 (m, 2H), 4.20 (m, 2H), 3.97 (br.s, 1H), 3.89 (br.s, 1H), 3.26 (sept, J = 6.8 Hz), 2.08 (s, 3H), 1.16 (d, J = 6.9 Hz, 6H), 1.15 (d, J = 6.9 Hz, 6H).

10 ***N*-{[6-(2-[(2-(trifluoromethyl)phenyl)amino]methyl)-1-naphthyl]pyridin-2-yl]methyl}aniline (6e)**

Anal. calc. for C₃₆H₃₆F₃N₃: C, 76.17; H, 6.39; N, 7.40. Found: C, 75.92; H, 6.30; N, 7.24.

¹H NMR (CDCl₃): δ 7.92 (d, J = 8.6 Hz, 1H), 7.89 (m, 1H), 7.82 (m, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.36-7.51 (m, 6H), 7.24 (m, 1H), 7.04-7.12 (m, 3H), 6.68 (m, 1H), 6.64 (m, 1H),
15 4.80 (m, 1H), 4.26-4.39 (m, 4H), 4.11 (br.s, 1H), 3.31 (sept, J = 6.75 Hz, 2H), 1.17 (d, J = 6.8 Hz, 6H), 1.16 (d, J = 6.8 Hz, 6H).

***N*-{[6-(2-[(2-Fluorophenyl)amino]methyl)-1-naphthyl]pyridin-2-yl]methyl}-2,6-diisopropylaniline (6f)**

20 Anal. calc. for C₃₅H₃₆FN₃: C, 81.20; H, 7.01; N, 8.12. Found: C, 80.98; H, 7.16; N, 8.30.

¹H NMR (CDCl₃): δ 7.91 (d, J = 8.4 Hz, 1H), 7.89 (m, 1H), 7.81 (m, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.45-7.50 (m, 2H), 7.35-7.42 (m, 3H), 7.04-7.12 (m, 3H), 6.87-6.95 (m, 2H), 6.54-6.64 (m, 2H), 4.40 (br.s, 2H), 4.31 (m, 2H), 4.27 (m, 2H), 3.30 (sept, J = 6.8 Hz, 2H), 1.17 (d, J = 6.8 Hz, 6H), 1.16 (d, J = 6.8 Hz, 6H).

25 ***N*-{[1-(6-[(2,6-Diisopropylphenyl)amino]methyl]pyridin-2-yl)-2-naphthyl]methyl}-2,3-dimethylaniline (6g)**

Anal. calc. for C₃₇H₄₁N₃: C, 84.21; H, 7.83; N, 7.96. Found: C, 84.37; H, 7.99; N, 7.89.

¹H NMR (CDCl₃): δ 7.91 (d, J = 8.2 Hz, 1H, 4-H in naphthyl), 7.89 (m, 1H, 8-H in naphthyl), 7.79 (m, 1H, 4-H in Py), 7.67 (d, J = 8.6 Hz, 1H, 3-H in naphthyl), 7.48 (m, 1H, 7-H in naphthyl), 7.37-7.45 (m, 4H, 3,5-H in Py and 5,6-H in naphthyl), 7.04-7.11 (m, 3H, 3,4,5-H in 2,6-diisopropylphenyl), 6.93 (m, 1H, 5-H in 2,3-dimethylphenyl), 6.56 (m, 1H, 4-H in 2,3-dimethylphenyl), 6.44 (m, 1H, 6-H in 2,3-dimethylphenyl), 4.23-4.36 (m, 4H, 2,3-

dimethylphenyl-NHCH₂ and 2,6-diisopropylphenyl-NHCH₂), 4.02 (br.s, 1H, NH), 3.98 (br.s, 1H, NH), 3.29 (sept, J = 6.8 Hz, 2H, CHMe₂), 2.24 (s, 3H, 3-Me in 2,3-dimethylphenyl), 2.01 (s, 3H, 2-Me in 2,3-dimethylphenyl), 1.17 (d, J = 6.8 Hz, 6H, CHMeMe'), 1.15 (d, J = 6.8 Hz, 6H, CHMeMe').

5 **N-[[1-(6-[(2,6-Diisopropylphenyl)amino]methyl]pyridin-2-yl)-2-naphthyl]methyl]indan-4-amine (6h)**

Anal. calc. for C₃₈H₄₁N₃: C, 84.56; H, 7.66; N, 7.79. Found: C, 84.49; H, 7.75; N, 7.62.

¹H NMR (CDCl₃): δ 7.90 (d, J = 8.5 Hz, 1H, 4-H in naphthyl), 7.88 (m, 1H, 8-H in naphthyl), 7.79 (m, 1H, 4-H in Py), 7.67 (d, J = 8.5 Hz, 1H, 3-H in naphthyl), 7.35-7.49 (m, 10 5H, 3,5-H in Py and 5,6,7-H in naphthyl), 7.03-7.10 (m, 3H, 3,4,5-H in 2,6-diisopropylphenyl), 6.97 (m, 1H, 3-H in indanyl), 6.60 (m, 1H, 4-H in indanyl), 6.35 (m, 1H, 2-H in indanyl), 4.21-4.36 (m, 4H, indanyl-NHCH₂ and 2,6-diisopropylphenyl-NHCH₂), 4.04 (br.s, 1H, NH), 3.88 (br.s, 1H, NH), 3.28 (sept, J = 6.8 Hz, 2H, CHMe₂), 2.86 (m, 2H, 5,5'-H in indanyl), 2.62 (m, 2H, 7,7'-H in indanyl), 2.03 (m, 2H, 6,6'-H in indanyl), 1.15 (d, J = 6.8 15 Hz, 6H, CHMeMe'), 1.14 (d, J = 6.8 Hz, 6H, CHMeMe').

N-[[1-(6-[(2,6-Diisopropylphenyl)amino]methyl]pyridin-2-yl)-2-naphthyl]methyl]-5,6,7,8-tetrahydronaphthalen-1-amine (6i)

Anal. calc. for C₃₉H₄₃N₃: C, 84.59; H, 7.83; N, 7.59. Found: C, 84.44; H, 7.69; N, 20 7.65.

