

SUPPORTED OLEFIN POLYMERIZATION CATALYSTS COMPRISING SUBSTITUTED 2-HYDROXYTHIOPHENE COMPOUNDS

FIELD

[0001] Olefin polymerization catalysts, materials, and methods.

INTRODUCTION

[0002] Polyolefins are made by generally known methods comprising polymerizing one or more olefin monomers in solution phase catalyzed by homogeneous catalysts, or in slurry phase or gas phase catalyzed by heterogeneous catalysts.

[0003] Homogeneous catalysis generally refers to reactions where a soluble catalyst and a reactant it acts upon are in the same phase (same state of matter), and in unrestricted contact. This is almost always liquid phase. The catalyst in pure form and the reactant in pure form at standard temperature and pressure (23° C., 101 kilopascals) may be a solid or a gas, but when the catalyst and reactant are dissolved in the same solution they are both in the liquid phase.

[0004] Liquid phase olefin polymerizations mean solution reactions where a homogeneous olefin polymerization catalyst and the reactant—one or more olefin monomers—are dissolved and react in a same hydrocarbon solvent. When the olefin monomer comprises ethylene, the polymerizations are run in hydrocarbon solutions at temperatures from 120° to 250° C., and usually 150° to 190° C., which is above the 115° to 135° C. melting temperature range of polyethylenes.

[0005] Homogeneous olefin polymerization catalysts must have at least partial solubility in the hydrocarbon solvent so that, at the relatively low catalyst concentrations and high temperatures used, the entire amount of the catalyst is dissolved in solution. In practice these catalysts are free (unsupported) ligand-metal complex molecules and the hydrocarbon solvent is alkanes or aromatic hydrocarbons.

[0006] Structures of free ligand-metal complex molecules may be precisely determined using small molecule structure characterization techniques such as proton-nuclear and carbon-nuclear magnetic resonance (¹H-NMR and/or ¹³C-NMR) spectroscopy or x-ray crystallography. This knowledge enables researchers to make rational design modifications to the homogeneous catalyst to study its structure-activity relationships and structure-product property relationships.

[0007] Heterogeneous catalysis generally refers to reactions where an insoluble catalyst and a reactant it acts upon are in different phases (different states of matter). Reaction occurs at interfaces between phases.

[0008] Heterogeneous catalysts may be made by a general strategy of heterogenization of homogeneous catalysts or homogeneous precatalysts and activators onto solid supports to

yield heterogeneous catalysts in the form of supported catalyst systems. Different supported catalyst systems may require different support materials. For example, Ziegler-Natta catalysts use magnesium chloride and supported metallocene catalysts use silica. Supported catalyst structures cannot be precisely determined.

[0009] In gas phase/solid phase olefin polymerizations, called gas phase polymerizations, the supported catalyst system (a heterogeneous olefin polymerization catalyst) is in a solid phase and the reactant—one or more olefin monomers—is in a gas or vapor phase. Reaction occurs at solid phase/gas phase interfaces.

[0010] In liquid phase/solid phase olefin polymerizations, called slurry phase polymerizations, the supported catalyst system (a heterogeneous olefin polymerization catalyst) is in a solid phase and the reactant—one or more olefin monomers—is dissolved in a hydrocarbon solvent to give a solution that constitutes the liquid phase. Reaction occurs at solid phase/liquid phase interfaces.

[0011] When the olefin monomer comprises ethylene, the gas phase and slurry phase polymerizations are run at from 75° to 120° C., below melting temperatures of most polyethylenes.

[0012] For these and other reasons, supported catalyst systems produce significantly different performance results and product properties than those of their counterpart homogeneous olefin polymerization catalysts. Thus, homogeneous olefin polymerization catalysis/solution phase polymerizations are not predictive of heterogeneous olefin polymerization catalysis/gas or slurry phase polymerizations.

SUMMARY

[0013] We claim a supported catalyst system comprising a substituted 2-hydroxythiophene compound and a support material; and a method of making the supported catalyst system. Also claimed are a gas phase or slurry phase polymerization process employing the supported catalyst system; and a polyolefin made by the gas phase or slurry phase polymerization process. Also claimed are the substituted 2-hydroxythiophene compound and a precatalyst comprising the substituted 2-hydroxythiophene compound, a metal atom, and a leaving group. Also claimed are methods of making the precatalyst and the substituted 2-hydroxythiophene compound.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Figure 1 shows Scheme 1 directed to a synthesis of an intermediate compound.

[0015] Figure 2 shows Scheme 2 directed to a synthesis of a substituted 2-hydroxythiophene compound (I).

[0016] Figure 3 shows Scheme 3 directed to a synthesis of a precatalyst of formula (II).

[0017] Figure 4 shows Scheme 4 directed to the making of a spray-dried supported catalyst system (III) or a conventionally-dried supported catalyst system (IV).

[0018] Figure 5 shows Scheme 5 directed to a synthesis of a bis(iodophenoxy)methylene-germanium compound.

[0019] Figure 6 has pictorial illustrations of representative chain structures of LLDPE, LDPE, and HDPE.

DETAILED DESCRIPTION

[0020] We claim a supported catalyst system comprising a substituted 2-hydroxythiophene compound and a support material; and a method of making the supported catalyst system. Also claimed are a gas phase or slurry phase polymerization process employing the supported catalyst system; and a polyolefin made by the gas phase or slurry phase polymerization process. Also claimed are the substituted 2-hydroxythiophene compound and a precatalyst comprising the substituted 2-hydroxythiophene compound, a metal atom, and a leaving group. Also claimed are methods of making the precatalyst and the substituted 2-hydroxythiophene compound.

Synthesis of the Supported Catalyst System

[0021] There are two general strategies for making the supported catalyst system comprising a substituted 2-hydroxythiophene compound. A first strategy comprises heterogenizing a homogeneous olefin polymerization precatalyst comprising the substituted 2-hydroxythiophene compound ("homogenous precatalyst"). A second strategy comprises heterogenizing a homogeneous olefin polymerization catalyst comprising the substituted 2-hydroxythiophene compound ("homogeneous catalyst").

[0022] There are two main contacting routes for the first heterogenization strategy comprising heterogenizing the homogeneous precatalyst. A first route comprises contacting a solution of the homogeneous precatalyst in a hydrocarbon solvent onto a solid support that has been pretreated with an activator (also called a cocatalyst), yielding the supported catalyst system. An example of the solid support that has been pretreated with an activator is the spray-dried methylaluminoxane/hydrophobic fumed silica ("SMAO"), which may be used as a convenient way of making an embodiment of the supported catalyst system for use in slurry phase polymerization. A second route comprises contacting an activator with solid support that has been pretreated with the homogeneous precatalyst, yielding the supported catalyst system.

[0023] A third contacting route is used for the second heterogenization strategy comprising heterogenizing the homogeneous catalyst. This third route comprises contacting a solution of the homogeneous precatalyst in a hydrocarbon solvent with an activator to give the homogeneous catalyst dissolved in hydrocarbon solvent, and then contacting the solution with the solid support, yielding the supported catalyst system.

[0024] The second and third contacting routes are disfavored for use with solid supports that give side reactions with either the homogeneous precatalyst or homogeneous catalyst. The

first heterogenization strategy comprising the first contacting route usually does not suffer from this potential problem.

[0025] The heterogenization strategies and contacting routes independently make the supported catalyst system as a suspension of solid particles thereof in a liquid consisting essentially of the hydrocarbon solvent and any hydrocarbon-soluble compounds. The hydrocarbon-soluble compounds may include unreacted activator (e.g., methyl aluminoxane or triethylaluminum) and/or by-products and side products from the heterogenization reaction and/or the activation reaction.

[0026] In some embodiments the suspension, including any hydrocarbon-soluble compounds, from the contacting route is fed into a gas phase or slurry phase polymerization reactor to polymerize olefin monomer. Prior to or during the feeding step the suspension may or may not be stored for a period of time in a storage tank and/or may or may not be diluted with additional hydrocarbon solvent, which may be the same as or different than the hydrocarbon solvent used in the contacting route.

[0027] In other embodiments the suspension from the contacting route is not fed into a gas phase or slurry phase polymerization reactor. Instead the contacting route used to make the supported catalyst system is followed by a separating step, which is performed prior to any feeding of the supported catalyst system into a gas phase or slurry phase polymerization reactor. In such embodiments the separating step comprises physically removing the supported catalyst system solids from the liquid portion of the suspension obtained from the contacting route, or vice versa physically removing the liquid portion from the supported catalyst system solids.

[0028] In some embodiments the separating step comprises a filtering step, a decanting step, or an evaporating step. The separating step may also comprise a combination of any two or more separating steps.

[0029] The filtering step may comprise contacting the suspension with a filter to yield a filtrate consisting of the liquid portion and a filtercake consisting of the supported catalyst system (solids). The filtercake may be washed with fresh hydrocarbon solvent and/or dried.

[0030] The decanting step may comprise pouring off or suctioning off the liquid portion of the suspension, yielding a decanted or suctioned liquid and the supported catalyst system (solids) as a "paste" consisting of the supported catalyst system (solids) and a small remainder of undecanted or unsuctioned liquid. The paste may be used as is in a polymerization or dried or slurried with fresh hydrocarbon solvent.

[0031] The drying step may comprise removing volatile constituents from the suspension, yielding the supported catalyst system (solids) as a dry powder. The volatile constituents may include any volatile components of the hydrocarbon-soluble compounds mentioned earlier, such as any volatile unreacted activator and/or volatile by-products and side products from

the heterogenization reaction and/or the activation reaction. The drying step may comprise slowly evaporating volatile constituents from the suspension, which is slowly concentrated, yielding a “conventionally-dried” embodiment of the dry powder of the supported catalyst system. Alternatively, the drying step may comprise spray-drying the suspension so as to rapidly remove (flash off) volatile constituents from the suspension, yielding a “spray-dried” embodiment of the dry powder of the supported catalyst system.

[0032] The combination of any two or more separating steps may comprise, for example, the decanting step followed by the evaporating step or two sequential decanting steps.

[0033] The spray-dried supported catalyst system embodiments can have higher catalyst efficiencies, higher catalyst productivities, faster light-offs, and can produce polyethylene polymers having different properties in gas phase polymerizations than the conventionally-dried embodiments of the supported catalyst system have in gas phase polymerizations. Thus, the spray-dried supported catalyst system embodiments may be preferred over the conventionally-dried supported catalyst system embodiments for gas phase polymerizations. Nonetheless, the conventionally-dried supported catalyst system embodiments are also completely useful and effective for gas phase polymerizations.

[0034] There may be little or no difference between the spray-dried supported catalyst system embodiments and the conventionally-dried supported catalyst system embodiments in slurry phase polymerizations, or there may be significant differences. However, any given spray-dried supported catalyst system, or any given conventionally-dried supported catalyst system, may perform quite differently in gas phase polymerizations than in slurry phase polymerizations.

[0035] All dry powder embodiments of the supported catalyst system are versatile for gas phase and slurry phase polymerizations because they can be fed as a dry powder, or suspended in alkanes or mineral oil and the resulting suspension fed, into gas phase or slurry phase olefin polymerization reactors. Catalyst feeders for both methods are commercially available.

[0036] The supported catalyst system, no matter its physical constitution (e.g., as dry powder or as a powder suspended in hydrocarbon solvent) is useful for catalyzing gas phase or a slurry phase olefin polymerization of one or more olefin monomers to make polyolefins such as polyethylene polymers.

Technical Advantages

[0037] Homogeneous olefin polymerization catalysis in a solution phase reaction with the counterpart homogeneous catalyst comprising a substituted 2-hydroxythiophene compound is quite different than heterogeneous olefin polymerization catalysis in a gas phase or slurry phase reaction with the supported catalyst system. The former is not predictive of the latter and polyolefin products obtained from the latter are different than polyolefin products obtained

from the former in various properties such as polymer weight average molecular weight, melt rheology, and branching.

[0038] The supported catalyst system and polyolefins made by the supported catalyst system via gas phase or slurry phase olefin polymerization have technical advantages relative to the counterpart homogeneous catalyst and polyolefin made by the homogeneous catalyst via solution phase olefin polymerization. These technical advantages include one or more of increased catalyst efficiencies or productivities, improved behavior in gas phase reactors, and differing product polyolefin polymer properties and morphologies. These technical advantages result in different types of unpredictable results: performance differences between the inventive supported catalyst system and a comparative homogeneous olefin polymerization catalyst; property differences between an inventive polyolefin and a comparative polyolefin; performance differences between different embodiments of the inventive supported catalyst system; and property differences between different embodiments of the inventive polyolefin. Further, the spray-dried embodiments of the supported catalyst system tend to have more technical advantages than the conventionally dried embodiments of the supported catalyst system.

[0039] Without being bound by theory, we believe that the technical advantages of the inventive supported catalyst system, comprising the substituted 2-hydroxythiophene compound, in gas phase or slurry phase polymerizations are functions of one or more of the following factors: (a) effects of the solid support, (b) performance differences between different embodiments of the supported catalyst system depending on if the embodiment was made via heterogenization according to the first, second, or third route, (c) the different effects of the conventional drying method versus the spray-drying method used to make dried powders of the supported catalyst system, (d) the effects of differences in process conditions between solution phase versus gas phase or slurry phase, (e) performance differences between different embodiments of the supported catalyst system in their gas phase reactor behavior, or (f) any combination of two or more of effects (a) to (e).

[0040] The (a) effects of the solid support may vary with the olefin—polar group-containing olefin monomers being especially sensitive to the solid support, and with the solid support's surface chemistry, which in turn is affected by whether or not it has been pretreated with a hydrophobing agent and the hydrophobing agent used.

[0041] The (b) effects of the route used to heterogenize the homogeneous olefin polymerization catalyst to make different embodiments of the supported catalyst system may vary depending upon if the first, second, or third route is used, or a different route.

[0042] The (c) effects of the drying method used to make the dry powder of the supported catalyst system may vary depending on whether or not the drying step is employed and the

type of the drying step, e.g., conventional drying versus spray-drying. In some embodiments the inventive method comprises spray-drying.

[0043] The differences in (d) process conditions comprise reaction temperature differences. Solution phase polymerizations of ethylene are run at temperatures from 140° to 250° C., typically 150° to 190° C., whereas gas phase and slurry phase polymerizations of ethylene are run at lower temperatures, from 70° to 120° C., usually from 75° to 115° C. These temperature differences affect catalyst efficiencies and productivities and polyethylene properties such as molecular weights (e.g., weight-average molecular weights), which may vary significantly at different reaction temperatures. For example, these relationship differences are at least in part due to differences in reaction rates for competing reactions comprising polyethylene chain propagation versus polyethylene chain termination in solution phase at 150° to 190° C. versus these competing reaction rates in gas phase or slurry phase at 75° to 115° C. For example, all other things being equal, if the ratio of the chain propagation reaction rate to the chain termination reaction rate increases as reaction temperature decreases, the catalyst efficiencies and productivities and molecular weights will increase (improve), whereas if the ratio decreases, these relationships decrease (worsen).

[0044] The performance differences between different embodiments of the supported catalyst system in (e) gas phase reactor behavior comprise kinetics of the supported catalyst system on its light-off kinetics for freshly fed catalyst, maximum temperature reached after feed (temperature will increase due to exothermic nature of olefin polymerization reactions), or the amount of ethylene uptake per unit weight of catalyst.

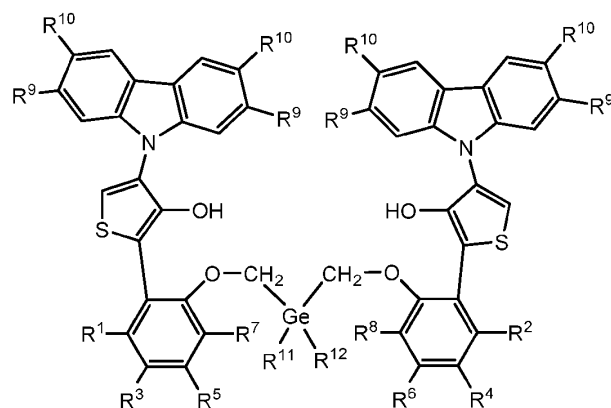
[0045] The (f) combinations of two or more of factors (a) to (e) are a further technical advantage of the inventive heterogeneous olefin polymerization catalyst comprising the substituted 2-hydroxythiophene compound and the polyolefin made via gas phase or slurry phase olefin polymerization catalyzed thereby.

[0046] In some embodiments the supported catalyst system comprising the substituted 2-hydroxythiophene compound has an improved activity in a gas phase and slurry phase polymerization reaction relative to that activity of its counterpart homogeneous olefin polymerization catalyst. For example, the improved activity may be an increased catalyst efficiency and/or an increased catalyst productivity. In some embodiments the supported catalyst system also makes a polyethylene product with one or more improved properties relative to those properties of a polyethylene product made by its counterpart homogeneous olefin polymerization catalyst in solution phase polymerization. For example, the improved property may be an increased weight-average molecular weight (M_w); an increased content of ultra-high molecular weight ("UHMW") constituents, e.g., M_w greater than 1,000,000 grams

per mole (g/mol); a z-average molecular weight greater than 2,000,000 grams per mole; an increased long chain branching (LCB) content; or a combination of any two or more thereof.

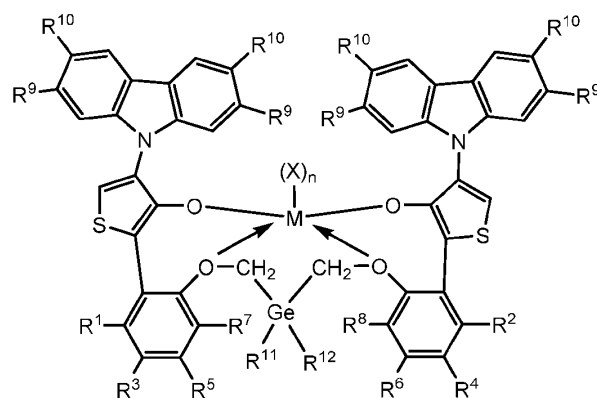
Additional embodiments

[0047] Another embodiment is a substituted 2-hydroxythiophene compound of formula (I):



[0048] (I), or a Group 1 or Group 2 metal salt thereof. R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, and R¹² are defined below.