¹H NMR (CDCl₃): δ 7.90 (d, J = 8.4 Hz, 1H, 4-H in naphthyl), 7.88 (m, 1H, 8-H in naphthyl), 7.78 (m, 1H, 4-H in Py), 7.66 (d, J = 8.4 Hz, 1H, 3-H in naphthyl), 7.36-7.49 (m, 5H, 3,5-H in Py and 5,6,7-H in naphthyl), 7.02-7.10 (m, 3H, 3,4,5-H in 2,6-diisopropylphenyl), 6.93 (m, 1H, 3-H in tetrahydronaphthyl), 6.46 (m, 1H, 4-H in 25 tetrahydronaphthyl), 6.37 (m, 1H, 2-H in tetrahydronaphthyl), 4.22-4.36 (m, 4H, tetrahydronaphthyl-NHCH₂ and 2,6-diisopropylphenyl-NHCH₂), 4.06 (br.s, 1H, NH), 3.91 (br.s, 1H, NH), 3.28 (sept, J = 6.7 Hz, 2H, CHMe₂), 2.70 (m, 2H, 5,5'-H in tetrahydronaphthyl), 2.36 (m, 2H, 8,8'-H in tetrahydronaphthyl), 1.79 (m, 2H, 7,7'-H in tetrahydronaphthyl), 1.70 (m, 2H, 6,6'-H in tetrahydronaphthyl), 1.15 (d, J = 6.7 Hz, 6H, 30 CHMeMe'), 1.14 (d, J = 6.7 Hz, 6H, CHMeMe').

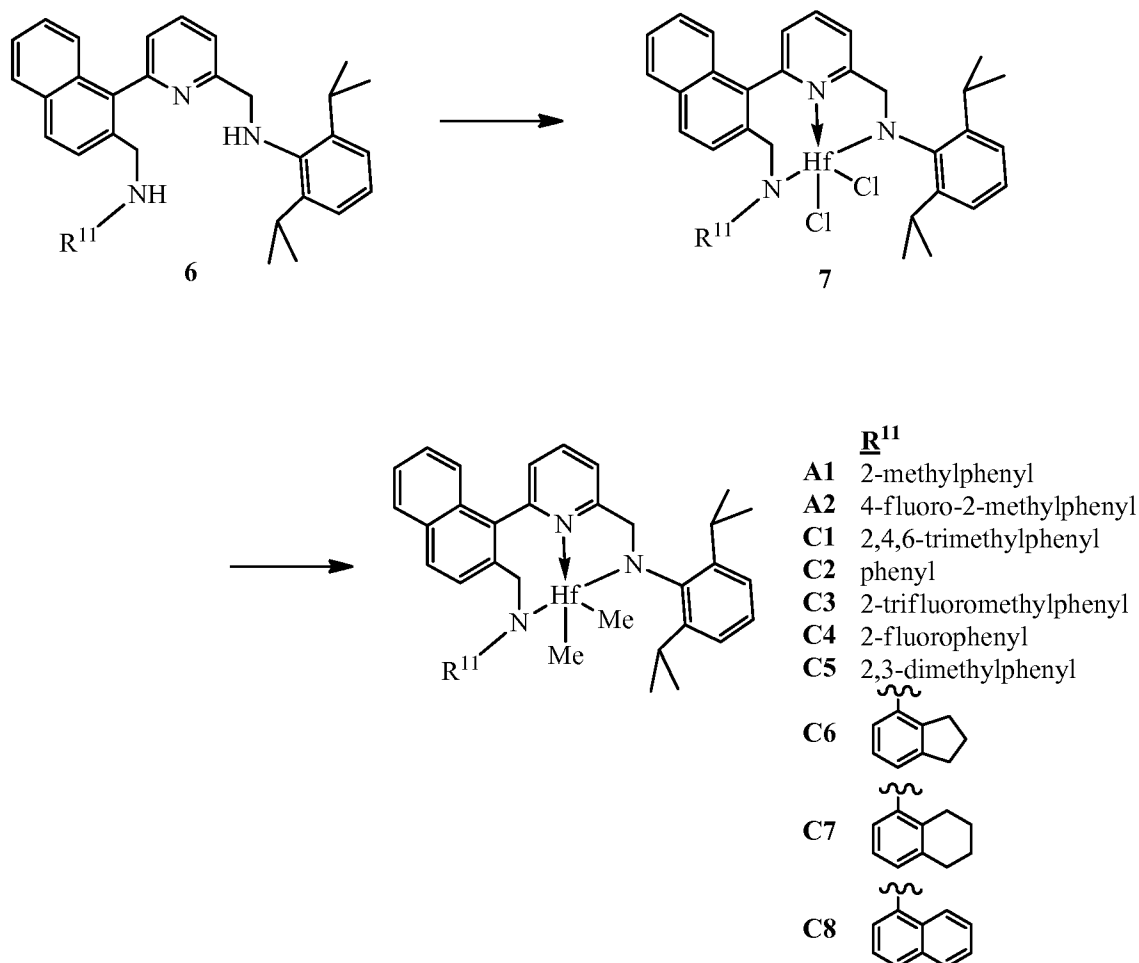
***N*-{[1-(6-[(2,6-Diisopropylphenyl)amino]methyl)pyridin-2-yl)-2-naphthyl]methyl}naphthalen-1-amine (6j)**

Anal. calc. for C₃₉H₃₉N₃: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.36; H, 7.32; N, 7.42.

5 ¹H NMR (CDCl₃): δ 7.92 (d, J = 8.4 Hz, 1H, 4-H in naphthylidene), 7.90 (m, 1H, 8-H in naphthylidene), 7.70-7.78 (m, 4H, 4-H in Py and 3,5-H in naphthylidene and 8-H in naphthyl), 7.17-7.51 (m, 9H, 3,5-H in Py and 6,7-H in naphthylidene and 3,4,5,6,7-H in naphthyl), 7.01-7.08 (m, 3H, 3,4,5-H in 2,6-diisopropylphenyl), 6.53 (m, 1H, 2-H in naphthyl), 4.91 (br.s, 1H, NH), 4.38 (m, 2H, CH₂NH-2,6-diisopropylphenyl), 4.23 (m, 2H, 10 CH₂NH-naphthyl), 3.99 (br.s, 1H, NH), 3.23 (sept, J = 6.7 Hz, 2H, CHMe₂), 1.13 (d, J = 6.7 Hz, 6H, CHMeMe'), 1.10 (d, J = 6.7 Hz, 6H, CHMeMe').

Synthesis of pyridyl diamide metal complexes

Shown below in Scheme 2 and also in Figure 2 are pyridyldiamide complexes and an outline of the general synthetic route used to prepare them. A detailed synthesis is presented 15 for complex A1. All other complexes were prepared analogously to complex A1.