[0049] Another embodiment is a precatalyst of formula (II):



[0050] (II). R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², M, X, and subscript n are defined below.

[0051] Another embodiment is a catalyst made by contacting the precatalyst of formula (II) with an activator. The catalyst is useful for polymerizing one or more olefin monomers.

[0052] Another embodiment is a supported catalyst system comprising the precatalyst of formula (II), a support material, and an activator.

[0053] Another embodiment is a method of making the supported catalyst system, the method comprising step (a) or comprising steps (b) and (c): (a) spray drying a mixture of an inert hydrocarbon solvent, the precatalyst of formula (II), the support material, and the activator to make the supported catalyst system; or (b) spray drying a mixture of an inert hydrocarbon

solvent, the support material and the activator to make a spray-dried supported activator, and (c) mixing the precatalyst of formula (II) with the spray-dried supported activator and an inert hydrocarbon solvent to make the supported catalyst system.

[0054] Another embodiment is a method of polymerizing an olefin monomer, the method comprising contacting the olefin monomer with the supported catalyst system, thereby making a polyolefin. The method may comprise a gas phase polymerization in a gas phase reactor under gas phase conditions or a slurry phase polymerization in a slurry phase reactor under slurry phase conditions.

[0055] Another embodiment is the polyolefin made by the method of polymerizing.

[0056] Independently in the formulas (I) and (II), R^1 and R^2 independently are H or a halogen. In some embodiments R^1 and R^2 are different, or R^1 and R^2 are identical. In some embodiments R^1 and R^2 are H. In other embodiments R^1 and R^2 are F.

[0057] Independently in the formulas (I) and (II), R^3 and R^4 independently are H, a halogen, a (C₁-C₁₅)hydrocarbyl, a (C₁-C₁₀)alkoxy, or a Si((C₁-C₁₀)alkyl)₃. In some embodiments R^3 and R^4 are different, or R^3 and R^4 are identical. In some embodiments R^3 and R^4 are a halogen, a (C₁-C₁₅)hydrocarbyl, a (C₁-C₁₀)alkoxy, or a Si((C₁-C₁₀)alkyl)₃. In some embodiments R^3 and R^4 are H. In other embodiments R^3 and R^4 are F. In some embodiments R^3 and R^4 are a (C₁-C₁₅)hydrocarbyl. In other embodiments R^3 and R^4 are a (C₁-C₁₀)alkoxy. In other embodiments R^3 and R^4 are a Si((C₁-C₁₀)alkyl)₃. In some embodiments R^3 and R^4 are identical and are both H, or both F, or both -C(CH₃)₃, or both -C(CH₂CH₃)₃, or both -C(CH₃)₂CH₂C(CH₃)₃, or both -OCH₃, or both -O(CH₂)₂C(CH₃)₃, or both -O(CH₂)₇CH₃, or both 4-*i*-(tert-butyl)phenyl, or both 1,3-di(*i*-tert-butyl)phenyl, or both -Si(CH₃)₂(CH₂)₇CH₃. In some embodiments each (C₁-C₁₅)hydrocarbyl independently is a (C₁-C₁₅)alkyl, a (C₁-C₅)alkyl, a (C₆-C₁₀)alkyl, a (C₆-C₁₅)aryl (e.g., phenyl or naphthyl), a (C₇-C₁₅)alkaryl (e.g., benzyl, 2-phenylethyl, or 1-phenylprop-1-yl), or a (C₇-C₁₅)alkaryl (e.g., 4-methylphenyl or 2,6-diisopropylphenyl).

[0058] Independently in the formulas (I) and (II), R^5 and R^6 independently are H or a halogen. In some embodiments R^5 and R^6 are different, or R^5 and R^6 are identical. In some embodiments R^5 and R^6 are H. In some embodiments R^5 and R^6 are F.

[0059] Independently in the formulas (I) and (II), R^7 and R^8 independently are H or a halogen. In some embodiments R^7 and R^8 are different, or R^7 and R^8 are identical. In some embodiments R^7 and R^8 are H. In some embodiments R^7 and R^8 are F.

[0060] In some embodiments R¹, R², R³, R⁴, R⁵, R⁶, R⁷, and R⁸ are H.

[0061] In some embodiments R³, R⁴, R⁵, and R⁶ are F and R¹, R², R⁷, and R⁸ are H. In some embodiments R¹, R², R³, R⁴, R⁵, and R⁶ are F and R⁷ and R⁸ are H. In some embodiments R³, R⁴, R⁵, R⁶, R⁷, and R⁸ are F and R¹ and R² are H.

[0062] In some embodiments R¹, R², R⁵, R⁶, R⁷, and R⁸ are H and R³ and R⁴ are as defined above with the proviso that R³ and R⁴ are not H.

[0063] Independently in the formulas (I) and (II), in some embodiments each R⁹ is H and each R¹⁰ is a (C₁-C₁₅)hydrocarbyl, alternatively a (C₁-C₁₀)alkyl or a (C₁-C₅)alkyl, phenyl, or substituted phenyl; or each R¹⁰ is H and each R⁹ is a (C₁-C₁₅)hydrocarbyl, alternatively a (C₁-C₁₀)alkyl or a (C₁-C₅)alkyl, phenyl, or substituted phenyl. In other embodiments each R⁹ is H and each R¹⁰ is a -Si((C₁-C₁₀)alkyl)₃, (C₁₀-C₁₈)aryl, or substituted (C₁₀-C₁₈)aryl; or each R¹⁰ is H and each R⁹ is a -Si((C₁-C₁₀)alkyl)₃, (C₁₀-C₁₈)aryl, or substituted (C₁₀-C₁₈)aryl. Each substituted phenyl has from 1 to 3 substituent groups independently selected from F, (C₁-C₁₀)alkyl, and (C₁-C₁₀)alkoxy; or F and (C₁-C₁₀)alkoxy; or (C₁-C₁₀)alkyl. In some embodiments each R⁹ is H and each R¹⁰ is tertiary-butyl, 4-tert-butylphenyl, 4-triethylmethylphenyl, 3,5-dimethylphenyl, 3,5-di-tert-butylphenyl, or 3,5-difluoro-4-octyloxyphenyl. In other embodiments each R¹⁰ is H and each R⁹ is 3,5-di-tert-butylphenyl.

[0064] Independently in the formulas (I) and (II), R¹¹ and R¹² independently are a (C₁-C₁₀)alkyl; or R¹¹ and R¹² independently are a (C₁-C₅)alkyl; or R¹¹ and R¹² independently are a (C₂-C₄)alkyl; or R¹¹ and R¹² independently are a (C₃)alkyl; or R¹¹ and R¹² are isopropyl.

[0065] In some embodiments R¹ and R² are different, or R¹ and R² are identical; or R¹ and R² are H; or R¹ and R² are F; or R³ and R⁴ are different, or R³ and R⁴ are identical, or R³ and R⁴ are a halogen, a (C₁-C₁₅)hydrocarbyl, a (C₁-C₁₀)alkoxy, or a Si((C₁-C₁₀)alkyl)₃, or R³ and R⁴ are a (C₁-C₁₀)alkyl or a (C₁-C₁₀)alkoxy; or R⁵ and R⁶ are different, or R⁵ and R⁶ are identical, or R⁵ and R⁶ are H, or R⁵ and R⁶ are F; or R⁷ and R⁸ are different, or R⁷ and R⁸ are identical, or R⁷ and R⁸ are H, or R⁷ and R⁸ are F; or each R⁹ is H and each R¹⁰ is tertiary-butyl, 4-tert-butylphenyl, 4-triethylmethylphenyl, 3,5-dimethylphenyl, 3,5-di-tert-butylphenyl, or 3,5-difluoro-4-octyloxyphenyl; or each R¹⁰ is H and each R⁹ is 3,5-di-tert-butylphenyl; or each R¹¹ and R¹² is identical; or each R¹¹ and R¹² is a (C₁-C₁₀)alkyl or a

(C₁-C₅)alkyl; or each R¹¹ and R¹² is isopropyl; or a combination of the foregoing definitions of R¹ to R¹².

[0066] Independently in formula (II), M is Ti, Hf, or Zr. In some embodiments M is Hf or Zr, or M is Ti, or M is Hf, or M is Zr.

[0067] Independently in formula (II), subscript n is 1 or 2. In some embodiments subscript n is 2.

[0068] Independently in formula (II), each X independently is a leaving group, at least one of which is displaceable when precatalyst (II) is contacted with an activator. In some embodiments each X independently is selected from a monodentate ligand independently chosen from a hydrogen atom, a (C₁-C₅₀)hydrocarbyl, a (C₁-C₅₀)heterohydrocarbyl, a (C₁-C₅₀)organoheteryl, a halogen atom, a dialkylamino, or a dialkyl carbamate. Each heteroatom in a heterohydrocarbyl or organoheteryl may be O, N, S, Si, or P. In some embodiments each heteroatom is O, N, or Si, or each heteroatom is Si. In some embodiments each X is a halogen, a (C₁-C₈)alkyl group, a Si((C₁-C₈)alkyl)₃ group, a CH₂Si((C₁-C₁₀)alkyl)₃ group, or benzyl. In some embodiments each X is benzyl or each X is Cl and subscript n is 2; or each X is benzyl and subscript n is 2.

[0069] The subscript n and X are chosen so that the precatalyst of formula (II) is overall (i.e., formally) charge-neutral.

[0070] Independently in formula (I) and (II), in some embodiments R¹ and R² are identical, R³ and R⁴ are identical, R⁵ and R⁶ are identical, R⁷ and R⁸ are identical, each R⁹ is identical, each R¹⁰ is identical, each R¹¹ is identical, and each R¹² is identical. In some such embodiments R¹ and R² are H; R³ and R⁴ are a halogen, a (C₁-C₁₅)hydrocarbyl, a (C₁-C₁₀)alkoxy, or a Si((C₁-C₁₀)alkyl)₃; R⁵ and R⁶ are H; and R⁷ and R⁸ are H. In some such embodiments R³ and R⁴ are as defined earlier. In some embodiments each X is identical. In some of these embodiments M is Hf. In some of these embodiments M is Zr.

[0071] Independently in formula (I) and (II), in some embodiments R¹ and R² are H, R³ and R⁴ are each a (C₁-C₁₅)alkyl or a (C₁-C₁₀)alkoxy, R⁵ and R⁶ are H, R⁷ and R⁸ are H, each R⁹ is H, each R¹⁰ is the same and is tertiary-butyl, 4-tert-butylphenyl, 4-triethylmethylphenyl, 3,5-dimethylphenyl, or 3,5-di-tert-butylphenyl, and each R¹¹ and R¹² is isopropyl. In other embodiments R¹ and R² are H, R³ and R⁴ are a (C₇-C₉)alkyl or a (C₇-C₉)alkoxy, R⁵ and R⁶ are H, R⁷ and R⁸ are H, each R⁹ is H, each R¹⁰ is tertiary-butyl, and each R¹¹ and R¹² is isopropyl. In some embodiments each R³ and R⁴ is (CH₃)₃CCH₂C(CH₃)₂- or CH₃(CH₂)₇O-

[0072] Independently in formula (I) and (II), in some embodiments R^1 and R^2 are F, or R^5 and R^6 are F, or R^7 and R^8 are F, or at least four thereof are F.

[0073] Independently in formula (I) and (II), in some embodiments R^1 and R^2 are the same, R^3 and R^4 are the same, R^5 and R^6 are the same, R^7 and R^8 are the same, each R^9 is the same, each R^{10} is the same, R^{11} and R^{12} are the same, and, in formula (II), each X is the same.

[0074] In some embodiments the substituted 2-hydroxythiophene compound of formula (I) is free of a Group 1 or Group 2 metal, i.e., has the structure drawn for formula (I). In other embodiments the substituted 2-hydroxythiophene compound is the Group 1 or Group 2 metal salt thereof.

[0075] The Group 1 or Group 2 metal salt may be made by replacing the hydrogen atom of one of the hydroxyl groups or replacing each of the hydrogen atoms of both hydroxyl groups, of the substituted 2-hydroxythiophene compound in formula (I) with a Group 1 or Group 2 metal atom. This may be done by reacting the compound of formula (I) with a Group 1 or Group 2 metal reactant. The Group 1 or Group 2 metal reactant may be a Group 1 or Group 2 metal hydroxide, a Group 1 or Group 2 metal hydride, a Group 1 or Group 2 metal alkoxide, or an alkyl Group 1 or Group 2 metal. In some embodiments the Group 1 or Group 2 metal atom or metal atoms independently is Li, Na, K, Ca, or Mg. The quantity of Group 1 or Group 2 metal reactant is chosen so that the Group 1 or Group 2 metal salt of the precatalyst of formula (I) is overall (i.e., formally) charge-neutral.

[0076] In some embodiments the substituted 2-hydroxythiophene compound of formula (I) is selected from the group consisting of compounds 1 to 3 in TABLE 1.

[0077] TABLE 1: Compound 3 is a prophetic example.

Cmpd No.	R^1 / R^2 each is	R^3 / R^4 each is	R^5 / R^6 each is	R^7 / R^8 each is	R^9	R^{10}	R^{11} / R^{12} each is
1	H	t-Octyl	H	H	H	t-Bu	i-Pr
2	H	OctylO	H	H	H	t-Bu	i-Pr
3	H	H	H	H	H	3,5-dtBP	i-Pr
4	H	F	H	H	H	t-Bu	i-Pr

[0078] wherein "Cmpd No." is compound number, t-Bu is tertiary-butyl; t-Octyl is $(CH_3)_3CCH_2C(CH_3)_2-$; OctylO is $CH_3(CH_2)_7O-$; 35dtBP is 3,5-di-tert-butylphenyl; and i-Pr is isopropyl (i.e., $(CH_3)_2CH-$).

[0079] In some embodiments is the precatalyst of formula (II) selected from the group consisting of precatalyst numbers 1 to 6 in TABLE 2.

[0080] TABLE 2: Precatalysts 5 to 6 are prophetic examples.

Precatalyst No.	Make from Formula (I) Compound No.	M	X each is	n
1	1	Zr	Benzyl	2
2	1	Hf	Benzyl	2
3	2	Zr	Benzyl	2
4	2	Hf	Benzyl	2
5	3	Zr	Benzyl	2
6	3	Hf	Benzyl	2
7	1	Zr	Cl	2
8	4	Zr	Benzyl	2
9	4	Hf	Benzyl	2

[0081] In some embodiments is the supported catalyst system selected from the group consisting of spray-dried supported catalyst system numbers SCS 1 to 7 and the undried supported catalyst system number SCS 8 in TABLE 3.

[0082] TABLE 3: spray-dried supported catalyst system 5 to 6 are prophetic examples.

SCS No.	Made from Formula (II) Precatalyst No.	Support Material	Activator	Catalyst Drying Method
SCS 1	1	HPFS1	MAO	Spray
SCS 2	2	HPFS1	MAO	Spray
SCS 3	3	HPFS1	MAO	Spray
SCS 4	4	HPFS1	MAO	Spray
SCS 5	5	HPFS1	MAO	Spray
SCS 6	6	HPFS1	MAO	Spray
SCS 7	7	HPFS1	MAO	Spray
SCS 8	1	SMAO		None (undried)
SCS 9	8	SMAO		None (undried)
SCS 10	9	SMAO		None (undried)

[0083] wherein “HPFS1” is a hydrophobic fumed silica made from untreated fumed silica and a hydrophobing agent that is dichlorodimethylsilane; and “MAO” is methylaluminoxane; and wherein “SMAO” is spray dried methylaluminoxane/HPFS1, wherein HPFS1 is made from untreated fumed silica and a hydrophobing agent that is dichlorodimethylsilane.

[0084] In some embodiments the supported catalyst system is that which has been shown to make by gas phase polymerization an ethylene/1-hexene copolymer having a weight-average

molecular weight greater than 1,000,000 grams per mole and/or a z-average molecular weight greater than 2,000,000 grams per mole.

[0085] In some embodiments the substituted 2-hydroxythiophene compound of formula (I) is Cmpd. no. 1, 2, or 3; or Cmpd. no. 1 or 2; or Cmpd. no. 1; or Cmpd. no. 2; or Cmpd. no. 3.

[0086] In some embodiments the precatalyst of formula (II) is Precat. No. 1, 2, 3, 4, 5, 6, 7, 8, or 9; or Precat. no. 1, 2, 3, or 4; or Precat. No. 5 and 6; or Precat. No. 1; or Precat. No. 2; or Precat. No. 3; or Precat. No. 4; or Precat. No. 5; or Precat. No. 6.

[0087] In some embodiments the spray-dried supported catalyst system is SCS no. 1, 2, 3, 4, 5, 6 or 7; or SCS no. 1, 2, 3, or 4; or SCS. No. 5 or 6; or SCS. No. 1; or SCS No. 2; or SCS No. 3; or SCS No. 4; or SCS No. 5; or SCS No. 6. In some embodiments the supported catalyst system is undried supported catalyst system no. SCS 8, 9, or 10.

[0088] Embodiments also include a method of making a polyolefin in a gas phase polymerization process, the method comprising contacting one or more olefin monomers with the supported catalyst system, described above, in a gas phase polymerization reactor under gas phase polymerization conditions to make a polyolefin polymer. In some embodiments the one or more olefin monomers comprise ethylene or propylene and optionally a 1-alkene having from 4 to 20 carbon atoms (" C_4 - C_{20} 1-alkene") and the polyolefin polymer that is made comprises a polyethylene polymer selected from a polyethylene homopolymer or an ethylene/ C_4 - C_{20} 1-alkene copolymer or a polypropylene polymer selected from a polypropylene homopolymer or a propylene/ C_4 - C_{20} 1-alkene copolymer. In some embodiments the one or more olefin monomers comprises ethylene and 1-butene, 1-hexene, or 1-octene and the polyethylene polymer is an ethylene/1-butene copolymer, an ethylene/1-hexene copolymer, or an ethylene/1-octene copolymer. In some of the foregoing embodiments making the polyethylene polymer, the polyethylene polymer has a weight-average molecular weight greater than 1,000,000 grams per mole and/or a z-average molecular weight greater than 2,000,000 grams per mole.

[0089] In some embodiments the method of polymerizing comprises gas phase polymerization and has any one of limitations (i) to (v): (i) wherein the one or more olefin monomers comprises ethylene or a combination of ethylene and propylene or a combination of ethylene and a C_4 - C_{20} alpha-olefin and wherein the polyolefin polymer is an ethylene homopolymer or an ethylene/propylene copolymer or an ethylene/ C_4 - C_{20} alpha-olefin copolymer; (ii) wherein the one or more olefin monomers comprises ethylene or a combination of ethylene and a C_4 - C_{20} alpha-olefin and the polyolefin polymer is an ethylene homopolymer or an ethylene/ C_4 - C_{20} alpha-olefin copolymer; wherein the ethylene homopolymer or an ethylene/ C_4 - C_{20} alpha-olefin copolymer has a weight-average molecular

weight 1,000,000 grams per mole or greater, or a z-average molecular weight of 2,000,000 grams per mole or greater, or both; or (iii) wherein the one or more olefin monomers comprises a combination of ethylene and a (C₄-C₂₀)alpha-olefin and wherein the polyolefin polymer is an ethylene/(C₄-C₂₀)alpha-olefin copolymer having a polydispersity index (PDI) of a ratio of weight-average molecular weight to number-average molecular weight (M_w/M_n) of greater than or equal to 4.0, or a broad molecular weight distribution of a ratio of z-average molecular weight to weight-average molecular weight (M_z/M_w) greater than or equal to 3.5, or both; (iv) any one of limitations (i) to (iii) wherein the (C₄-C₂₀)alpha-olefin is 1-hexene; (v) a combination of limitations (ii) and (iii) or a combination of limitations (ii), (iii), and (iv).

[0090] Embodiments also include a method of making a polyolefin in a slurry phase polymerization process, the method comprising contacting one or more olefin monomers with the supported catalyst system, described above, in a slurry phase polymerization reactor under slurry phase polymerization conditions to make a polyolefin polymer. In some embodiments the method has any one of limitations (i) and (ii): (i) wherein the one or more olefin monomers comprises ethylene or a combination of ethylene propylene or a combination of ethylene and a (C₄-C₂₀)alpha-olefin and the polyolefin polymer comprises an ethylene homopolymer or an ethylene/propylene copolymer of an ethylene/(C₄-C₂₀)alpha-olefin copolymer. In some embodiments the one or more olefin monomers comprises a combination of ethylene and 1-hexene and the polyolefin polymer comprises an ethylene/1-hexene copolymer.

Synthesis of the compound of formula (I) and the precatalyst of formula (II)

[0091] The compound of formula (I) and the precatalyst of formula (II) can be synthesized according to Schemes 1 to 4 shown in Figures 1 to 4. Reaction workup procedures are standard and described later in the Examples. Structures are characterized by proton-nuclear magnetic resonance (¹H-NMR) spectroscopy and carbon-13 nuclear magnetic resonance (¹³C-NMR) spectroscopy.

[0092] Figure 1 depicts synthetic Scheme 1 showing the conversion of starting material (1) to intermediate compound (5). In Scheme 1, 3-bromo-2-hydroxy-thiophene-1-carboxylic acid methyl ester (1) was obtained from a commercial supplier. In step A, compound (1) is saponified with sodium hydroxide (NaOH) in aqueous 1,4-dioxane at 80° C. to give 3-bromo-2-hydroxy-thiophene-1-carboxylate sodium salt. The carboxylate was heated with concentrated hydrochloric acid at 60° C. to give 3-bromo-2-hydroxythiophene. In step B the 3-bromo-2-hydroxythiophene was reacted with lithium hydroxide monohydrate (LiOH·H₂O), ethoxychloromethane (ClCH₂OCH₂CH₃, also called chloromethyl ethyl ether) in 1,4-dioxane/tetrahydrofuran (1:4, v/v) at 0° C. to make 3-bromo-2-ethoxymethoxythiophene (2).

In step C, 1.0 mole equivalent of compound (2) was reacted with 2.20 mole equivalents of carbazole (3), 2.00 mole equivalents of cuprous oxide (Cu_2O), and 10 mole equivalents of potassium carbonate (K_2CO_3), and 3 mole equivalents of potassium acetate (KOAc) in deoxygenated xylenes at 140 C. and 4.0 mole equivalents of N,N'-dimethylethylenediamine ("DMEDA") to make 2-ethoxymethoxy-3-carbazolylthiophene (4). In step D, 1 mole equivalent of compound (4) was reacted with 1.25 mole equivalents of n-butyl lithium at -35° C for 4 hours, and then 2.0 mole equivalents of neat isopropoxyboropinacolato ester ("i-PrOBPin") was added and the temperature allowed to warm to ambient temperature to make intermediate compound (5). The synthesis continues in Scheme 2 shown in Figure 2.

[0093] Figure 2 depicts synthetic Scheme 2 showing the conversion of intermediate compound (5) to the substituted 2-hydroxythiophene compound of formula (I). In Step E, 3 mole equivalents of compound (5) were reacted with 1 mole equivalent of a 1,3-bis(iodophenoxy)methylene germanium compound (6) wherein R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^{11} , and R^{12} are as defined for formula (I) and 9 mole equivalents of potassium phosphate tribasic (K_3PO_4) in the presence of a catalyst (e.g., bis(di-tert-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II)) or "Pd(AmPhos) Cl_2 ") to make a bis(ethoxymethyl)-protected compound. The bis(ethoxymethyl)-protected compound was then used in Step F comprising deprotective hydrolysis with concentrated hydrochloric acid in dichloromethane/1,4-dioxane (1:1, v/v) under nitrogen at 23° C. to make the substituted 2-hydroxythiophene compound of formula (I).

[0094] Figure 3 depicts synthetic Scheme 3 showing the conversion of the substituted 2-hydroxythiophene compound of formula (I) to an embodiment of the precatalyst of formula (II). In Step G, 1.0 mole equivalent of the substituted 2-hydroxythiophene compound of formula (I) is azeotropically dried using toluene. Then, to a solution of compound (I) was added 1.15 mole equivalent of a Group 4 metal salt of formula $\text{M}(\text{X})_{n+2}$, wherein M, X, and subscript n are as defined for formula (II), dropwise, and the reaction mixture was stirred at 23° C for 30 minutes. The reaction mixture was filtered through a 0.45 micrometer (μm) polytetrafluoroethylene filter, and the filtrate was concentrated to give the precatalyst of formula (II). Examples of the Group 4 metal salt of formula $\text{M}(\text{X})_{n+2}$ are zirconium tetrachloride (ZrCl_4), zirconium tetrabenzyl (ZrBn_4), zirconium dibenzylidichloride (ZrBn_2Cl_2), hafnium tetrachloride (HfCl_4), hafnium dibenzylidichloride (HfBn_2Cl_2), and hafnium tetrabenzyl (HfBn_4). Benzyl, abbreviated "Bn", is phenylmethyl, which is a monoradical of formula $-\text{CH}_2\text{C}_6\text{H}_5$. The ZrCl_4 , ZrBn_2Cl_2 , HfCl_4 , or HfBn_2Cl_2 make embodiments of the precatalyst of formula (II) wherein M is Zr or Hf and each X is Cl. These embodiments may be converted to other embodiments of the precatalyst of formula (II). For example, the embodiments of the precatalyst of formula (II) wherein each X

is Cl may be reacted with n mole equivalents of an alkylmagnesium halide or of an alkyl lithium to make the precatalyst of formula (II) wherein each X is alkyl. The embodiments of the precatalyst of formula (II) wherein M is Zr or Hf and each X is benzyl (Bn) are made directly from the $ZrBn_4$ or $HfBn_4$. Alternatively, the embodiments of the precatalyst of formula (II) wherein M is Zr or Hf and each X is benzyl (Bn) may be made from the embodiments of the precatalyst of formula (II) wherein M is Zr or Hf and each X is Cl by reacting them with n mole equivalents of a benzylmagnesium halide or benzyl lithium.

[0095] Figure 4 depicts synthetic Scheme 4. In Step H of Scheme 4, the precatalyst of formula (II) is activated by an activator and supported on a support material in an inert hydrocarbon liquid, such as alkanes or toluene, to make a supported catalyst system suspended in the inert hydrocarbon liquid. In Step I(i), the suspension of the supported catalyst system is spray-dried as described herein to make a spray-dried supported catalyst system ("sd-SCS") embodiment. Alternatively, in Step I(ii) the suspension of the supported catalyst system is conventionally dried as described herein to make a conventionally-dried supported catalyst system ("cd-SCS") embodiment. The catalyst activity and catalyst productivity of an sd-SCS embodiment made from a given precatalyst of formula (II) are different than, and typically superior to, the catalyst activity and catalyst productivity of a cd-SCS embodiment made from the same precatalyst of formula (II).

[0096] Figure 5 depicts synthetic Scheme 5. In Scheme 5, 1,3-bis(iodophenoxy)methylene germanium compound (6) shown in Scheme 2 in Figure 2 is made from phenols (6a) and (6c) and dichloromethyl-di-isopropylgermanium (6b) in the presence of potassium phosphate (K_3PO_4) in dimethylformamide (DMF) at 80° to 100° C.

Supported Catalyst System

[0097] The supported catalyst system is a heterogeneous olefin polymerization catalyst. The heterogenization of the precatalyst of formula (II) with support material and activator to make the supported catalyst system may be carried out according to any one of the heterogenization routes described earlier. The supported catalyst system is formulated for use in gas phase or slurry phase polymerizations of olefin monomers.

[0098] The supported catalyst system is made from the precatalyst of formula (II), an activator, and a solid support. The supported catalyst system may comprise additional components such as by-products and side products of the preparation of the supported catalyst system and any unreacted activator that may remain in preparations that use an excess amount of activator relative to the amount of the precatalyst of formula (II).

[0099] The catalysts of the supported catalyst system may be unsupported when contacted with an activator, which may be the same or different for the different catalysts. Alternatively, the catalysts may be disposed by spray-drying onto a solid support material prior to being

contacted with the activator(s). The solid support material may be uncalcined or calcined prior to being contacted with the catalysts. The solid support material may be a hydrophobic fumed silica (e.g., a fumed silica treated with dimethyldichlorosilane, which is $((\text{CH}_3)_2\text{SiCl}_2)$, which is commercially available from Cabot Corporation as Cabosil™ TS-610 fumed silica. The bimodal (unsupported or supported) catalyst system may be in the form of a powdery, free-flowing particulate solid.

Support Material

[00100] The support material used in the supported catalyst system may be an inorganic oxide solid. The terms “support”, “solid support”, “support material”, and “solid support material” mean the same thing as used herein and refer to a porous inorganic substance or organic substance. In some embodiments, the support material may be an inorganic oxide, which includes Group 2, 3, 4, 5, 13 or 14 metal oxides, alternatively Group 13 or 14 metal oxides. Examples of inorganic oxide-type support materials are silica, magnesia, alumina, titania, zirconia, thoria, and mixtures of any two or more of such inorganic oxides. Examples of such mixtures are silica-chromium, silica-alumina, and silica-titania. The support material may be untreated or the support material may be treated with a hydrophobing agent. In some embodiments the support material is a hydrophobic fumed silica.

[00101] The inorganic oxide support material is porous and has variable surface area, pore volume, and average particle size. In some embodiments, the surface area is from 50 to 1000 square meter per gram (m^2/g) and the average particle size is from 1 to 300 micrometers (μm), alternatively 20 to 300 μm . Alternatively, the pore volume is from 0.5 to 6.0 cubic centimeters per gram (cm^3/g) and the surface area is from 200 to 600 m^2/g . Alternatively, the pore volume is from 1.1 to 1.8 cm^3/g and the surface area is from 245 to 375 m^2/g . Alternatively, the pore volume is from 2.4 to 3.7 cm^3/g and the surface area is from 410 to 620 m^2/g . Alternatively, the pore volume is from 0.9 to 1.4 cm^3/g and the surface area is from 390 to 590 m^2/g . Each of the above properties are measured using conventional techniques known in the art.

[00102] The support material may comprise silica, alternatively amorphous silica (not quartz), alternatively a high surface area amorphous silica (e.g., from 500 to 1000 m^2/g). Such silicas are commercially available from several sources including the Davison Chemical Division of W.R. Grace and Company (e.g., Davison 952 and Davison 955 products), and PQ Corporation (e.g., ES70 product). The silica may be in the form of spherical particles, which may be obtained by a spray-drying process. Alternatively, MS3050 product is a silica from PQ Corporation that is not spray-dried. As procured, these silicas are not calcined (i.e., not dehydrated). Silica that is calcined prior to purchase may also be used as the support material.

[00103] In some embodiments the solid support is a hydrophobic fumed silica. The hydrophobic fumed silica is made by contacting an untreated fumed silica, having surfaces containing silicon-bonded hydroxyl groups (Si-OH groups), with a hydrophobing agent, described later. In some embodiments the hydrophobing agent is a silicon-based hydrophobing agent, containing on average per molecule one or more functional groups reactive with a Si-OH group, to give the hydrophobic fumed silica. The silicon-based hydrophobing agent may be selected from $(\text{CH}_3)_2\text{SiCl}_2$, a polydimethylsiloxane, hexamethyldisilazane (HMDZ), and a $(\text{C}_1\text{-C}_{10})\text{alkylSi}((\text{C}_1\text{-C}_{10})\text{alkoxy})_3$ (e.g., an octyltrialkoxysilane such as octyltriethoxysilane, i.e., $\text{CH}_3(\text{CH}_2)_7\text{Si}(\text{OCH}_2\text{CH}_3)_3$). In some embodiments the silicon-based hydrophobing agent is dimethyldichlorosilane, i.e., $(\text{CH}_3)_2\text{SiCl}_2$. In some embodiments the support material is a dimethyldichlorosilane-treated fumed silica, such as that sold as product TS-610 from Cabot Corporation.

[00104] The support material may be uncalcined or calcined. The calcined support material is made prior to being contacted with a precatalyst, activator, and/or hydrophobing agent, by heating the support material in air to give a calcined support material. The calcining comprises heating the support material at a peak temperature from 350° to 850° C., alternatively from 400° to 800° C., alternatively from 400° to 700° C., alternatively from 500° to 650° C. and for a time period from 2 to 24 hours, alternatively from 4 to 16 hours, alternatively from 8 to 12 hours, alternatively from 1 to 4 hours, thereby making the calcined support material. If the support material has not been heated in this way it is an uncalcined support material.

Hydrophobing Agent

[00105] The hydrophobing agent is an organic compound or an organosilicon compound that forms a stable reaction product with surface hydroxyl groups of a fumed silica. The organosilicon compound may be a polydiorganosiloxane compound or an organosilicon monomer, which contains silicon bonded leaving groups (e.g., Si-halogen, Si-acetoxy, Si-oximo ($\text{Si-ON}=\text{C}<$), Si-alkoxy, or Si-amino groups) that react with surface hydroxyl groups of untreated fumed silica to form Si-O-Si linkages with loss of water molecule as a by-product. The polydiorganosiloxane compound, such as a polydimethylsiloxane, contains backbone Si-O-Si groups wherein the oxygen atom can form a stable hydrogen bond to a surface hydroxyl group of fumed silica. The silicon-based hydrophobing agent may be trimethylsilyl chloride, dimethyldichlorosilane, a polydimethylsiloxane fluid, hexamethyldisilazane, an octyltrialkoxysilane (e.g., octyltrimethoxysilane), and a combination of any two or more thereof.

Activator

[00106] The activator used in the heterogenization method may be any compound capable of reacting with the precatalyst of formula (II) to yield an active olefin polymerization catalyst. The

activator may be a Lewis acid, a non-coordinating ionic activator, or an ionizing activator, or a Lewis base.

[00107] In some embodiments the activator is an aluminum based activator. The molar ratio of activator's metal (Al) to a particular catalyst compound's metal (Group 4 metal, e.g., Ti, Zr, or Hf) may be 7,000:1 to 0.5:1, alternatively 3,500:1 to 1:1, alternatively 1,000:1 to 0.5:1, alternatively 300:1 to 1:1, alternatively 150:1 to 1:1. Suitable activators are commercially available. In some embodiments the aluminum based activator is an alkylaluminum or an alkylaluminumoxane (alkylalumoxane). Any alkyl group may be used. In some embodiments each alkyl of the alkylaluminum or alkylaluminumoxane independently may be a (C₁-C₈)alkyl, alternatively a (C₁-C₇)alkyl, alternatively a (C₁-C₆)alkyl, alternatively a (C₁-C₄)alkyl.

[00108] The alkylaluminum may be a trialkylaluminum, alkylaluminum halide, or alkylaluminum alkoxide (diethylaluminum ethoxide). The trialkylaluminum may be trimethylaluminum, triethylaluminum ("TEAL"), tripropylaluminum, or tris(2-methylpropyl)aluminum. The alkylaluminum halide may be diethylaluminum chloride. The alkylaluminum alkoxide may be diethylaluminum ethoxide.