Scheme 2. Synthesis of pyridyldiamide complexes**Complex A1.**

Toluene (50 mL) was added to the pyridyldiamine **6a** (2.07 g, 4.03 mmol) and
 5 Hf(NMe₂)₂Cl₂(dme) (dme = 1,2-dimethoxyethane) (1.73 g, 4.03 mmol) to form a yellow
 solution. The mixture was heated to 95°C in the dark. After 2.5 hours the suspension was
 cooled to ambient temperature for a couple of hours. The resulting solid was collected on a
 glass frit and washed with toluene (2 x 5 mL) and then dried under reduced pressure to afford
 2.4 grams of the intermediate dichloride derivative as a white solid. Proton NMR
 10 spectroscopy indicated the presence of 0.46 equivalents of toluene. This dichloride derivative
 (2.40 g, 2.99 mmol) was combined with CH₂Cl₂ (100 mL) and cooled to -40°C. A solution
 of Me₂Mg (15.3 mL, 3.59 mmol) in Et₂O was added dropwise. After 0.5 h the mixture was
 allowed to warm to ambient temperature. The volatiles were then evaporated and the residue
 was extracted with CH₂Cl₂ and filtered. The volatiles were removed to afford the crude
 15 product that was washed with pentane. Drying under reduced pressure afforded product as a

white solid (2.01 g, 93.3%). ¹H NMR (400 MHz, CD₂Cl₂): 8.2-6.9 (aryls, 16H), 5.07 (AB quartet, Δν = 130 Hz, J = 20 Hz), 4.49 (br, 1H), 4.14 (br, 1H), 3.74 (sept, 1H), 3.02 (br sept 1H), 2.30 (br, 3H), 1.4-1.0 (m, 11H), 0.89 (t, 2H), 0.55 (d, 3H), -0.80 (s, 3H), -1.13 (s, 3H).

Complex A2.

5 ¹H NMR (500 MHz, CD₂Cl₂): 8.09 (br, 2H), 7.97 (d, 1H), 7.75-7.48 (m, 6H), 7.1-6.94 (m, 5H), 6.78 (br, 1H), 5.20 (d, 1H), 4.90 (br d, 1H), 4.5-3.7 (v br, 2H), 3.73 (sept, 1H), 3.1-1.8 (v br, 3H), 1.17 (d, 6H), 1.09 (d, 3H), 0.63 (br s, 3H), -0.80 (s, 3H), -1.14 (br s, 3H).

Complex C3.

NMR characterization data is broad and complex.

10 **Complex C4.**

¹H NMR (400 MHz, CD₂Cl₂): 8.2-6.9 (m, 15H), 5.03 (AB quartet, 2H), 4.42 (AB quartet, 2H), 3.74 (sept, 1H), 3.07 (sept, 1H), 1.15 (m, 9H), 0.62 (d, 3H), -0.65 (s, 3H), -1.09 (s, 3H).

Complex C5.

15 Proton NMR data is complex and broad and suggests the presence of multiple rotational isomers.

Complex C6.

20 ¹H NMR (400 MHz, CD₂Cl₂): 8.2-7.5 (m, 9H), 7.1-6.7 (m, 6H), 5.01 (AB quartet, 2H), 4.38 (AB quartet, 2H), 3.73 (sept, 1H), 2.9 (m, 4H), 2.6 (m, 1H), 2.01 (m, 2H), 1.16 (d, 3H), 1.10 (m, 6H), 0.51 (d, 3H), -0.70 (s, 3H), -1.14 (s, 3H).

Complex C7.

Proton NMR data is complex and broad and suggests the presence of multiple rotational isomers.

Complex C8.

25 Proton NMR data is complex and broad and suggests the presence of multiple rotational isomers.

Polymerizations Examples

General polymerization procedures for parallel pressure reactor

30 Both propylene homopolymerizations and ethylene-propylene copolymerizations were carried out in a parallel pressure reactor, as generally described in US 6,306,658; US 6,455,316; US 6,489,168; WO 00/09255; and Murphy et al., J. Am. Chem. Soc., 2003, 125, pp. 4306-4317, each of which is fully incorporated herein by reference for US purposes. Although the specific quantities, temperatures, solvents, reactants, reactant ratios, pressures,

and other variables are frequently changed from one polymerization run to the next, the following describes a typical polymerization performed in a parallel pressure reactor.

A pre-weighed glass vial insert and disposable stirring paddle were fitted to each reaction vessel of the reactor, which contains 48 individual reaction vessels. The reactor was then closed and propylene (typically 1 mL) was introduced to each vessel as a condensed gas liquid. If ethylene was added as a comonomer, it was added before the propylene as a gas to a pre-determined pressure (typically 10-80 psi) while the reactor vessels were heated to a set temperature (typically 40°C). Then solvent (typically isohexane) was added to bring the total reaction volume, including the subsequent additions, to 5 mL and the reactor vessels were heated to their set temperature (usually between 50°C and 110°C). At this time scavenger and/or co-catalyst and/or a chain transfer agent, such as tri-n-octylaluminum in toluene or bis(diisobutylaluminum) oxide in hexane (typically 100-1000 nmol) was added.

The contents of the vessel were stirred at 800 rpm. An activator solution (typically 1.0-1.2 molar equivalents of dimethyl anilinium tetrakis-pentafluorophenyl borate dissolved in toluene or 100-1000 molar equivalents of methyl alumoxane (MAO) in toluene) was then injected into the reaction vessel along with 500 microliters of toluene, followed by a toluene solution of catalyst (typically 0.40 mM in toluene, usually 20-40 nanomols of catalyst) and another aliquot of toluene (500 microliters). Equivalence is determined based on the mol equivalents relative to the moles of the transition metal in the catalyst complex.

The reaction was then allowed to proceed until a pre-determined amount of pressure had been taken up by the reaction. Alternatively, the reaction may be allowed to proceed for a set amount of time. At this point, the reaction was quenched by pressurizing the vessel with compressed air. After the polymerization reaction, the glass vial insert containing the polymer product and solvent was removed from the pressure cell and the inert atmosphere glove box, and the volatile components were removed using a Genevac HT-12 centrifuge and Genevac VC3000D vacuum evaporator operating at elevated temperature and reduced pressure. The vial was then weighed to determine the yield of the polymer product. The resultant polymer was analyzed by Rapid GPC (see below) to determine the molecular weight, by FT-IR (see below) to determine percent ethylene incorporation, and by DSC (see below) to determine melting point.

To determine various molecular weight related values by GPC, high temperature size exclusion chromatography was performed using an automated "Rapid GPC" system as generally described in US 6,491,816; US 6,491,823; US 6,475,391; US 6,461,515; US 6,436,292; US 6,406,632; US 6,175,409; US 6,454,947; US 6,260,407; and US 6,294,388;

each of which is fully incorporated herein by reference for US purposes. This apparatus has a series of three 30 cm x 7.5 mm linear columns, each containing PLgel 10 μ m, Mix B. The GPC system was calibrated using polystyrene standards ranging from 580 - 3,390,000 g/mol. The system was operated at an eluent flow rate of 2.0 mL/minutes and an oven temperature of 165°C. 1,2,4-trichlorobenzene was used as the eluent. The polymer samples were dissolved in 1,2,4-trichlorobenzene at a concentration of 0.1 - 0.9 mg/mL. 250 μ L of a polymer solution was injected into the system. The concentration of the polymer in the eluent was monitored using an evaporative light scattering detector. The molecular weights presented are relative to linear polystyrene standards and are uncorrected.

Differential Scanning Calorimetry (DSC) measurements were performed on a TA-Q100 instrument to determine the melting point of the polymers. Samples were pre-annealed at 220°C for 15 minutes and then allowed to cool to room temperature overnight. The samples were then heated to 220°C at a rate of 100°C/minutes and then cooled at a rate of 50°C/min. Melting points were collected during the heating period. The weight percent of ethylene incorporated in the ethylene-propylene copolymers was determined by rapid FT-IR spectroscopy on a Bruker Equinox 55+ IR in reflection mode. Samples were prepared in a thin film format by evaporative deposition techniques. Weight percent ethylene was obtained from the ratio of peak heights at 744-715 and 1189-1126 cm^{-1} . This method was calibrated using a set of ethylene/propylene copolymers with a range of known wt% ethylene content.

Comparison of Al Scavenger Effect on Molecular Weight of Polypropylene

The homopolymerization of propylene was performed in a parallel pressure reactor using a catalyst system consisting of complex **C1** and $[\text{PhNHMe}_2]\text{B}(\text{C}_6\text{F}_5)_4$ activator. The choice of scavenger was found to have a large effect on molecular weight of the resulting polymer. Over all concentration ranges explored bis(diisobutylaluminum)oxide (DIBALO) and PMAO-IPTM (a polymethylaluminoxane available from AkzoNobel, Pasadena, Texas) scavengers yielded higher molecular weight polymer relative to Oct_3Al scavenger. Overall, DIBALO gave the best results with the least reduction in molecular weight, even at high concentrations of scavenger. These data are presented in Figure 2.

Comparison of catalyst reactivity

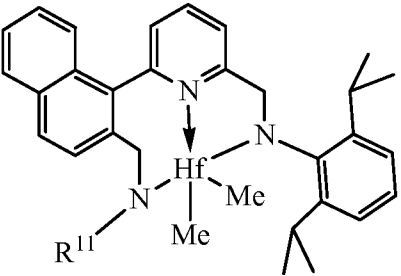
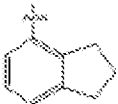
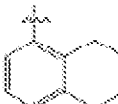
Effect of substitution at R¹¹ position on propylene homopolymerization.

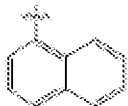
The effect of substitution at the R¹¹ (Formula I) position on propylene polymerization can be determined by comparing the performance of complexes **A1** (R¹¹ = 2-methylphenyl) and **A2** (R = 4-fluoro-2-methylphenyl) to those of comparatives **C1** through **C8** when all complexes have been activated under identical conditions. These experiments were

performed and the results are shown in Table 2. Catalysts mixtures formed with **A1** and **A2** were found to be significantly more active for propylene polymerization at both 85 and 100°C than related catalysts formed from complexes **C1** through **C8** (see Table 1). This indicates a preferred structure for the R¹¹ group, which is a single ortho substitution, preferably by a methyl group, with additional optional substitution at the 4 position. The use of an R¹¹ group that contains no substitution (e.g. **C2**), 2,6-disubstitution (e.g. **C1**), ortho substitution by a fluorocarbon group (e.g. **C3**), ortho substitution by a halogen (e.g. **C4**), or 2,3-disubstitution with (e.g. **C6-C8**) or without (e.g. **C5**) ring formation all gave relatively poor activities.

Table 1.

Effect of substitution at **R¹¹** position on propylene polymerization. Conditions: isohexane solvent, propylene added = 1 mL, total volume = 5 mL, complex = 30-40 nmol, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate activator (1.1 equivalents relative to complex), tri-n-octylaluminum (300 nmol). Activities are given as kilograms of PP/mmol of Hf/hour. Complexes marked with an asterisk (*) are comparative examples.

			
Complex	R ¹¹	Activity at 85°C	Activity at 100°C
A1	2-methylphenyl	187	61
A2	4-fluoro-2-methylphenyl	171	63
C1*	2,4,6-trimethylphenyl	68	13
C2*	Phenyl	20	4
C3*	2-trifluoromethylphenyl	<1	<1
C4*	2-fluorophenyl	<1	<1
C5*	2,3-dimethylphenyl	86	9
C6*		15	3
C7*		2	1

C8*		<1	<1
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Ethylene-Propylene Copolymerization in a Continuous Reactor

All of the examples were produced in a 0.5-liter continuous stirred-tank reactor operated in a solution process. The autoclave reactor was equipped with a stirrer, a water-cooling/steam-heating element with a temperature controller, and a pressure controller.
 5 Solvents and monomers were first purified by passing through a three-column purification system. Purification columns were regenerated periodically whenever there was evidence of lower activity of polymerization.

Isohexane was used as a solvent. The solvent was fed into the reactor using a Pulsar
 10 pump and its flow rate was controlled by a mass flow controller. Ethylene was delivered as a gas solubilized in the chilled solvent/monomer mixture. The compressed, liquefied propylene feed was controlled by a mass flow controller. The solvent and monomer were fed into a manifold first. The mixture of solvent and monomers were then chilled to about -15°C by passing through a chiller prior to feeding into the reactor through a single tube. The
 15 collected samples were first air-dried in a hood to evaporate most of the solvent and unreacted monomers, and then dried in a vacuum oven at a temperature of about 90°C for about 12 hours. The vacuum oven dried samples were weighed to obtain yields. Ethylene and propylene conversion was calculated basing on the polymer yield, composition and the amount of monomers fed into the reactor. Catalyst activity (also referred as to catalyst
 20 productivity) was calculated based the yield and the feed rate of catalyst (catalyst only). All the reactions were carried out at a gauge pressure of about 2.4 MPa.

Catalyst used in the following examples was complex A1 and N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate. Both the complex A and activator were first dissolved in toluene and the solutions were kept in an inert atmosphere. The solutions of complex A1 and
 25 activator were fed into the reactor using a separated ISCO syringe pump. The activator feed rate were adjusted according the catalyst feed rate so the molar ratio of catalyst to activator was about 1:1. Both tri-n-octylaluminum (TNOAL) solution (available from Sigma Aldrich, Milwaukee, WI) and bis(diisobutylaluminium)oxide solution (available from Akzo Nobel) were further diluted in isohexane and used as a scavenger. The detailed process condition
 30 and some analytical results are summarized in Table 3.