[00109] The alkylaluminumoxane may be a methylaluminoxane (MAO), ethylaluminoxane, 2-methylpropyl-aluminumoxane, or a modified methylaluminoxane (MMAO).

[00110] In some embodiments the activator is the MAO.

Supported Catalyst System

[00111] Once the precatalyst of formula (II) and the activator are in contact with each other, whether in the presence or absence of the solid support, as the case may be for the first, second or third heterogenization routes described earlier, an active catalyst species and an activator species are made *in situ*. The active catalyst species comprises a ligand derived from the substituted 2-hydroxythiophene compound of formula (I) and an activator species. The activator species has a different structure or composition than the activator from which it is derived. The activation reaction may also generate one or more by-products. The corresponding activator species may be a derivative of the Lewis acid, non-coordinating ionic activator, ionizing activator, Lewis base, alkylaluminum, or alkylaluminumoxane, respectively. An example of the derivative of the by-product is a methylaluminoxane species that is formed by devolatilizing during spray-drying of a supported catalyst system made with methylaluminoxane.

[00112] The supported catalyst system may be made by the heterogenization routes described earlier. These routes typically include use of an inert hydrocarbon liquid as solvent or carrier.

[00113] In some embodiments the precatalyst and support material are contacted together in the inert hydrocarbon liquid to give a suspension of a supported precatalyst in the inert

hydrocarbon liquid, then the suspension is contacted with the activator to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[00114] In other embodiments the precatalyst and activator are contacted together in an inert hydrocarbon liquid to give a solution of a catalyst in the inert hydrocarbon liquid, then the solution is contacted with the support material to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[00115] In other embodiments the activator and the support material are contacted together in an inert hydrocarbon liquid to give a suspension of a supported activator in the inert hydrocarbon liquid, then the suspension is contacted with the precatalyst to give a suspension of the supported catalyst system in the inert hydrocarbon liquid, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[00116] In other embodiments the precatalyst, activator, and support material are contacted together simultaneously in an inert hydrocarbon liquid to give a suspension of the supported catalyst, and then the inert hydrocarbon liquid is removed to give the supported catalyst system.

[00117] The removing of the inert hydrocarbon liquid from the suspension of the supported catalyst system may include a step of decanting some of the inert hydrocarbon liquid from the suspension. In some embodiments the decanting method comprises pouring off excess inert hydrocarbon liquid from the suspension to give a concentrated suspension of the supported catalyst system.

[00118] The removing of the inert hydrocarbon liquid from the suspension of the supported catalyst system may comprise a step of drying the supported catalyst system. The drying step may comprise a conventional drying method or a spray-drying method.

[00119] The conventional drying method comprises a method of slowly increasing the mass or molar amount of less volatile chemical constituent(s) per unit volume of a continuous mixture comprising more volatile and less volatile chemical constituent(s) by gradually removing the more volatile chemical constituent(s) from the less volatile constituent(s) of the continuous mixture to give a concentrate having a higher mass or molar amount of the less volatile chemical constituent(s) per unit volume than did the continuous mixture, wherein the rate of gradual removing is limited by a relatively small evaporative surface area to mass ratio (compared to spray-drying). The concentrate may be a precipitated solid.

[00120] The spray-drying method comprises rapidly forming a particulate solid comprising less volatile chemical constituents via aspiration of a bulk mixture of the less volatile chemical constituents and more volatile chemical constituents through a nebulizer using a hot gas, wherein the aspiration forms particulates collectively having a large evaporative surface area

to mass ratio compared to that of concentrating. The particle size and shape of the particulate solid formed by spray-drying may be different than those of a precipitated solid.

[00121] In some embodiments the spray-dried supported catalyst system may be made at laboratory scale according to the following spray-drying procedure in a nitrogen-purged glove box: charge an oven-dried glass jar with anhydrous deoxygenated toluene and a solid support material. The contents are stirred at room temperature until well dispersed as a slurry. To the slurry is added a 10 % solution by weight of methylaluminoxane (MAO) in toluene. The resulting mixture is stirred for 15 minutes, then a quantity of the precatalyst of formula (II) is added. The resulting reaction mixture is stirred at room temperature for an additional 30 to 60 minutes to activate the precatalyst, yielding the supported catalyst system suspended in toluene. This suspension is spray-dried using a spray drier apparatus (e.g., a Büchi Mini Spray Dryer model B-290 from BUCHI Corporation, New Castle, Delaware, USA) with the following parameters: Set Temperature 140° C., Outlet Temperature 75° C. (minimum), aspirator setting 95 rotations per minute (rpm), and pump speed 150 rpm. The spray-drying process yields the spray-dried supported catalyst system as an anhydrous solid powder. In some embodiments the solid support material that has been treated with a hydrophobing agent, such as a hydrophobic fumed silica that has been treated with dimethyldichlorosilane. The foregoing procedure may be scaled up to manufacturing size quantities using generally known methods.

Comparing Advantages of Undried, Conventionally-Dried, and Spray-Dried Embodiments of the Supported Catalyst System

[00122] The present invention contemplates both the conventionally dried supported catalyst system embodiments, the spray-dried supported catalyst system embodiments, and the decanted but undried supported catalyst system embodiments. The decanted but undried supported catalyst system embodiments are useful in catalyzing slurry phase polymerizations and are convenient form for adding the supported catalyst system to a slurry phase reactor.

[00123] The conventionally dried supported catalyst system embodiments may have higher catalyst efficiencies, and thus greater polyolefin productivities, than do comparative unsupported catalysts made from the same precatalyst and activator in the absence of the support material.

[00124] The spray-dried supported catalyst system embodiments may have higher catalyst efficiencies, and thus greater polyolefin productivities, than do the conventionally dried supported catalyst system embodiments. Therefore, the spray-dried embodiments of the supported catalyst system may have still higher catalyst efficiencies, and thus still greater polyolefin productivities, than do comparative unsupported catalysts made from the same precatalyst and activator in the absence of the support material.

[00125] Many spray-dried supported catalyst system embodiments also make polyolefins having improved resin properties. For example, some spray-dried supported catalyst system

embodiments make polyolefins having increased content of long chain branching (LCB), whereas other spray-dried supported catalyst system embodiments and the conventionally dried catalyst system embodiments do not. In another example, some spray-dried supported catalyst system embodiments make polyolefins having ultrahigh molecular weight contents, whereas other spray-dried supported catalyst system embodiments and the conventionally dried catalyst system embodiments do not.

[00126] The supported catalyst system may be used in slurry phase or gas phase olefin polymerization reactions to enhance the rate of polymerization of monomer and/or comonomer(s). In some aspects the olefin polymerization reaction is conducted in a gas phase reactor in the gas phase, or in a slurry phase reactor in the slurry phase.

Method of Polymerizing One or More Olefin Monomers

[00127] In embodiments of the method of polymerizing an olefin monomer, the method comprising contacting the olefin monomer with the supported catalyst system, thereby making a polyolefin, wherein the olefin polymerization is conducted in a gas phase reactor under gas phase process conditions or the olefin polymerization is conducted in a slurry phase reactor under slurry phase conditions. In some embodiments the method comprises polymerizing ethylene only and makes a polyethylene homopolymer. In other embodiments the method comprises polymerizing ethylene and propylene and makes an ethylene/propylene copolymer, or polymerizing ethylene and a (C₄-C₈)alpha-olefin and makes an ethylene/(C₄-C₈)alpha-olefin copolymer. In some embodiments the (C₄-C₈)alpha-olefin is 1-butene, 1-hexene, or 1-octene; or 1-butene or 1-hexene; or 1-butene; or 1-hexene; or 1-octene; and the ethylene/(C₄-C₈)alpha-olefin copolymer is ethylene/1-butene copolymer, ethylene/1-hexene copolymer, or ethylene/1-octene copolymer; or ethylene/1-butene copolymer or ethylene/1-hexene copolymer; or ethylene/1-butene copolymer; or ethylene/1-hexene copolymer; or ethylene/1-octene copolymer.

Polymerization Reactors and Process Conditions

[00128] The method of polymerizing an olefin monomer may be carried out in any gas phase olefin polymerization reactor or slurry phase olefin polymerization reactor and under any gas phase polymerization process conditions or slurry phase polymerization conditions.

[00129] Reactors and process conditions for gas phase and slurry phase olefin polymerization reactions are well-known. For example slurry phase reactors and process conditions include those described in US 3,324,095. The gas phase polymerization reactor and process conditions may employ stirred-bed gas-phase polymerization reactor (SB-GPP reactor) or a fluidized-bed gas-phase polymerization reactor (FB-GPP reactor). The gas phase reactor and process conditions may include an induced condensing agent and be conducted in condensing mode polymerization such as described in US 4,453,399; US 4,588,790; US

4,994,534; US 5,352,749; US 5,462,999; and US 6,489,408. The gas phase reactor and process conditions may be a fluidized bed reactor/method as described in US 3,709,853; US 4,003,712; US 4,011,382; US 4,302,566; US 4,543,399; US 4,882,400; US 5,352,749; US 5,541,270; EP-A-0 802 202; and Belgian Patent No. 839,380. These patents disclose gas phase polymerization processes wherein the polymerization medium is either mechanically agitated or fluidized by the continuous flow of the gaseous monomer and diluent. Other useful gas phase processes include series or multistage polymerization processes such as described in US 5,627,242; US 5,665,818; US 5,677,375; EP-A-0 794 200; EP-B1-0 649 992; EP-A-0 802 202; and EP-B-634421.

[00130] In some embodiments the gas phase reactor and process conditions comprise a single gas phase reactor and single set of process conditions.

[00131] In other embodiments the gas phase reactor and process conditions comprise two gas phase reactors in series and two sets of process conditions. In such embodiments a first olefin polymerization is conducted in a first gas phase reactor under a first gas phase process conditions, then the resulting polyolefin is transferred into a second gas phase reactor, wherein a second olefin polymerization reaction is conducted under a second set of process conditions. The supported catalyst system may be used in the first olefin polymerization and not the second olefin polymerization, or in the second olefin polymerization and not the first olefin polymerization, or in both the first and second olefin polymerizations. The supported catalyst system used in both the first and second olefin polymerizations may be the same embodiment or different embodiments.

[00132] In some embodiments the olefin polymerization comprises a slurry phase reactor and process conditions and a gas phase reactor and process conditions in series, or vice versa. In some embodiments a first olefin polymerization is conducted in the slurry phase reactor under the slurry phase process conditions, then the slurry phase polyolefin is transferred into the gas phase reactor and a second olefin polymerization is conducted under gas phase conditions. The supported catalyst system may be used in the first olefin polymerization and not the second olefin polymerization, or in the second olefin polymerization and not the first olefin polymerization, or in both the first and second olefin polymerizations. The supported catalyst system used in both the first and second olefin polymerizations may be the same embodiment or different embodiments.

Polyolefin

[00133] The product of the olefin polymerization method is a polyolefin.

[00134] In some embodiments the polyolefin is a low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), a medium-density polyethylene (MDPE), or a high-density polyethylene (HDPE). These polyethylenes have different polymer chain structures, which are pictorially illustrated in Figure 6, and are a result of the different polymerization process

conditions and initiators or catalysts used to make them. In general an LLDPE is distinguished from LDPE by the initiator or catalyst and the polymerization process conditions used to make them, which leads to differences in their amounts of long chain branching. LDPE is made by a free radical polymerization process (e.g., initiated by small amounts of organic peroxide) at high pressure and as such LDPE inherently has a significant amount of long chain branching as shown in Figure 6. LLDPEs that are made using traditional Ziegler-Natta catalysts, which do not generate long chain branching, are linear and free of long chain branching as illustrated in Figure 6. In general an LLDPE is distinguished from HDPE by density and by the amount of short chain branching (SCB). LLDPEs have densities less than 0.940 g/cm^3 , whereas HDPE has densities greater than or equal to 0.940 g/cm^3 . Also, LLDPEs have a significant amount of short chain branching, whereas HDPEs have far lesser amounts of short chain branching; see Figure 6.

[00135] In some embodiments the polyethylene may have no detectable long-chain branching content, i.e., 0 long-chain branches ("LCB") per 1000 carbon atoms. In other embodiments the polyethylene may have a long-chain branching content from 0.01 to 2 long-chain branches ("LCB") per 1000 carbon atoms (LCB/1000C), alternatively from 0.01 LCB/1000C to 1.0 LCB/1000C, alternatively from 0.1 LCB/1000C to 1.0 LCB/1000C. As used herein having a LCB content means having an amount of long chain branching that is detectable by the ^{13}C -NMR spectroscopy, which currently has a lower detection limit of 0.004 LCB/1000C. LCB content from greater than 0.000 LCB/1000C to less than 0.010 LCB/1000C are excluded herein.

[00136] The long chain branching content of the inventive polyolefin may be directly or indirectly characterized by any one of the following measurements (i) to (iv): (i) directly by carbon-13 nuclear magnetic resonance (NMR) spectroscopy; (ii) indirectly by a melt flow ratio (I_{21}/I_2) equation described below; (iii) indirectly by a melt flow ratio (I_{21}/I_2) range; or (iv) Mark-Houwink analysis using a triple detector gel permeation chromatography (triple detector GPC). In some embodiments the characterization may comprise a combination of measurements (i) and (ii), a combination of measurements (i) and (iv), a combination of measurements (i) and (iii), a combination of measurements (ii) and (iii), a combination of measurements (ii) and (iv), a combination of measurements (iii) and (iv), or a combination of measurements (i), (ii), (iii), and (iv).

[00137] In some embodiments the polyethylene may have ultra-high molecular weight ("UHMW") content. In some embodiments the polyethylene may have UHMW tail in a GPC plot. The UHMW content of these polyethylene embodiments may be measured by GPC, and is a polymer weight average molecular weight of 1,000,000 g/mol or greater. The UHMW tail is any one of limitations (i) to (iii): (i) a z-average molecular weight of 1,000,000 g/mol or

greater, (ii) a ratio of z-average molecular weight to weight-average molecular weight (M_z/M_w) of 3.5 or greater, or (iii) both limitations (i) and (ii).

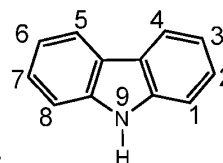
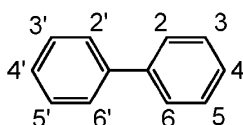
[00138] The polyolefin may be formulated with one or more additives useful in polyethylene articles, such as but not limited to, additives useful in polyethylene films, additives useful in polyethylene pipes, or additives useful in blow molded polyethylene articles. In some embodiments the one or more additives comprise additives useful for films such as one or more antioxidants, one or more ultraviolet (UV) light stabilizers, one or more colorants, and/or one or more anti-microbial agents.

Definitions

[00139] *Activator*: a compound for converting a precatalyst having no or negligible catalytic activity into a catalyst having orders of magnitude higher catalytic activity.

[00140] *Alpha-olefin*: is a terminal monoalkene of formula $H_2C=CH(CH_2)_kCH_3$ wherein subscript k is an integer of 0 or higher, or 1 or higher; abbreviated “ α -olefin”.

[00141] *Biphenyl*: a compound of this structure and position numbering:



[00142] *Carbazole*: is a compound of structure and position numbering:

[00143] *Dry*: precatalysts, activators, catalysts and calcined support materials may have a moisture content from 0 to less than 5 parts per million based on total parts by weight. Dry may also refer to being free of an organic solvent such as toluene or hexanes when used to describe an embodiment of a supported catalyst system as a dry powder.

[00144] *Fumed silica*: a pyrogenic silica produced in a flame. An amorphous silica powder made by fusing microscopic droplets into branched, chainlike, three-dimensional secondary particles, which agglomerate into tertiary particles. Not quartz.

[00145] *Heteroatoms*: as used herein, generic heteroatom-containing organic groups wherein the specific heteroatom or heteroatoms is not or are not explicitly or implicitly indicated, such as is the case for “heterohydrocarbyl” groups and “organoheteryl” groups, inherently contain one or more heteroatoms selected from the group consisting of O, S, N, P, and Si; or O, S, N, and Si; or O, N, and Si; or O and N; or O; or N; or Si; or S; or P. In contrast, examples of heteroatom-containing organic groups wherein the heteroatom is explicitly or implicitly

indicated are: alkoxy groups wherein the heteroatom implicitly is O' and amino groups wherein the heteroatom implicitly is N; alkylO- groups wherein the heteroatom explicitly is O; and -CH₂Si(alkyl)₃ groups wherein the heteroatom explicitly is Si.

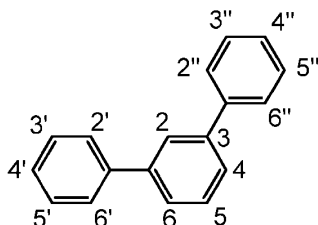
[00146] *Hydrocarbyl*, *heterohydrocarbyl*, and *organoheteryl* have their IUPAC Gold Book meanings. The hydrocarbyl is a monovalent radical that in unsubstituted embodiments consists of one or more carbon atoms and hydrogen atoms, wherein the monovalent radical is on a carbon atom. Examples are alkyl and aryl. The heterohydrocarbyl group is a monovalent radical that in unsubstituted embodiments consists of one or more carbon atoms and at least one heteroatom, wherein the monovalent radical is a carbon atom. Examples are ethoxymethyl and -CH₂Si(alkyl)₃. The organoheteryl group is a monovalent radical that in unsubstituted embodiments consists of one or more carbon atoms and at least one heteroatom, wherein the monovalent radical is a heteroatom. Examples alkoxy and -Si(alkyl)₃.

[00147] *Inert*: not (appreciably) reactive. The term "inert" as applied to the purge gas or olefin monomer feed means a molecular oxygen (O₂) content from 0 to less than 5 parts per million based on total parts by weight of the purge gas or olefin monomer feed. As applied to a hydrocarbon (unsubstituted) solvent means free of carbon-carbon double and triple bonds, free of molecular oxygen (0 to less than 5 ppm O₂), and free of moisture ("dry", 0 to less than 5 ppm H₂O). Examples are hydrocarbon solvents that may be inerted (dried and purged of O₂) are unsubstituted alkanes (e.g., hexanes and heptane), unsubstituted arenes (e.g., benzene and naphthalene), and unsubstituted alkylarenes (e.g., toluene, xylenes, and fluorene).

[00148] *Metallocene catalyst*. Homogeneous or heterogeneous molecule that contains an unsubstituted- or substituted-cyclopentadienyl ligand-metal complex and enhances olefin polymerization reaction rates. With respect to number of catalytic sites, typically unsupported metallocene catalyst molecules are substantially single site or dual site and supported metallocene catalysts are multi-sited, meaning two or more sites or speciations. The unsubstituted cyclopentadienyl is a monoanion of formula [C₅H₅]⁻. As used herein "substituted cyclopentadienyl" includes monocyclic derivatives of cyclopentadienyl, such as propylcyclopentadienyl and pentamethylcyclopentadienyl, and multicyclic derivatives of cyclopentadienyl, such as bicyclic derivatives indenyl and tetrahydroindenyl and tricyclic derivatives fluorenyl, tetrahydrofluorenyl, and octahydrofluorenyl, and substituted derivatives thereof. Examples of substituted-cyclopentadienyl ligands are unsubstituted indenyl, alkyl-substituted indenyl, unsubstituted 4,5,6,7-tetrahydroindenyl, alkyl-substituted 4,5,6,7-tetrahydroindenyl, unsubstituted fluorenyl, and alkyl-substituted fluorenyl, unsubstituted

1,2,3,4-tetrahydrofluorenyl, alkyl-substituted 1,2,3,4-tetrahydrofluorenyl, unsubstituted 1,2,3,4,5,6,7,8-octahydrofluorenyl, and alkyl-substituted 1,2,3,4,5,6,7,8-octahydrofluorenyl.

[00149] *Meta-terphenyl*: also named 3-phenyl-1,1'-biphenyl, is a compound of this structure



and position numbering:

[00150] *Modality of Molecular Weight Distribution* in reference to a polyolefin indicates the nature of the polyolefin's molecular weight distribution greater than a molecular weight of 1,000 grams/mole ($\text{Log}(\text{MW}) > 3.0$) and less than a molecular weight of 10,000,000 grams /mole ($\text{Log}(\text{MW}) < 7.0$) in a plot of $dW/d\text{Log}(\text{MW})$ on the y-axis versus $\text{Log}(\text{MW})$ on the x-axis to give a Gel Permeation Chromatograph (GPC) chromatogram, wherein $\text{Log}(\text{MW})$ and $dW/d\text{Log}(\text{MW})$ are as defined herein and are measured by the High Temperature Gel Permeation Chromatography (GPC) Test Method described later. Only peaks between $\text{log}(\text{MW})$ 3.0 and $\text{log}(\text{MW})$ 7.0 count for modality. The modality of the polyolefin may be unimodal (only 1 peak between $\text{log}(\text{MW})$ 3.0 and $\text{log}(\text{MW})$ 7.0) or multimodal (2 or more peaks between $\text{log}(\text{MW})$ 3.0 and $\text{log}(\text{MW})$ 7.0). The modality of the multimodal polyolefin may be bimodal (only 2 peaks between $\text{log}(\text{MW})$ 3.0 and $\text{log}(\text{MW})$ 7.0), trimodal (only 3 peaks between $\text{log}(\text{MW})$ 3.0 and $\text{log}(\text{MW})$ 7.0), or higher modal (4 or more peaks between $\text{log}(\text{MW})$ 3.0 and $\text{log}(\text{MW})$ 7.0). Any two peaks between $\text{log}(\text{MW})$ 3.0 and $\text{log}(\text{MW})$ 7.0 may be separated by a distinguishable local minimum therebetween or one peak may merely be a shoulder on the other. Deconvolution of a GPC plot between $\text{log}(\text{MW})$ 3.0 and $\text{log}(\text{MW})$ 7.0 may be used to determine if there are any hidden peaks, which would then be counted for modality.

[00151] *Multi-site catalyst*: any catalyst that makes a polyethylene having a polydispersity index (PDI , M_w/M_n) greater than 2.0.

[00152] *Olefin monomer*: unsubstituted hydrocarbon containing a carbon-carbon double bond.

[00153] *Polyolefin*: a straight chain or branched chain macromolecule consisting of carbon and hydrogen, or plurality of macromolecules, and having six or more constituent units derived by polymerizing an olefin monomer or two or more olefin comonomers.

[00154] *Precatalyst*: a catalyst precursor compound, also called a "precatalyst". A precatalyst has none or very little catalytic activity itself, but upon being contacted with an activator the precatalyst is converted into a catalyst compound. The precatalyst may be a ligand-metal complex such as the precatalysts described herein.

[00155] *Prophetic example.* An embodiment that has not been actually made, but which can be readily made from the teachings provided herein and which the inventor(s) expect will have the described inventive features and advantages, and is included to support the claimed scope.

[00156] *Single-site catalyst.* An organic ligand-metal complex useful for enhancing rates of polymerization of olefin monomers and having at most two discreet binding sites at the metal available for coordination to an olefin monomer molecule prior to insertion on a propagating polymer chain.

[00157] *Single-site non-metallocene catalyst.* A single-site catalyst that is free of an unsubstituted or substituted cyclopentadienyl ligand.

[00158] *System (chemical):* an interrelated arrangement of different chemical constituents so as to form a functioning whole.

[00159] *Ziegler-Natta catalyst:* a titanium catalyst supported on magnesium dichloride solids, and, optionally, a silica.

[00160] In the event of a disagreement between a chemical name and its structure, the structure controls and determines the identity of the compound in question. In the event of a disagreement between a chemical name and its description by reference to formula (I) or (II), and substituent groups R[#] (e.g., R¹, R², etc.) and X, the description referring to the formula (I) or (II), and substituent R[#] and X groups controls and determines the identity of the compound in question.

Experimental Methods

[00161] *Preparing Test Plaques, Sheets, or Specimens:* see ASTM D4703-10, *Standard Practice for Compression Molding Thermoplastic Materials into Test Specimens, Plaques, or Sheets.*

[00162] *Density Test Method:* measured according to ASTM D792-13, *Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement*, Method B (for testing solid plastics in liquids other than water, e.g., in liquid 2-propanol). Units are grams per cubic centimeter (g/cm³).

[00163] *Long Chain Branching (LCB) Value Test Method:* the amount of the LCB occurring in the EB LLDPE resins can be measured using a combination of nuclear magnetic resonance (NMR) techniques described in Z. Zhou, S. Pesek, J. Klosin, M. Rosen, S. Mukhopadhyay, R. Cong, D. Baugh, B. Winniford, H. Brown, K. Xu, "Long chain branching detection and quantification in LDPE with special solvents, polarization transfer techniques, and inverse gated ¹³C NMR spectroscopy", *Macromolecules*, 2018, 51, 8443; Z. Zhou, C. Anklin, R. Cong, X. Qiu, R. Kuemmerle, "Long-chain branch detection and quantification in ethylene-hexene LLDPE with ¹³C NMR", *Macromolecule*, 2021, 54, 757; and Z. Zhou, C. Anklin, R. Kuemmerle,

R. Cong, X. Qiu, J. DeCesare, M. Kapur, R. Patel, "Very sensitive ^{13}C NMR method for the detection and quantification of long-chain branches in ethylene-hexene LLDPE", *Macromolecule*, 2021, 54, 5985. The chemical shift range for LCB calculation is between 38.12 ppm to 38.22 ppm.

[00164] *Melt Flow Test Methods*. Melt flow index values of polyethylenes were measured via the rate of extrusion of molten polymers through a die of specified length and diameter, under prescribed conditions of temperature, load, piston position in the barrel and duration, employing a melt indexer and test methods according to ASTM D1238-13 at 190° C. The load is 2.16 kg ("I₂"), 5.0 kg ("I₅"), or 21.6 kg ("I₂₁").

[00165] *Differential Scanning Calorimetry Test Method*. Melt temperature was determined via Differential Scanning Calorimetry according to ASTM D 3418-08. In general, a scan rate of 10° C/min on a sample of 10 milligrams (mg) was used, and the second heating cycle was used to determine T_m .

Gel-permeation chromatography (GPC) Test Method:

[00166] Weight-average molecular weight (M_w), number-average molecular weight (M_n), and z-average molecular weight (M_z) were measured using a High Temperature Gel Permeation Chromatography (Polymer Laboratories), equipped with a differential refractive index detector (DRI). The M_w and M_n values obtained were used to calculate polydispersity index (PDI), wherein $PDI = M_w/M_n$. Three Polymer Laboratories PLgel 10 μm Mixed-B columns were used. The nominal flow rate was 1.0 mL/min, and the nominal injection volume was 300 μL . The various transfer lines, columns, and differential refractometer (the DRI detector) were contained in an oven maintained at 160°C. The solvent for the experiment was 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 was then filtered through a 0.1 μm Teflon filter. The TCB was then degassed with an online degasser before entering the GPC instrument. The polymer solutions were prepared by placing dry polymer in glass vials, adding the desired amount of TCB, then heating the mixture at 160 °C with continuous shaking for about 2 hours. All quantities were measured gravimetrically. The injection concentration was 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 was purged. The flow rate in the apparatus was then increased to 1.0 ml/minute, and the DRI was allowed to stabilize for 8 hours before injecting the first sample. The molecular weight was determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards. The MW was calculated at each elution volume with following equation:

$$\log M_x = \frac{\log(K_x / K_{PS})}{a_x + 1} + \frac{a_{PS} + 1}{a_x + 1} \log M_{PS}$$

where the variables with subscript "X" stand for the test sample while those with subscript "PS" stand for PS. In this method, $a_{PS}=0.67$ and $K_{PS}=0.00017$, while a_x and K_x were obtained from published literature. Specifically, $a/K = 0.695/0.000579$ for PE and $0.705/0.0002288$ for PP.

[00167] The concentration, c , at each point in the chromatogram was calculated from the baseline-subtracted DRI signal, IDRI, using the following equation: $c = KDRI \cdot IDRI / (dn/dc)$, where KDRI is a constant determined by calibrating the DRI, and (dn/dc) is the refractive index increment for the system. Specifically, $dn/dc = 0.109$ for polyethylene. The mass recovery was calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume. All molecular weights are reported in g/mol unless otherwise noted. In event of conflict between the GPC-DRI procedure and the "Rapid GPC," the GPC-DRI procedure immediately above shall be used. The comonomer content (i.e., 1-hexene) incorporated in the polymers (weight %) was determined by rapid FT-IR spectroscopy on the dissolved polymer in a GPC measurement. Comonomer content can be determined with respect to polymer molecular weight by use of an infrared detector such as an IR5 detector in a gel permeation chromatography measurement, as described in *Analytical Chemistry* 2014, 86(17), 8649-8656. "Toward Absolute Chemical Composition Distribution Measurement of Polyolefins by High-Temperature Liquid Chromatography Hyphenated with Infrared Absorbance and Light Scattering Detectors" by Dean Lee, Colin Li Pi Shan, David M. Meunier, John W. Lyons, Rongjuan Cong, and A. Willem deGroot. *Analytical Chemistry* 2014 86 (17), 8649-8656.

[00168] For some of the polymer samples, weight-average molecular weight (M_w), number-average molecular weight (M_n), and z-average molecular weight (M_z) were measured using a chromatographic system consisting of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5) and 4-capillary viscometer (DV) coupled to a Precision Detectors (Now Agilent Technologies) 2-angle laser light scattering (LS) detector Model 2040. For all absolute Light scattering measurements, the 15 degree angle is used for measurement. The autosampler oven compartment was set at 165° Celsius and the column compartment and detectors were set at 155° Celsius. The columns used were 4 TOSOH TSKgel GMHHR-H (30) HT 30-micron particle size, mixed pore size columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent

source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[00169] Calibration of the GPC column set was performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000 and were arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. Individually prepared polystyrene standards of 10,000,000 and 15,000,000 g/mol, both from Agilent Technologies, were also prepared, at 0.5 and 0.3 mg/mL respectively. The polystyrene standards were pre-dissolved at 80 °C with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160°C for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).

[00170] $M_{polyethylene} = A \times (M_{polystyrene})^B$ (EQ1), wherein M is the molecular weight, A has a value of 0.3992, and B equals 1.0.

[00171] A third order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[00172] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 12,000 for the 4 TOSOH TSKgel GMHHR-H (30) HT 30-micron particle size, mixed pore size columns.

[00173] Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples were weight-targeted at 1 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 3 hours at 165° Celsius under “low speed” shaking.

[00174] The calculations of $Mn_{(GPC)}$, $Mw_{(GPC)}$, and $Mz_{(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2 to 4, using PolymerChar GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the

polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

$$[00175] \quad M_{n(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(IR_i / M_{polyethylene_i} \right)} \quad (EQ2).$$

$$[00176] \quad M_{W(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (EQ3).$$

$$[00177] \quad M_{Z(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (EQ4).$$

[00178] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 5. Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/-0.5% of the nominal flowrate.

[00179] Flowrate(effective) = Flowrate(nominal) * (RV(FM Calibrated) / RV(FM Sample))
(EQ 5).

[00180] For polymer samples prepared via slurry polymerization in a parallel pressure reactor (PPR), high temperature GPC analysis was performed using a Dow Robot Assisted Delivery (RAD) system equipped with a PolymerChar infrared detector (IR5) and Agilent PLgel Mixed A columns. Decane (10μL) was added to each sample for use as an internal flow marker. Samples were first diluted in 1,2,4-trichlorobenzene (TCB) stabilized with 300ppm butylated hydroxyl toluene (BHT) at a concentration of 10mg/mL and dissolved by stirring at 160°C for 120 minutes. Prior to injection samples were further diluted with TCB stabilized with BHT to a

concentration of 2 mg/mL. Samples (250 μ L) were eluted through one PL-gel 20 μ m (50 x 7.5mm) guard column followed by two PL-gel 20 μ m (300 x 7.5mm) Mixed-A columns maintained at 160 $^{\circ}$ C with TCB stabilized with BHT at a flowrate of 1.0 mL/min. The total run time was 24 minutes. To calibrate for molecular weight (MW) Agilent EasiCal polystyrene standards (PS-1 and PS-2) were analyzed to create a 3rd order MW calibration curve. Molecular weight units were converted from polystyrene (PS) to polyethylene (PE) using a daily Q-factor calculated around 0.4 using the average of 5 Dow 38-4 reference samples of known MW. Hexene incorporation was determined by use of a linear calibration developed by analyzing copolymer samples with known compositions.

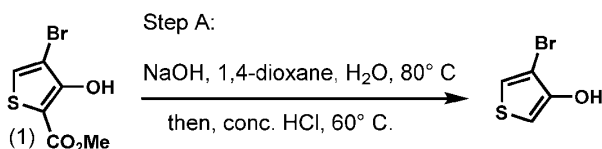
[00181] *Liquid chromatography-mass spectrometry (LC-MS) Measurements* were performed using a Waters e2695 Separations Module coupled with a Waters 2424 ELS detector, a Waters 2998 PDA detector, and a Waters 3100 ESI mass detector. LC-MS separations were performed on an XBridge C18 3.5 μ m 2.1x50 mm column using a 5:95 to 100:0 acetonitrile to water gradient with 0.1% formic acid as the ionizing agent. HRMS analyses were performed using an Agilent 1290 Infinity LC with a Zorbax Eclipse Plus C18 1.8 μ m 2.1x50 mm column coupled with an Agilent 6230 TOF Mass Spectrometer with electrospray ionization.

[00182] *Nuclear magnetic resonance (NMR) spectra* were recorded on Bruker 400 NMR, Bruker 500 NMR, Varian 400-MR and VNMR5-500 spectrometers. ¹H NMR data are reported as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet and m = multiplet), integration, and assignment). Chemical shifts for ¹H NMR data are reported in ppm downfield from internal tetramethylsilane (TMS, δ scale) using residual protons in the deuterated solvent as references. ¹³C NMR data were determined with ¹H decoupling, and the chemical shifts are reported downfield from tetramethylsilane (TMS, δ scale) in ppm versus the using residual carbons in the deuterated solvent as references.

EXAMPLES

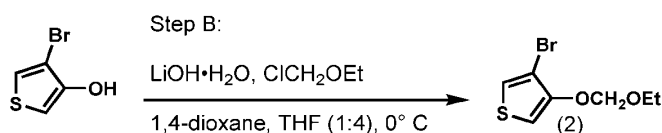
[00183] Actual examples are not indicated as such, whereas prophetic examples, if any, are marked prophetic. Syntheses of commercially available compounds are not shown. Unless otherwise noted the following conditions are used. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether were purified *via* passage through activated alumina and, in some cases, Q-5 reactant. Solvents used for experiments performed in a nitrogen-filled glovebox were further dried by storage over activated 3 $\text{\AA}$ molecular sieves. Glassware for moisture-sensitive reactions was dried in an oven overnight prior to use.