Table 3

	Run 1	Run 2
Polymerization temperature (°C)	85	85
Propylene feed rate (g/min)	14	14
Ethylene feed rate (SLPM)	0.7	0.7
Isohexane feed rate (g/min)	55.5	55.5
Catalyst feed rate (mol/min)	2.445E-07	2.445E-07
Scavenger	TNOAL (25wt% in hexane)	bis(diisobutylaluminum oxide) 20 wt% in hexane
Scavenger feed rate (mol/min)	4.13E-06	4.12E-06
Polymer yield (gram/min)	6.16	5.98
Mn_LS (g/mol)	495,459	808,487
Mw_LS (g/mol)	1,250,617	1,699,686
Mz_LS (g/mol)	1,958,911	4,877,757
Ethylene content (wt %)	13.9	14.6

By comparing run 1 to run 2 (Table 3), the use of bis(diisoaluminum)oxide in place of tri-n-octylaluminum as scavenger yields product with significantly higher molecular weight.

5 The weight percent of ethylene in the product was determined by NMR spectroscopy as described by Cheung in J. Poly. Sci. Part B 1987, 25, p. 2355. Molecular weights were determined by GPC-MALLS as described earlier.

All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text, provided however that any priority document not named in the initially filed application or filing documents is NOT incorporated by reference herein. As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including" for purposes of Australian law. Likewise, whenever a composition, an element, or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of," "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

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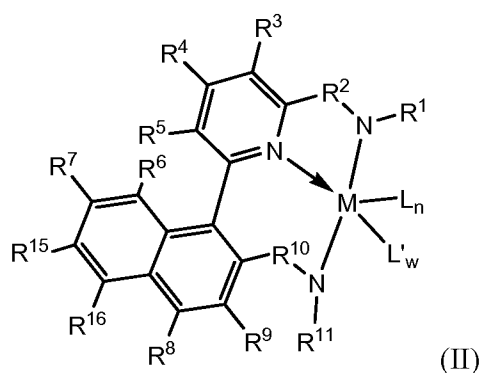
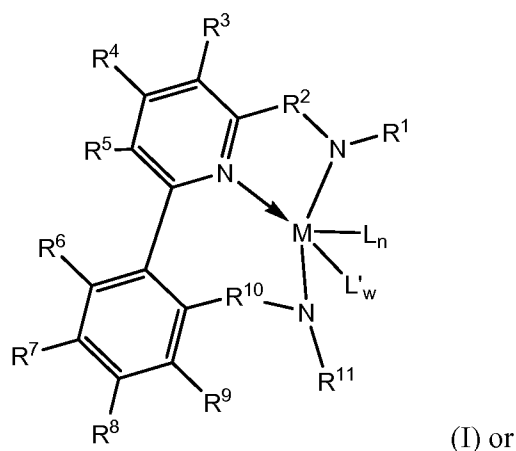
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CLAIMS

What is claimed is:

1. A method to prepare a polyolefin comprising the step:
contacting an olefinic monomer or olefinic monomers with a pyridyldiamido
5 transition metal catalyst, optionally an activator, and an aluminum containing scavenger that
has an oxygen to aluminum (O/Al) molar ratio from about 0.25 and about 1.5.
2. The method of claim 1, wherein the olefinic monomers are one or more of ethylene, a
propylene, a butylene, a hexene or an octene.
3. The method of claim 1, wherein the olefinic monomer is ethylene or propylene.
- 10 4. The method of claim 1, wherein the olefinic monomers are propylene and ethylene.
5. The method of claim 1, further comprising a trialkyl aluminum compound present in a
concentration of from about 1 micromolar to about 50 micromolar.
6. The method of any of claims 1 through 5, wherein the activator is a non-coordinating
anion activator.
- 15 7. The method of claim 6, wherein the non-coordinating activator is one or more of
N,N'-dimethylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium
tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium
tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
20 triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, or triphenylcarbenium
tetrakis(perfluorophenyl)borate.
8. The method of claim 1, wherein the activator is present from about 0.1 molar
equivalents to about 10 molar equivalents, based on the transition metal catalyst.
9. The method of claim 8, wherein the concentration of activator present is about 1
25 molar equivalent.
10. The method of any of claims 1 through 9, wherein the pyridyldiamido transition metal
catalyst is represented by the formula (I) or (II):



wherein:

M is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal;

5 R^1 and R^{11} are each independently selected from the group consisting of hydrocarbyls, and substituted hydrocarbyls, or silyl groups;

R^2 and R^{10} are each, independently, $-E(R^{12})(R^{13})-$ with E being carbon, silicon, or germanium, and each R^{12} and R^{13} being independently selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R^{12} and R^{13} may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R^{12} and R^{13} may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings;

15 R^3 , R^4 , and R^5 are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R^3 & R^4 and/or R^4 & R^5) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

R⁶, R⁷, R⁸, R⁹, R¹⁵, and R¹⁶ are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R⁶ & R⁷, and/or R⁷ & R¹⁵, and/or R¹⁶ & R¹⁵, and/or R⁸ & R⁹) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

n is 0, 1, 2, 3, or 4;

10 L' is neutral Lewis base;

w is 0, 1, 2, 3, or 4; and

wherein n + w is no greater than 4.

11. The method of claim 10, wherein M is Ti, Zr, or Hf.

12. The method of claim 10, wherein R⁶, R⁷, R⁸, R⁹, R¹⁵, and R¹⁶, are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl; each L is independently selected from the group consisting of halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, and alkynyl; each L' is independently selected from the group consisting of ethers, thio-ethers, amines, nitriles, imines, pyridines, and phosphines; the R² group(s) are selected from the group consisting of CH₂, CMe₂, SiMe₂, SiEt₂, SiPr₂, SiBu₂, SiPh₂, Si(aryl)₂, and Si(alkyl)₂, CH(aryl), CH(Ph), CH(alkyl), CH(2-isopropylphenyl), where alkyl is a C₁ to C₄₀ alkyl group, aryl is a C₅ to C₄₀ aryl group; the R¹⁰ group(s) are selected from the group consisting of CH₂, CMe₂, SiMe₂, SiEt₂, SiPr₂, SiBu₂, SiPh₂, Si(aryl)₂, and Si(alkyl)₂, CH(aryl), CH(Ph), CH(alkyl), CH(2-isopropylphenyl), where alkyl is a C₁ to C₄₀ alkyl group, aryl is a C₅ to C₄₀ aryl group, and Ph is phenyl.