[00184] *Example 1: synthesis of 3-bromo-2-hydroxythiophene (example of step A).*



[00185] To a suspension of 3-bromo-2-hydroxythiophene-1-carboxylic acid methyl ester (1) (10.020 grams, 42.267 mmol, 1.00 eq) in 1,4-dioxane (100 mL) and H₂O (450 mL) under nitrogen was added NaOH (50.000 g, 1.250 mol, 29.6 eq) all at once. The pale yellow mixture was equipped with a reflux condenser and placed in a mantle (i.e., heating mantle) heated to 80 °C. After stirring (500 rpm) for 2.5 hours, thin layer chromatography (TLC) of the resulting golden yellow solution indicated complete conversion of (1) to a product having a lower R_f spot. The reaction mixture was removed from the mantle, allowed to gradually cool to 23 °C, and placed in an ice water bath for 60 minutes. Then, concentrated HCl (175 mL, 37%) was added over 10 minutes, and the resulting white heterogeneous mixture was removed from the ice water bath, placed in a mantle heated to 60 °C, and stirred vigorously (1000 rpm) for 5 hours. The now pale golden yellow solution was removed from the mantle, allowed to cool gradually to 23 °C, diluted with Et₂O (100 mL), stirred vigorously for 2 minutes, poured into a separatory funnel, partitioned, organics were washed with aqueous HCl (2 x 100 mL, 1 Normal ("N")), residual organics were extracted from the aqueous layer using Et₂O (2 x 50 mL), dried over solid Na₂SO₄, decanted, and the Et₂O was removed via rotary evaporation to afford 3-bromo-2-hydroxythiophene as a solution in 1,4-dioxane (100 mL). The solution of 3-bromo-2-hydroxythiophene is used in step B without concentration or purification. An aliquot was removed, fully concentrated *in vacuo*, and NMR is consistent with pure 3-bromo-2-hydroxythiophene as a mixture of keto-enol tautomers where * indicates keto-enol tautomer: ¹H NMR (400 MHz, Chloroform-*d*) δ (8.34 (s, 1H)*), 7.12 (d, *J* = 3.7 Hz, 1H), 6.43 (d, *J* = 3.7 Hz, 1H), 5.49 (s, 1H), (3.72 (s, 2H)*). ¹³C NMR (101 MHz, Chloroform-*d*) δ (210.23*), 195.46, 160.19, (149.69*), 121.43, (111.65*), (103.07*), 100.24, (37.05*).

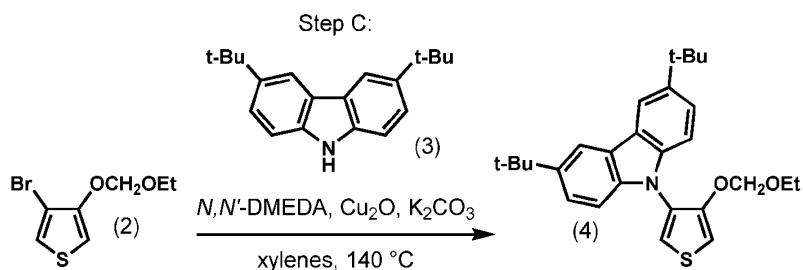
[00186] Example 2: synthesis of 3-bromo-2-ethoxymethoxythiophene (2) (example of step B).



[00187] The solution of the 3-bromo-2-hydroxythiophene in 1,4-dioxane (100 mL) from Step A was diluted with non-anhydrous, non-deoxygenated THF (400 mL). Then H₂O (6 mL) was added. The solution was placed in an ice water bath, sparged with nitrogen for 1 hour, placed under a positive flow of nitrogen upon which solid lithium hydroxide-monohydrate (3.544 g,

84.453 mmol, 2.00 eq) was added. The now dark red-brown solution, was stirred vigorously (1000 rpm) for 1 hour, then neat chloromethyl ethyl ether (11.8 mL, 126.80 mmol, 3.00 eq, "ClCH₂OEt") was added via syringe in a quick dropwise manner. After stirring for 2 hours at 0 °C the dark brown solution was diluted with aqueous NaOH (200 mL, 1 N), stirred for 2 minutes, THF was removed *in vacuo*, the biphasic mixture was diluted with CH₂Cl₂ (100 mL), suction filtered over a pad of diatomaceous earth, rinsed with CH₂Cl₂ (4 x 50 mL), the dark brown filtrate was poured into a separatory funnel, partitioned, organics were washed with aqueous NaOH (2 x 100 mL, 1 N), residual organics were extracted from the aqueous using CH₂Cl₂ (2 x 50 mL), combined, dried over solid Na₂SO₄, decanted, and carefully concentrated to afford a golden brown oil which was diluted with CH₂Cl₂ (25 mL), suction filtered over a pad of silica gel, rinsed with CH₂Cl₂ (4 x 50 mL), and the filtrate was concentrated to afford the 3-bromo-2-ethoxymethoxythiophene (2) as a golden yellow oil (9.534 g, 40.209 mmol, 95% two steps). NMR is consistent with compound (2): ¹H NMR (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 3.6 Hz, 1H), 6.61 (d, *J* = 3.5 Hz, 1H), 5.19 (s, 2H), 3.73 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.51, 121.50, 103.84, 101.55, 95.07, 64.53, 15.05.

[00188] Example 3: synthesis of 2-ethoxymethoxy-3-(3',6'-di-*tert*-butylcarbazolyl)lthiophene (4) (example of step C).

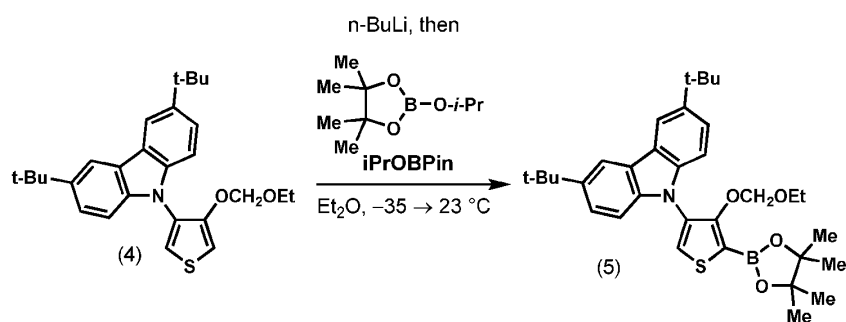


[00189] Step C. In a nitrogen filled continuous purge glovebox, a mixture of the bromothiophene (2) (5.883 g, 24.811 mmol, 1.00 eq), 3,6-di-*tert*-butylcarbazole (15.252 g, 54.585 mmol, 2.20 eq), Cu₂O (7.100 g, 49.622 mmol, 2.00 eq), and K₂CO₃ (34.290 g, 248.11 mmol, 10.00 eq) was suspended in deoxygenated anhydrous xylenes (200 mL), *N,N'*-DMEDA (10.7 mL, 99.244 mmol, 4.00 eq) was added, the mixture was equipped with a reflux condenser and a rubber septa, removed from the glovebox, placed under nitrogen, placed in a mantle heated to 140 °C, stirred vigorously (1000 rpm) for 48 hours, removed from the mantle, the now deep red-black mixture was allowed to cool gradually to 23 °C, CH₂Cl₂ (100 mL) was added, the mixture was stirred for 5 mins, suction filtered over a pad of silica gel, rinsed with CH₂Cl₂ (4 x 75 mL), concentrated, the golden brown amorphous solid was suspended in hexanes (50 mL), placed in a mantle heated to 60 °C, after stirring (300 rpm) for 1 hr, the golden brown mixture was removed from the heating mantle, allowed to gradually

cool to 23 °C, the mixture was suction filtered, the residual white solid was rinsed with hexanes (4 x 20 mL), the golden brown filtrate solution was concentrated onto Diatomaceous earth, and purified via silica gel chromatography using an ISCO chromatography purification system; 15% CH₂Cl₂ in hexanes to make the thiophene-carbazole (4) as a white amorphous foam (7.699 g, 17.673 mmol, 71%). NMR is consistent with compound (4). ¹H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 1.9 Hz, 2H), 7.45 (dd, *J* = 8.6, 2.0 Hz, 2H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 3.6 Hz, 1H), 3.56 (q, *J* = 7.1 Hz, 2H), 1.47 (s, 18H), 1.16 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 150.87, 142.60, 139.70, 127.62, 123.44, 123.08, 120.21, 116.07, 109.57, 102.36, 94.78, 64.37, 34.70, 32.03, 15.01.

[00190] Example 4: synthesis of 2-ethoxymethoxy-3-(3',6'-di-*tert*-butylcarbazolyl)-2-pinacoloborylthiophene (5) (example of step D).

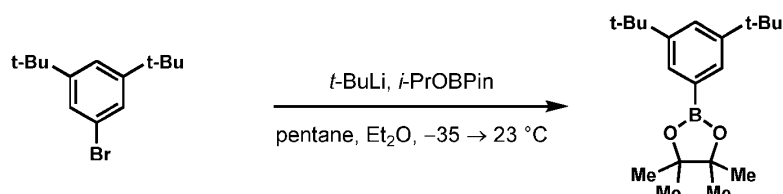
Step D:



[00191] Step D. A golden yellow solution of the thiophene carbazole (4) (3.000 g, 6.887 mmol, 1.00 eq) in anhydrous deoxygenated Et₂O (75 mL) in a nitrogen filled continuous purge glovebox was placed in the freezer (-35 °C), and allowed to precool for 14 hours upon which a precooled solution of *n*-butyl lithium (*n*-BuLi) (3.50 mL, 8.608 mmol, 1.25 eq, titrated 2.5 M in hexanes) was added in a quick dropwise manner. The pale orange solution was allowed to sit in the freezer for 4 hours upon which the isopropoxyboropinacolboronic acid pinacol ester ("i-PrOBPin") (2.81 mL, 13.774 mmol, 2.00 eq) was added neat. The now golden yellow solution was allowed to stir at 23 °C for 2 hours, the now white heterogeneous mixture was removed from the glovebox, diluted with an aqueous phosphate buffer (20 mL, pH = 8, 0.05 M), concentrated via rotary evaporation, the mixture was diluted with CH₂Cl₂ (25 mL) and water (25 mL), poured into a separatory funnel, partitioned, organics were washed with water (1 x 25 mL), residual organics were extracted with CH₂Cl₂ (2 x 25 mL), combined, dried over solid Na₂SO₄, decanted, concentrated, the resultant golden yellow foam was dissolved in CH₂Cl₂ (10 mL), suction filtered through a short pad of silica gel, rinsed with CH₂Cl₂ (4 x 20 mL), and the golden yellow filtrate solution was concentrated to afford the thiophene-boropinacolboronic acid pinacol ester (5) as a pale golden yellow foam (2.581 g, 4.596 mmol, 67%). NMR was consistent with approximately

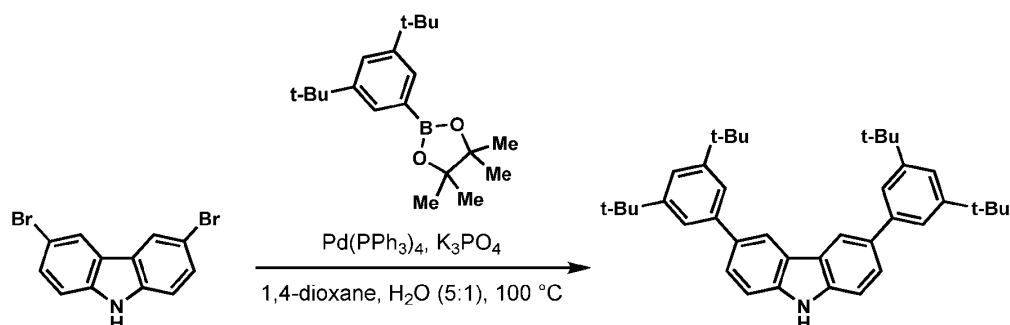
72% pure compound (5). **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.11 – 8.08 (m, 2H), 7.62 (d, *J* = 0.9 Hz, 1H), 7.45 (dt, *J* = 8.6, 1.4 Hz, 2H), 7.23 (dd, *J* = 8.7, 0.7 Hz, 2H), 4.88 (d, *J* = 0.8 Hz, 2H), 2.96 – 2.88 (m, 2H), 1.46 (s, 18H), 1.38 (s, 12H), 0.58 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 158.93, 142.70, 139.53, 130.88, 127.58, 123.65, 123.00, 115.86, 109.77, 98.24, 84.20, 64.53, 34.71, 32.03, 24.80, 14.14. The 72% pure compound (5) was used in the subsequent reaction without further purification.

[00192] Example 5: synthesis of 3,5-di-*tert*-butyl-pinocolatoborylbenzene.



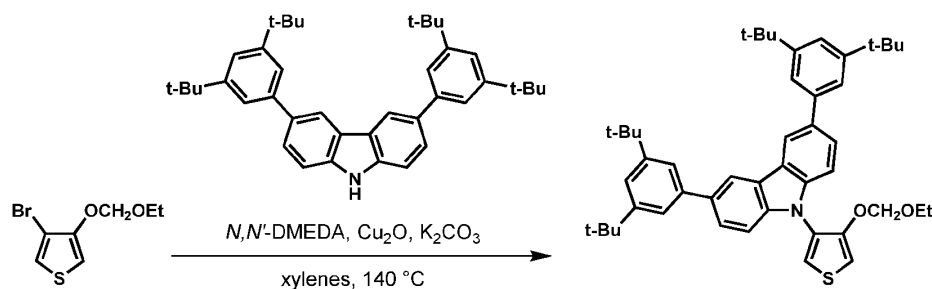
[00193] A clear colorless solution of *t*-BuLi (6.60 mL, 11.143 mmol, 3.00 eq, non-titrated 1.70 M in pentane) in pentane (30 mL) in a nitrogen filled glovebox was placed in the freezer (-35 °C) for 14 hours upon which a pre-cooled solution of the 3,5-di-*tert*-butylphenyl bromide (1.000 g, 3.714 mmol, 1.00 eq) in anhydrous deoxygenated Et₂O (10 mL) was added in a dropwise manner. The now clear pale yellow mixture was allowed to sit in the freezer for 3 hours upon which the now canary golden yellow mixture was removed from the freezer and neat *i*-PrOBPin (1.50 mL, 7.428 mmol, 2.00 eq) was added via syringe in a quick dropwise manner. The now pale yellow mixture was stirred vigorously (1000 rpm) at 23 °C for 2 hours, removed from the glovebox, neutralized with an aqueous phosphate buffer (50 mL, pH = 8, 0.05 M), the white heterogeneous mixture was suction filtered over a pad of diatomaceous earth, rinsed with CH₂Cl₂ (4 x 20 mL), the pale yellow biphasic mixture was poured into a separatory funnel, partitioned, organics were washed with an aqueous phosphate buffer (2 x 25 mL, pH = 8, 0.05 M), residual organics were extracted from the aqueous layer using CH₂Cl₂ (2 x 25 mL), combined, dried over solid Na₂SO₄, decanted, concentrated to afford a pale yellow amorphous viscous oil which was dissolved in CH₂Cl₂ (10 mL), suction filtered over a pad of silica gel, rinsed with CH₂Cl₂ (4 x 20 mL), and the pale yellow filtrate solution was concentrated to afford the 3,5-di-*tert*-butylphenyl boropinacolate ester as a white foam (1.021 g, 3.229 mmol, 87%). NMR indicated product. **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 2.0 Hz, 2H), 7.58 (t, *J* = 2.0 Hz, 1H), 1.38 (s, 18H), 1.38 (s, 12H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 149.81, 128.79, 125.55, 83.53, 34.82, 31.53, 24.89.

[00194] Example 6: synthesis of 3,6-bis(3',5'-di-*tert*-butylphenyl)carbazole.



[00195] A mixture of the carbazole (1.062 g, 3.267 mmol, 1.00 eq), 3,5-di-*t*-butylphenyl boropinacolate ester (3.100 g, 9.801 mmol, 3.00 eq), $\text{Pd}(\text{PPh}_3)_4$ (0.755 g, 0.6534 mmol, 0.20 eq), and K_3PO_4 (6.241 g, 29.403 mmol, 9.00 eq) equipped with a reflux condenser was evacuated, then back-filled with nitrogen, this evacuation/re-fill process was repeated 3x more, freshly deoxygenated 1,4-dioxane (30 mL) and H_2O (5.0 mL) were added simultaneously via syringes, the golden yellow mixture was placed in a mantle heated to 100 °C, stirred vigorously (1000 rpm) for 48 hours, removed from the mantle, allowed to cool gradually to 23 °C, the golden yellow suspension was suction filtered through silica gel, rinsed with CH_2Cl_2 (4 x 20 mL), the yellow filtrate solution was concentrated onto diatomaceous earth, and purified via silica gel chromatography; hexanes – 50% CH_2Cl_2 in hexanes to afford the disubstituted carbazole as a white foam (1.551 g, 2.852 mmol, 87%). NMR is consistent with pure 3,6-bis(3',5'-di-*t*-butylphenyl)carbazole. **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.34 – 8.29 (m, 2H), 8.10 (s, 1H), 7.68 (dd, J = 8.4, 1.8 Hz, 2H), 7.54 (d, J = 1.7 Hz, 4H), 7.51 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 1.8 Hz, 2H), 1.43 (s, 36H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 151.03, 141.57, 139.25, 134.55, 126.04, 123.93, 122.02, 120.74, 119.18, 110.71, 35.01, 31.60.

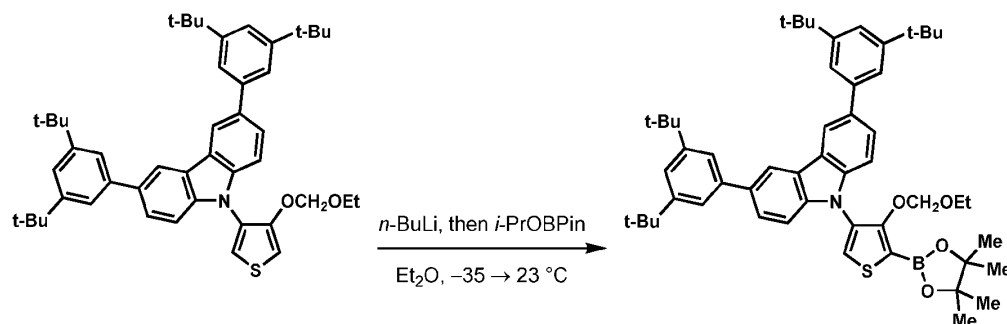
[00196] Example 7: synthesis of 2-ethyloxymethyloxy-3-[3,6-bis(3',5'-di-*t*-butylphenyl)carbazolyl]thiophene.



[00197] In a nitrogen filled continuous purge glovebox, a mixture of the bromothiophene (2) (1.000 g, 4.218 mmol, 1.00 eq), 3,6-bis(3',5'-di-*t*-butylphenyl)carbazole (3.485 g, 9.280 mmol, 2.20 eq), Cu_2O (1.208 g, 8.326 mmol, 2.00 eq), and K_2CO_3 (5.828 g, 42.174 mmol, 10.00 eq) was suspended in deoxygenated anhydrous xylenes (40 mL), *N,N'*-DMEDA (1.80

mL, 16.872 mmol, 4.00 eq) was added, the mixture was equipped with a reflux condenser and a rubber septa, removed from the glovebox, placed under nitrogen, placed in a mantle heated to 140 °C, stirred vigorously (1000 rpm) for 48 hours, removed from the mantle, the now deep red-black mixture was allowed to cool gradually to 23 °C, CH₂Cl₂ (100 mL) was added, the mixture was stirred for 5 mins, suction filtered over a pad of silica gel, rinsed with CH₂Cl₂ (4 x 75 mL), the golden brown filtrate was concentrated onto diatomaceous earth, and purified via silica gel chromatography using an ISCO chromatography purification system; hexanes - 5% EtOAc in hexanes to afford the thiophene-carbazole product as a clear colorless amorphous foam (2.448 g, 3.497 mmol, 83%). NMR is consistent with pure 2-ethyloxymethoxy-3-[3,6-bis(3',5'-di-tert-butylphenyl)carbazolyl]thiophene. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.35 (d, *J* = 1.7 Hz, 2H), 7.66 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.55 (d, *J* = 1.8 Hz, 4H), 7.48 – 7.43 (m, 3H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 3.6 Hz, 1H), 5.09 (s, 2H), 3.59 (q, *J* = 7.0 Hz, 2H), 1.44 (s, 36H), 1.18 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 151.05, 150.83, 141.62, 141.04, 134.98, 127.09, 125.98, 123.75, 122.08, 120.78, 120.71, 119.09, 110.37, 102.55, 94.83, 64.49, 35.02, 31.61, 15.06. HRMS (ESI): calc'd C₄₇H₅₇NO₂S [M+H]⁺ as 700.4183; found 700.4144.

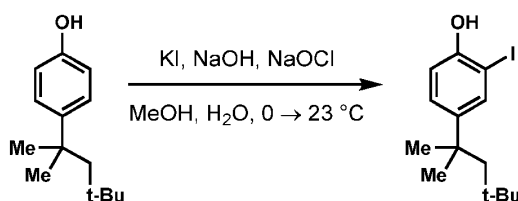
[00198] Example 8: synthesis of 2-ethyloxymethoxy-3-[3,6-bis(3',5'-di-tert-butylphenyl)carbazolyl]-1-pinocolatoborylthiophene



[00199] A golden yellow solution of the 2-ethyloxymethoxy-3-[3,6-bis(3',5'-di-tert-butylphenyl)carbazolyl]thiophene (2.448 g, 3.497 mmol, 1.00 eq) in anhydrous deoxygenated Et₂O (40 mL) in a nitrogen filled continuous purge glovebox was placed in the freezer (-35 °C), and allowed to precool for 14 hours upon which a precooled solution of *n*-BuLi (1.75 mL, 4.371 mmol, 1.25 eq, titrated 2.5 M in hexanes) was added in a quick dropwise manner. The pale orange solution was allowed to sit in the freezer for 4 hours upon which the isopropoxyboropinacol ester (1.43 mL, 6.994 mmol, 2.00 eq) was added neat. The now golden yellow solution was allowed to stir at 23 °C for 2 hours, then removed from the glovebox, the now white heterogeneous mixture was diluted with water (50 mL) and Et₂O (50 mL), poured into a separatory funnel, partitioned, organics were washed with water (1 x 25

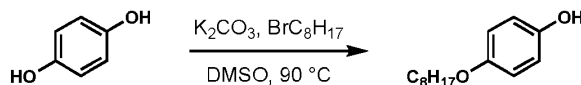
mL), residual organics were extracted with Et₂O (2 x 25 mL), combined, dried over solid Na₂SO₄, decanted, concentrated, and the golden yellow filtrate solution was concentrated to afford the thiophene-boropinacolate ester as a pale golden yellow foam (2.537 g, 2.641 mmol). NMR is consistent with approximately 86% pure *2-ethyloxymethyloxy-3-[3,6-bis(3',5'-di-tert-butylphenyl)carbazolyl]-1-pinocolatoborylthiophene*. **¹H NMR** (400 MHz, cdcl₃) δ 8.35 – 8.33 (m, 2H), 7.73 (s, 1H), 7.67 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.55 (d, *J* = 1.8 Hz, 4H), 7.46 (t, *J* = 1.8 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 4.98 (s, 2H), 2.96 (q, *J* = 7.1 Hz, 2H), 1.44 (s, 36H), 1.40 (s, 12H), 0.60 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (101 MHz, cdcl₃) δ 158.91, 151.13, 151.06, 141.55, 140.88, 134.99, 130.51, 127.81, 126.13, 123.65, 122.00, 120.80, 118.90, 110.62, 98.41, 84.30, 64.58, 35.02, 31.62, 24.82, 14.20. The product is used in the subsequent reaction without further purification.

[00200] Example 9: synthesis of 2-iodo-4-(1',1',3',3' -tetramethylbutyl)phenol.



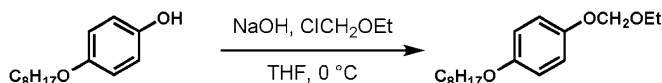
[00201] A clear colorless solution of 4-(1',1',3',3' -tetramethylbutyl)phenol (3.324 g, 16.110 mmol, 1.00 eq), potassium iodide (KI, 3.477 g, 20.943 mmol, 1.30 eq), and aqueous NaOH (21 mL, 20.943 mmol, 1.30 eq, 1 N) in methanol (100 mL) and water (50 mL) under nitrogen was placed in an ice bath and stirred vigorously for 1 hour, upon which precooled commercial aqueous bleach (26 mL, 20.943 mmol, 1.30 eq, 5.2% w/w) was added in a dropwise manner over 10 minutes. The now pale opaque yellow mixture was stirred for 2 hours at 0 °C, the mixture was removed from the ice water bath, stirred at 23 °C for 3 hours, upon which solid NaH₂PO₄ (20 g) was added followed by water (100 mL) and a saturated aqueous mixture Na₂S₂O₃ (100 mL) to reduce residual iodine.. The mixture was stirred vigorously for 10 minutes, diluted with CH₂Cl₂ (50 mL), the biphasic yellow mixture was poured into a separatory funnel, partitioned, organics were washed with aqueous Na₂S₂O₃ (2 x 50 mL), residual organics were extracted from the aqueous layer using CH₂Cl₂ (2 x 50 mL), combined, dried over solid Na₂SO₄, decanted, concentrated onto diatomaceous earth, and purified via silica gel chromatography; hexanes – 10% CH₂Cl₂ to give 2-iodo-4-(1',1',3',3' -tetramethylbutyl)phenol as a clear colorless amorphous foam (3.240 g, 9.340 mmol, 58%). NMR is consistent with pure 2-iodo-4-(1',1',3',3' -tetramethylbutyl)phenol: **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 2.3 Hz, 1H), 7.24 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.90 (dd, *J* = 8.6, 0.5 Hz, 1H), 5.11 (s, 1H), 1.68 (s, 2H), 1.32 (s, 6H), 0.73 (s, 9H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 152.34, 144.65, 135.66, 128.14, 114.23, 85.38, 56.87, 37.93, 32.35, 31.81, 31.55.

[00202] *Example 10: synthesis of 4-octyloxyphenol.*



[00203] To a mixture of hydroquinone (20.000 g, 181.64 mmol, 1.00 eq) and K_2CO_3 (100.40 g, 726.56 mmol, 4.00 eq) in DMSO (600 mL) was added 1-bromooctane (40.8 mL, 236.13 mmol, 1.30 eq). The mixture was placed under nitrogen, placed in a mantle heated to 90 °C, stirred (500 rpm) for 36 hours, removed from the mantle, allowed to cool to ambient temperature, water (200 mL) and KH_2PO_4 (100 grams) were added, and stirred for approximately 10 mins. Then, EtOAc/hexanes (200 mL, 1:1) was added, the biphasic mixture was poured into a separatory funnel, partitioned, organics were washed with water (3 x 100 mL), residual organics were extracted from the aqueous using EtOAc/hexanes (2 x 100 mL, 1:1), combined, dried over Na_2SO_4 , decanted, concentrated onto diatomaceous earth, and purified via silica gel chromatography using an ISCO; 40% – 80% CH_2Cl_2 in hexanes to afford 4-octylether phenol as a pale golden brown solid (16.646 g, 74.871 mmol, 41%). NMR indicated product. 1H NMR (400 MHz, $CDCl_3$) δ 6.84 – 6.73 (m, 4H), 5.11 (s, 1H), 3.92 (t, J = 6.6 Hz, 2H), 1.78 (p, J = 6.8 Hz, 2H), 1.46 (p, J = 7.0 Hz, 2H), 1.34 (ddd, J = 19.4, 10.1, 5.1 Hz, 8H), 0.99 – 0.84 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.24, 149.44, 116.07, 115.74, 68.91, 31.83, 29.38, 29.26, 26.06, 22.67, 14.11.

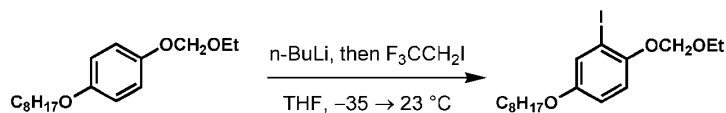
[00204] *Example 11: Synthesis of 4-octyloxyphenolmethyl ethyl ether.*



[00205] A clear, colorless solution of the iodo-phenol (18.405 g, 0.08278 mol, 1.00 eq) in THF (500 mL) was sparged under positive flow of nitrogen for 15 mins upon which an aqueous solution of NaOH (13.2 mL, 0.500 mol, 6.00 eq, 50 % w/w) was added via syringe in a quick dropwise manner. After stirring (500 rpm) for 60 mins at 23 °C, neat chloromethyl ethyl ether (23.0 mL, 0.24835 mol, 3.00 eq) was added via syringe in a quick dropwise manner to the clear pale yellow solution. After stirring for 3 hours at 23 °C, the now white heterogeneous mixture was diluted with aqueous NaOH (100 mL, 1 N), THF was removed via rotary evaporation, the resultant white biphasic mixture was diluted with CH_2Cl_2 (100 mL), poured into a separatory funnel, partitioned, organics were washed with aqueous NaOH (2 x 100 mL, 1 N), residual organics were extracted from the aqueous using CH_2Cl_2 (2 x 50 mL), combined, dried over solid Na_2SO_4 , decanted, and concentrated. The resultant pale yellow oil was diluted in CH_2Cl_2 (20 mL), suction filtered through a pad of silica gel, rinsed with CH_2Cl_2 (4 x 25 mL), and the filtrate was concentrated to afford the phenolic methyl ethyl ether as a clear amber oil (23.116 g, 0.08244 mol, 99%). NMR indicated product. 1H NMR (400 MHz, $cdcl_3$) δ 7.00 – 6.92 (m, 2H), 6.84 – 6.76 (m, 2H), 5.13 (s, 2H), 3.88 (t, J = 6.6 Hz, 2H), 3.71 (q, J = 7.1 Hz,

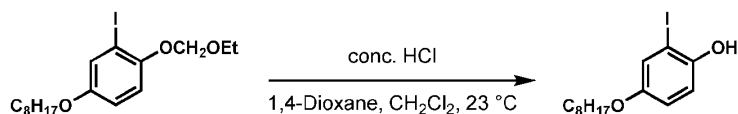
2H), 1.74 (dt, $J = 14.6, 6.7$ Hz, 2H), 1.43 (dq, $J = 10.2, 6.0$ Hz, 2H), 1.37 – 1.24 (m, 8H), 1.21 (t, $J = 7.1$ Hz, 3H), 0.92 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, cdcl_3) δ 154.19, 151.31, 117.50, 115.26, 94.00, 68.51, 63.99, 31.79, 29.35, 29.22, 26.03, 22.63, 15.09, 14.07.

[00206] Example 12: Synthesis of 2-iodo-4-octyloxyphenolmethyl ethyl ether.



[00207] Prior to use, the bisether was azeotropically dried using toluene (4 x 10 mL). A clear, colorless solution of the bisether (4.359 g, 15.545 mmol, 1.00 eq) in anhydrous deoxygenated THF (150 mL) in a continuous purge nitrogen filled glovebox was placed in a freezer (-35 °C) for 16 hours. $n\text{-BuLi}$ (10.9 mL, 27.204 mmol, 1.75 eq, 2.5 M in hexanes) was added, the dark amber solution was allowed to sit in the freezer for 20 hours, 2-iodo-1,1,1-trifluoroethane (3.8 mL, 38.863 mmol, 2.50 eq) was added neat in a quick dropwise manner, the now golden brown solution was allowed to remain in the freezer for 30 mins, removed, stirred (500 rpm) for 4 hours, the mixture was removed from the glovebox, neutralized with H_2O (50 mL), and THF was removed via rotary evaporation. The brown mixture was diluted with CH_2Cl_2 (50 mL) and water (50 mL), poured into a separatory funnel, partitioned, organics were extracted with CH_2Cl_2 (2 x 50 mL), combined, dried over Na_2SO_4 , decanted, concentrated onto diatomaceous earth, and purified by silica gel chromatography using an ISCO; hexanes – 20% CH_2Cl_2 in hexanes to afford the iodide as a clear colorless oil (5.208 g, 12.818 mmol, 82%). NMR indicated product. ^1H NMR (500 MHz, cdcl_3) δ 7.31 (d, $J = 2.9$ Hz, 1H), 7.00 (d, $J = 8.9$ Hz, 1H), 6.83 (dd, $J = 9.0, 2.9$ Hz, 1H), 5.19 (s, 2H), 3.88 (t, $J = 6.6$ Hz, 2H), 3.78 (q, $J = 7.1$ Hz, 2H), 1.74 (dq, $J = 8.9, 6.6$ Hz, 2H), 1.47 – 1.39 (m, 2H), 1.39 – 1.28 (m, 8H), 1.23 (d, $J = 7.1$ Hz, 3H), 0.91 – 0.85 (m, 3H). ^{13}C NMR (126 MHz, cdcl_3) δ 154.71, 150.48, 125.02, 116.25, 115.55, 94.60, 87.65, 68.74, 64.55, 31.80, 29.32, 29.24, 29.22, 25.99, 22.65, 15.07, 14.09.

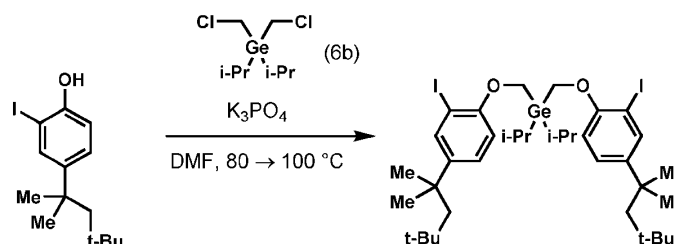
[00208] Example 13: Synthesis of 2-iodo-4-octyloxyphenol.



[00209] To a clear pale yellow solution of the iodo-phenol (17.510 g, 0.04310 mol, 1.00 eq) in 1,4-dioxane (50 mL) and CH_2Cl_2 (50 mL) under nitrogen at 23 °C was added conc. HCl (25 mL). After stirring (500 rpm) for 8 hours at 23 °C, the now golden brown mixture was diluted with water (100 mL) and CH_2Cl_2 (50 mL), poured into a separatory funnel, partitioned, organics were extracted from the aqueous using CH_2Cl_2 (2 x 25 mL), combined, dried over Na_2SO_4 , decanted, concentrated, CH_2Cl_2 (20 mL) was added, the dark brown solution was suction filtered over a pad of silica gel, rinsed with CH_2Cl_2 (4 x 25 mL), and the filtrate was

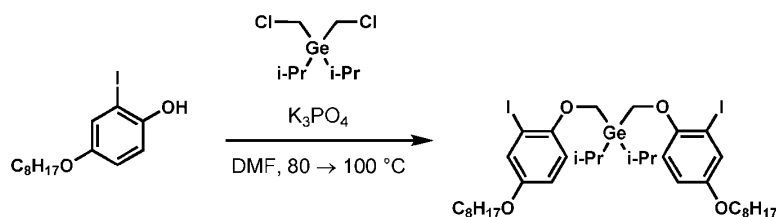
concentrated to afford the iodophenol as a clear amber oil (14.810 g, 0.04253 mol, 99%). NMR indicated product with minor impurities, which was used in the subsequent reaction without further purification. **¹H NMR** (400 MHz, CDCl_3) δ 7.17 (d, J = 2.8 Hz, 1H), 6.88 (d, J = 8.9 Hz, 1H), 6.80 (dd, J = 8.9, 2.9 Hz, 1H), 4.93 (s, 1H), 3.85 (t, J = 6.5 Hz, 2H), 1.81 – 1.65 (m, 2H), 1.41 (p, J = 6.9 Hz, 2H), 1.37 – 1.20 (m, 8H), 0.96 – 0.79 (m, 3H). **¹³C NMR** (101 MHz, CDCl_3) δ 153.51, 149.03, 123.45, 116.95, 115.04, 85.07, 68.94, 31.79, 29.32, 29.24, 29.21, 25.98, 22.64, 14.09.