13. The method of any of claim 10, wherein R¹¹ is an ortho alkyl substituted phenyl group, preferably the ortho alkyl substituent is a methyl, ethyl, iso-propyl, propyl, butyl, or isobutyl group.

14. The method of claim 13, wherein the remaining positions of the phenyl group are hydrogen atoms or the 4 and 6 positions are substituted by an alkyl group.

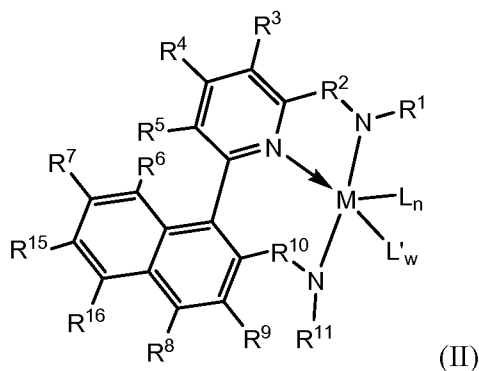
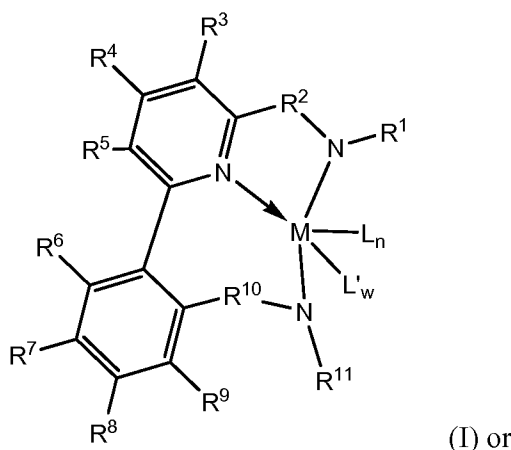
15. The method of any of claims 1 to 10, wherein the aluminum containing scavenger is represented by the formula ((R_z-Al)_yO)_x, wherein z is 1-2, y is 1-2, x is 1-100 and R is a C1-C12 hydrocarbyl group.

16. The method of claim 15, wherein R is a C4 to C10 hydrocarbyl group, preferably a methyl or t-butyl group, preferably R is t-butyl, z is 2, y is 2 and x is 1 or alumoxane.

17. The method of any of claims 1 through 10, wherein the aluminum containing scavenger is present from about 1 to about 5000 equivalents to 1 pyridyldiamido transition metal catalyst equivalent, preferably from about 500 to 1000 equivalents to 1 pyridyldiamido transition metal catalyst equivalent.

18. The method of any of claims 1 through 10, wherein the polyolefin has a molecular weight of from about 1000 Da to about 3,000,000 Da.

19. A pyridyldiamido transition metal catalyst represented by the formula (I) or (II):



wherein:

M is a Group 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12 metal;

15 R¹ is selected from the group consisting of hydrocarbyls, and substituted hydrocarbyls, or silyl groups, preferably a phenyl group substituted at the 2 and 6 positions, preferably with the same or different C1-C20 alkyl groups;

R¹¹ is a phenyl group substituted at the 2 position, preferably with a C1-C20 alkyl group and which is not substituted at the 3, 5, and/or 6 positions provided that the 4 position can be substituted with a group 17 element or a C1-C20 alkyl group;

R^2 and R^{10} are each, independently, $-E(R^{12})(R^{13})-$ with E being carbon, silicon, or germanium, and each R^{12} and R^{13} being independently selected from the group consisting of hydrogen, hydrocarbyls, and substituted hydrocarbyls, alkoxy, silyl, amino, aryloxy, halogen, and phosphino, R^{12} and R^{13} may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, or 7 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R^{12} and R^{13} may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings;

R^3 , R^4 , and R^5 are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, aryloxy, halogen, amino, and silyl, and wherein adjacent R groups (R^3 & R^4 and/or R^4 & R^5) may be joined to form a substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

R^6 , R^7 , R^8 , R^9 , R^{15} , and R^{16} are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl, and wherein adjacent R groups (R^6 & R^7 , and/or R^7 & R^{15} , and/or R^{16} & R^{15} , and/or R^8 & R^9) may be joined to form a saturated, substituted or unsubstituted hydrocarbyl or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

n is 0, 1, 2, 3, or 4;

L' is neutral Lewis base;

w is 0, 1, 2, 3, or 4; and

wherein $n + w$ is no greater than 4.

20. The pyridyldiamido transition metal catalyst of claim 19, wherein M is Ti, Zr, or Hf; and/or R^6 , R^7 , R^8 , R^9 , R^{15} , and R^{16} , are independently selected from the group consisting of hydrogen, hydrocarbyls, substituted hydrocarbyls, alkoxy, halogen, amino, and silyl; and/or each L is independently selected from the group consisting of halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, and alkynyl; and/or each L' is independently selected from the group consisting of ethers, thio-ethers, amines, nitriles, imines, pyridines, and phosphines; and/or the R^2 group(s) are selected from the group consisting of CH_2 , CMe_2 , $SiMe_2$, $SiEt_2$, $SiPr_2$, $SiBu_2$, $SiPh_2$, $Si(aryl)_2$, and $Si(alkyl)_2$,

CH(aryl), CH(Ph), CH(alkyl), CH(2-isopropylphenyl), where alkyl is a C₁ to C₄₀ alkyl group, and aryl is a C₅ to C₄₀ aryl group; and/or the R¹⁰ group(s) are selected from the group consisting of CH₂, CMe₂, SiMe₂, SiEt₂, SiPr₂, SiBu₂, SiPh₂, Si(aryl)₂, and Si(alkyl)₂, CH(aryl), CH(Ph), CH(alkyl), CH(2-isopropylphenyl), where alkyl is a C₁ to C₄₀ alkyl group, aryl is a C₅ to C₄₀ aryl group, and Ph is phenyl.

21. The pyridyldiamido transition metal catalyst of claim 19, wherein R¹¹ is an ortho alkyl substituted phenyl group, preferably the ortho alkyl substituent is a methyl, ethyl, isopropyl, propyl, butyl, or isobutyl group.

22. The pyridyldiamido transition metal catalyst of claim 21, wherein the remaining positions of the phenyl group are hydrogen atoms or the 4 position is substituted by a halogen or a C1-C20 alkyl group.

23. A catalyst system comprising optionally an activator, an aluminum containing scavenger that has an oxygen to aluminum (O/Al) molar ratio from about 0.25 to about 1.5 and the pyridyldiamido transition metal complex of any of claims 19 to 22.

24. The catalyst system of claim 23, wherein the optional activator is a non-coordinating anion.

25. The catalyst system of claim 23, wherein the optional activator is alumoxane.

26. The catalyst system of claim 23, wherein R¹¹ is a phenyl group substituted at the 2 position with a C1-C20 alkyl group.

27. The catalyst system of claim 24 wherein the activator is one or more of:

trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, tri(t-butyl)ammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate, tropillium tetraphenylborate, triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate triethylsilylium tetraphenylborate, benzene(diazonium)tetraphenylborate, trimethylammonium tetrakis(pentafluorophenyl)borate, triethylammonium tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, N,N-diethylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate, tropillium

tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylphosphonium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate, benzene(diazonium) tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, triethylammonium tetrakis-

5 (2,3,4,6-tetrafluorophenyl)borate, tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate, dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-

10 tetrafluorophenyl)borate, tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium

15 tetrakis(perfluoronaphthyl)borate, tripropylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate, tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium

20 tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate, trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate,

25 tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(t-butyl)ammonium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate, tropillium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate,

30 triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(n-butyl)ammonium tetrakis(3,5-

bis(trifluoromethyl)phenyl)borate, tri(t-butyl)ammonium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, N,N-dimethylanilinium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, N,N-diethylanilinium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-
 5 bis(trifluoromethyl)phenyl)borate, tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylphosphonium
 tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylsilylium tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, benzene(diazonium) tetrakis(3,5-
 bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
 10 dicyclohexylammonium tetrakis(pentafluorophenyl)borate; tri(o-tolyl)phosphonium
 tetrakis(pentafluorophenyl)borate, tri(2,6-dimethylphenyl)phosphonium
 tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate,
 triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium
 tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
 15 tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium
 tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
 N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium
 tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
 triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium
 20 tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
 trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium
 tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate,
 tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(t-butyl)ammonium
 tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
 25 N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-
 trimethylanilinium) tetrakis(perfluorobiphenyl)borate, tropillium
 tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
 triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium
 tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, and
 30 [4-t-butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B], (where Ph is phenyl and Me is methyl).

1/2

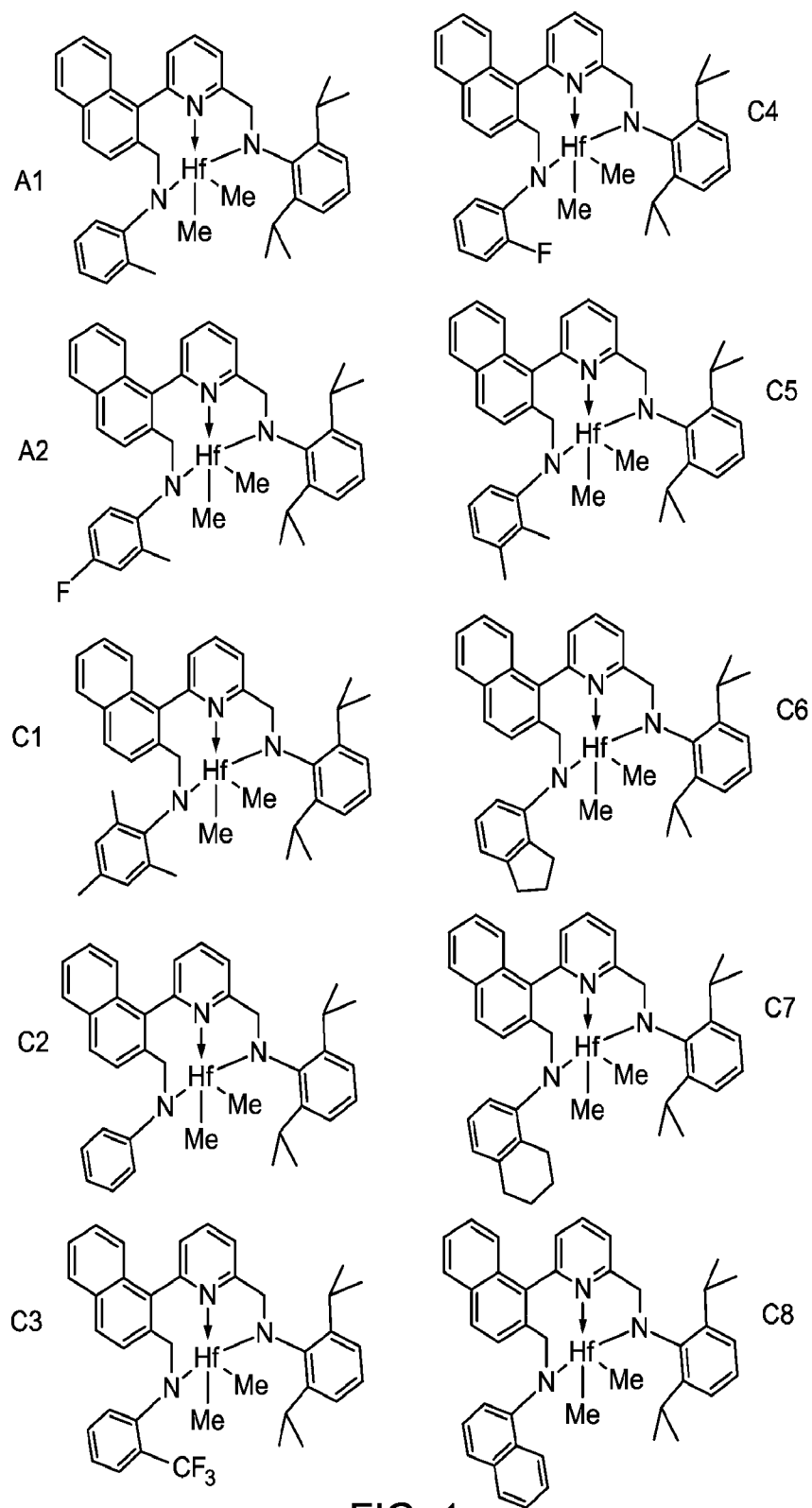


FIG. 1

2/2

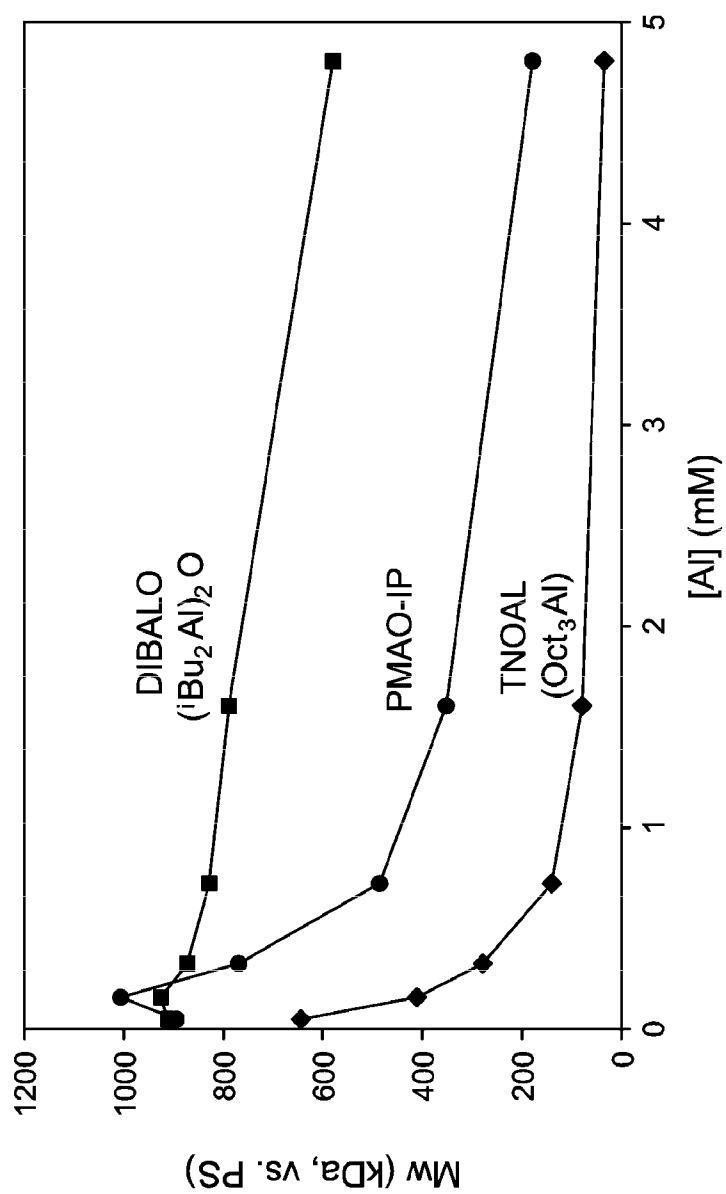


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2014/012186**A. CLASSIFICATION OF SUBJECT MATTER****C08F 10/00(2006.01)i, C08F 4/64(2006.01)i, C07D 213/16(2006.01)i**

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)

C08F 10/00; C07F 7/00; C08F 2/00; C08F 4/02; B01J 31/00; C08F 2/04; C08F 4/44; C08F 4/659; C08F 4/64; C07D 213/16

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: pyridyldiamido transition metal catalyst, polyolefin, olefin, ethylene, propylene, polymerization, activator, scavenger, aluminum, alumoxane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012-0071616 A1 (HAGADORN, J. R. et al.) 22 March 2012 See claims 1-4, 8, 17, 20-22; paragraphs [0051], [0177], [0127], [0163], [0176], [0187].	19-21
Y		1-9, 23-25, 27
A		22, 26
Y	US 6194527 B1 (CRIBBS, L. V.) 27 February 2001 See abstract; claim 1.	1-9, 23-25, 27
A		19-22, 26
A	US 2004-0220050 A1 (FRAZIER, K. A. et al.) 4 November 2004 See abstract; claims 1-10.	1-9, 19-27
A	US 6900321 B2 (BOUSSIE, T. R. et al.) 31 May 2005 See abstract; claims 1-17.	1-9, 19-27

☐ 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

02 May 2014 (02.05.2014)

Date of mailing of the international search report

02 May 2014 (02.05.2014)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2014/012186**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.: 11-14, 16
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:
Claims 11-14 and 16 are unclear because they refer to multiple dependent claims 10, 15 which do not comply with PCT Rule 6.4(a).
3. ☒ Claims Nos.: 10, 15, 17-18
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 fee, this Authority did not invite payment of any 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

Information on patent family members

International application No.

PCT/US2014/012186

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012-0071616 A1	22/03/2012	CN 103492398 A	01/01/2014
		EP 2688896 A2	29/01/2014
		US 2011-0224391 A1	15/09/2011
		US 2011-0301310 A1	08/12/2011
		US 8394902 B2	12/03/2013
		US 8674040 B2	18/03/2014
		WO 2012-134613 A2	04/10/2012
		WO 2012-134613 A3	14/03/2013
		WO 2012-134614 A1	04/10/2012
		WO 2012-134615 A1	04/10/2012
US 6194527 B1	27/02/2001	AU 2000-65360 A1	24/04/2001
		AU 6536000 A	24/04/2001
		CA 2391327 A1	29/03/2001
		EP 1246850 A1	09/10/2002
		EP 1246850 A4	30/06/2004
		MX PA02002104 A	07/11/2002
		WO 01-21669 A1	29/03/2001
		WO 01-21669 A1	29/03/2001
US 2004-0220050 A1	04/11/2004	AT 432950 T	15/06/2009
		CA 2523286 A1	18/11/2004
		CA 2523286 C	27/11/2012
		CN 1784431 A	07/06/2006
		CN 1784431 C0	16/04/2008
		DE 602004021374 D1	16/07/2009
		EP 1622947 A1	08/02/2006
		EP 1622947 B1	03/06/2009
		ES 2324167 T3	31/07/2009
		JP 04-625802 B2	02/02/2011
		JP 2006-525314 A	09/11/2006
		JP 2006-525314 T	09/11/2006
		US 6953764 B2	11/10/2005
		WO 2004-099268 A1	18/11/2004
US 6900321 B2	31/05/2005	AU 2566202 A	21/05/2002
		AU 4151702 A	18/06/2002
		EP 1334139 A2	13/08/2003
		US 2002-137845 A1	26/09/2002
		US 2002-142912 A1	03/10/2002
		US 2002-147288 A1	10/10/2002
		US 2002-156279 A1	24/10/2002
		US 2002-173419 A1	21/11/2002
		US 2002-177711 A1	28/11/2002
		US 2004-122247 A1	24/06/2004
		US 2004-209765 A1	21/10/2004
		US 2006-135722 A1	22/06/2006
		US 6706829 B2	16/03/2004
		US 6713577 B2	30/03/2004

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/012186

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		US 6727361 B2	27/04/2004
		US 6750345 B2	15/06/2004
		US 6828397 B2	07/12/2004
		US 7018949 B2	28/03/2006
		US 7087690 B2	08/08/2006
		WO 02-38628 A2	16/05/2002
		WO 02-38628 A3	22/05/2003
		WO 02-46249 A2	13/06/2002
		WO 02-46249 A3	13/02/2003
		WO 02-46249 A9	01/05/2003