[00210] Example 14: synthesis of bis[2-iodo-4-(1',1',3',3'-tetramethylbutyl)phenoxy)methyl]-di-isopropylgermanium.



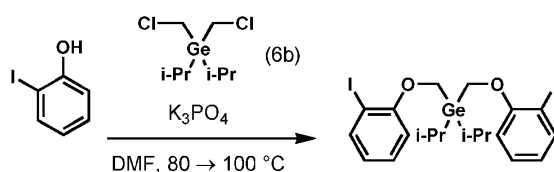
[00211] A solid mixture of the 2-iodo-4-*t*-octyl phenol (1.610 g, 4.845 mmol, 2.50 eq) and K_3PO_4 (1.646 g, 7.752 mmol, 4.00 eq) under nitrogen was suspended in DMF (30 mL), bis-chloromethyl di-*isopropyl* germanium (0.500 g, 1.938 mmol, 1.00 eq) was added neat, and the mixture was placed in a mantle heated to 80 °C. After stirring (300 rpm) for 16 hours, the golden brown solution was heated to 100 °C, stirred for 2 hours, removed from the mantle, allowed to cool to ambient temperature, the resultant golden brown mixture was diluted with water (25 mL) and hexanes (25 mL), the biphasic mixture was poured into a separatory funnel, partitioned, organics were washed with aqueous NaOH (2 x 25 mL, 1 N), residual organics were extracted with hexanes (2 x 25 mL), combined, dried over solid Na_2SO_4 , decanted, concentrated onto diatomaceous earth, and purified via silica gel chromatography; 0% - 10% CH_2Cl_2 in hexanes to afford the bis[2-iodo-4-(1',1',3',3'-tetramethylbutyl)phenoxy)methyl]-di-isopropylgermanium as a clear colorless oil (0.985 g, 1.159 mmol, 60%). NMR is consistent with the compound. **¹H NMR** (500 MHz, CDCl_3) δ 7.70 (d, J = 2.3 Hz, 2H), 7.29 – 7.26 (m, 2H), 6.91 (d, J = 8.7 Hz, 2H), 4.16 (s, 4H), 1.73 (p, J = 7.5 Hz, 2H), 1.68 (s, 4H), 1.31 (s, 12H), 1.29 (d, J = 7.5 Hz, 12H), 0.73 (s, 18H). **¹³C NMR** (126 MHz, CDCl_3) δ 157.33, 144.34, 137.02, 126.96, 110.23, 85.81, 58.10, 56.83, 37.89, 32.36, 31.87, 31.60, 19.80, 14.00.

[00212] Example 15: synthesis of bis[2-iodo-4-(octyloxy)phenoxy)methyl]-di-isopropylgermanium.



[00213] A solid mixture of the 2-iodo-4-octylether phenol (1.159 g, 3.328 mmol, 2.10 eq) and K_3PO_4 (1.682 g, 7.925 mmol, 5.00 eq) under nitrogen was suspended in DMF (30 mL), bis-chloromethyl di-*isopropyl* germanium (0.409 g, 1.585 mmol, 1.00 eq) was added neat, and the mixture was placed in a mantle heated to 80 °C. After stirring (300 rpm) for 16 hours, the golden brown solution was heated to 100 °C, stirred for 2 hours, removed from the mantle, allowed to cool to ambient temperature, the resultant dark brown / black mixture was diluted with water (25 mL) and hexanes (25 mL), the biphasic mixture was poured into a separatory funnel, partitioned, organics were washed with aqueous NaOH (2 x 25 mL, 1 N), residual organics were extracted with hexanes (2 x 25 mL), combined, dried over solid Na_2SO_4 , decanted, concentrated onto diatomaceous earth, and purified via silica gel chromatography; 0% - 30% CH_2Cl_2 in hexanes to afford the bis-iodide as a clear pale yellow amorphous oil (0.978 g, 1.109 mmol, 70%). NMR indicated product. 1H NMR (500 MHz, $cdCl_3$) δ 7.31 (d, J = 2.9 Hz, 2H), 6.91 (d, J = 9.0 Hz, 2H), 6.85 (dd, J = 8.9, 2.8 Hz, 2H), 4.12 (s, 4H), 3.87 (t, J = 6.6 Hz, 4H), 1.78 – 1.67 (m, 6H), 1.46 – 1.38 (m, 4H), 1.36 – 1.23 (m, 20H), 1.28 (d, J = 7.5 Hz, 12H), 0.92 – 0.86 (m, 6H). ^{13}C NMR (126 MHz, $cdCl_3$) δ 154.18, 153.58, 125.38, 115.27, 111.33, 86.03, 68.90, 58.64, 31.82, 29.35, 29.29, 29.25, 26.00, 22.67, 19.80, 14.13, 13.98.

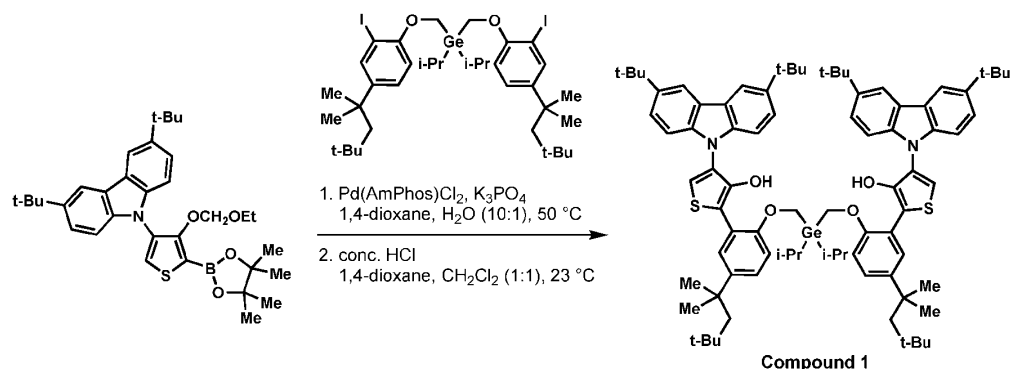
[00214] Example 16 (prophetic): synthesis of bis[2-iodophenoxy)methyl]-di-*isopropyl*germanium.



[00215] A mixture of 2-iodo-phenol (4.845 mmol, 2.50 eq) and K_3PO_4 (1.646 g, 7.752 mmol, 4.00 eq) under nitrogen is suspended in DMF (30 mL), bis-chloromethyl di-*isopropyl* germanium (0.500 g, 1.938 mmol, 1.00 eq) is added neat, and the mixture is placed in a mantle heated to 80 °C. After stirring (300 rpm) for 16 hours, the solution is heated to 100 °C, stirred for 2 hours, removed from the mantle, allowed to cool to ambient temperature, the resultant mixture is diluted with water (25 mL) and hexanes (25 mL), the mixture is poured into a separatory funnel, partitioned, organics are washed with aqueous NaOH (2 x 25 mL, 1 N), residual organics are extracted with hexanes (2 x 25 mL), combined, dried over solid Na_2SO_4 , decanted, concentrated onto diatomaceous earth, and purified via silica gel chromatography;

0% - 10% CH₂Cl₂ in hexanes to make bis[(2-iodo-phenoxy)methyl]-di-isopropylgermanium. NMR is expected to be consistent with the compound.

[00216] Example 17: synthesis of Compound 1: a compound of formula (I) wherein R¹, R², and R⁵ to R⁹ are H, R³ and R⁴ are each (CH₃)₃CCH₂C(CH₃)₂- ("t-Octyl"), each R¹⁰ is tertiary-butyl, and R¹¹ and R¹² are each isopropyl.

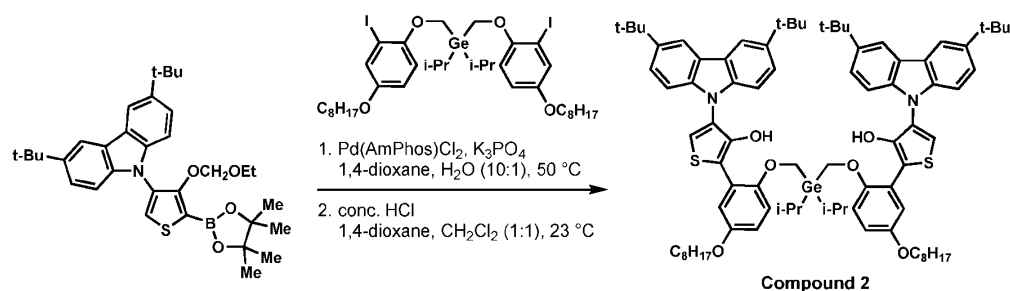


[00217] A solid mixture of the boronate ester (11.228 g, 13.995 mmol, 3.00 eq, approx. 70% pure), bis-iodide (3.966 g, 4.665 mmol, 1.00 eq), Pd(AmPhos)Cl₂ (0.661 g, 0.9330 mmol, 0.20 eq), and solid K₃PO₄ (8.912 g, 41.985 mmol, 9.00 eq) in a round-bottom flask equipped with a reflux condenser sealed with a rubber septa was evacuated, back-filled with nitrogen, the evacuation/nitrogen re-fill process was repeated 3x more, then freshly sparged deoxygenated 1,4-dioxane (50 mL) and H₂O (5.0 mL) were added via syringe, and the resultant canary yellow mixture was placed in a mantle heated to 50 °C. After stirring (300 rpm) for 36 hours, the now black mixture was removed from the mantle, allowed to cool to 23 °C, diluted with CH₂Cl₂ (20 mL), the biphasic mixture was suction filtered through a pad of silica gel, rinsed with CH₂Cl₂ (4 x 20 mL), the filtrate was concentrated onto diatomaceous earth, and purified via silica gel chromatography; 10% – 35% CH₂Cl₂ in hexanes to afford the protected coupled product as a golden brown foam (5.220 g). NMR indicated product with minor impurities. The mixture was used in the subsequent reaction without further purification.

[00218] To a solution of the aforementioned coupled product (6.220 g) in 1,4-dioxane and CH₂Cl₂ (50 mL, 1:1) under nitrogen at 23 °C was added aqueous conc. HCl (15 mL, 37% w/w). After stirring (300 rpm) for 24 hours, the dark brown mixture was diluted with water (50 mL) and CH₂Cl₂ (25 mL), the biphasic mixture was poured into a separatory funnel, partitioned, residual organics were extracted with CH₂Cl₂ (2 x 25 mL), combined, dried over solid Na₂SO₄, decanted, concentrated onto diatomaceous earth, and purified via silica gel chromatography; 10% - 30% CH₂Cl₂ in hexanes to afford the hydroxythiophene (compound 1) as a pale golden yellow amorphous foam (3.523 g, 2.612 mmol, 56% two steps). NMR indicated product. ¹H NMR (500 MHz, cdcl₃) δ 8.13 (dd, J = 2.0, 0.6 Hz, 4H), 7.45 – 7.41 (m, 6H), 7.31 (s, 2H), 7.22

(dd, $J = 8.6, 0.6$ Hz, 4H), 7.03 (dd, $J = 8.7, 2.5$ Hz, 2H), 6.91 (s, 2H), 6.59 (d, $J = 8.8$ Hz, 2H), 4.08 (s, 4H), 1.73 (s, 4H), 1.45 (s, 36H), 1.36 (s, 12H), 1.36 – 1.28 (m, 2H), 0.93 (d, $J = 7.5$ Hz, 12H), 0.75 (s, 18H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.05, 146.27, 144.07, 142.53, 139.92, 128.26, 127.31, 126.70, 123.47, 123.10, 121.11, 119.95, 116.09, 116.00, 112.74, 109.66, 59.56, 56.83, 38.10, 34.71, 32.39, 32.06, 31.91, 31.62, 19.40, 13.92.

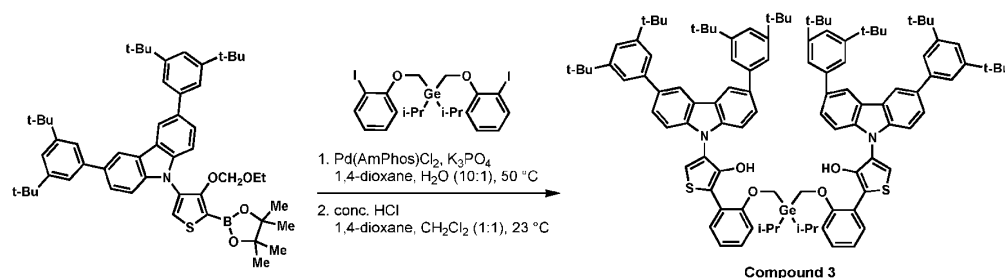
[00219] Example 18: synthesis of Compound 2: a compound of formula (I) wherein R^1 , R^2 , and R^5 to R^9 are H, R^3 and R^4 are each octyloxy, each R^{10} is tertiary-butyl, and R^{11} and R^{12} are each isopropyl.



[00220] A solid mixture of the boropinacolate ester (1.408 g, 1.504 mmol, 2.80 eq, approx. 60% pure), bis-iodide (0.473 g, 0.5373 mmol, 1.00 eq), Pd(AmPhos)Cl₂ (76.0 mg, 0.1075 mmol, 0.20 eq), and solid K₃PO₄ (1.026 g, 4.836 mmol, 9.00 eq) in a round-bottom flask equipped with a reflux condenser sealed with a rubber septa was evacuated, back-filled with nitrogen, the evacuation/nitrogen re-fill process was repeated 3x more, then freshly sparged deoxygenated 1,4-dioxane (15 mL) and H₂O (1.5 mL) were added via syringe, and the resultant canary yellow mixture was placed in a mantle heated to 50 °C. After stirring (300 rpm) for 36 hours, the now black mixture was removed from the mantle, allowed to cool to 23 °C, diluted with CH₂Cl₂ (20 mL), the biphasic mixture was suction filtered through a pad of silica gel, rinsed with CH₂Cl₂ (4 x 20 mL), the filtrate was concentrated onto diatomaceous earth, and purified via silica gel chromatography; 10% – 40% CH₂Cl₂ in hexanes to afford the protected coupled product as a dark purple amorphous foam (0.559 g). NMR indicated product with minor impurities. The mixture was used in the subsequent reaction without further purification. To a solution of the coupled product (0.559 g) in 1,4-dioxane and CH₂Cl₂ (10 mL, 1:1) under nitrogen at 23 °C was added aqueous conc. HCl (5 mL, 37% w/w). After stirring (300 rpm) for 20 hours, the dark purple-black mixture was diluted with water (25 mL) and CH₂Cl₂ (25 mL), the biphasic mixture was poured into a separatory funnel, partitioned, residual organics were extracted with CH₂Cl₂ (2 x 25 mL), combined, dried over solid Na₂SO₄, decanted, concentrated onto diatomaceous earth, and purified via silica gel chromatography; 10% - 40% CH₂Cl₂ in hexanes to afford the hydroxythiophene (compound 2) as a clear colorless amorphous foam (0.353 g, 0.2557 mmol, 48% two steps). NMR indicated product.

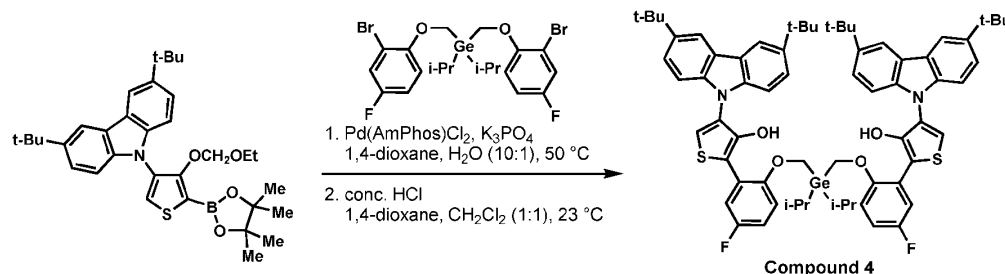
¹H NMR (500 MHz, cdCl_3) δ 8.12 (dd, $J = 1.9, 0.6$ Hz, 4H), 7.41 (dd, $J = 8.6, 1.9$ Hz, 4H), 7.31 (s, 2H), 7.21 – 7.17 (m, 6H), 6.96 (dd, $J = 2.2, 1.1$ Hz, 2H), 6.52 (d, $J = 2.3$ Hz, 4H), 3.97 (s, 4H), 3.91 (t, $J = 6.5$ Hz, 4H), 1.78 (p, $J = 6.7$ Hz, 4H), 1.44 (s, 36H), 1.42 – 1.22 (m, 22H), 0.95 – 0.87 (m, 18H). **¹³C NMR** (126 MHz, cdCl_3) δ 154.29, 150.34, 146.59, 142.55, 139.85, 127.44, 123.46, 123.10, 123.05, 120.22, 115.99, 115.73, 115.41, 115.29, 114.76, 109.66, 68.56, 60.61, 34.70, 32.04, 31.85, 29.42, 29.36, 29.29, 26.10, 22.70, 19.34, 14.15, 13.82.

[00221] Example 19 (prophetic): synthesis of Compound 3: a compound of formula (I) wherein R^1 to R^9 are H, each R^{10} is 3,5-di(tertiary-butyl)phenyl (“35dtBP”), and R^{11} and R^{12} are each isopropyl.



[00222] Compound 3 is made in a manner similar to the procedure of Example 18.

[00223] Example 20: synthesis of Compound 4: a compound of formula (I) wherein R^1 , R^2 , and R^5 to R^9 are H, R^3 and R^4 are each fluoro, each R^{10} is tertiary-butyl, and R^{11} and R^{12} are each isopropyl.

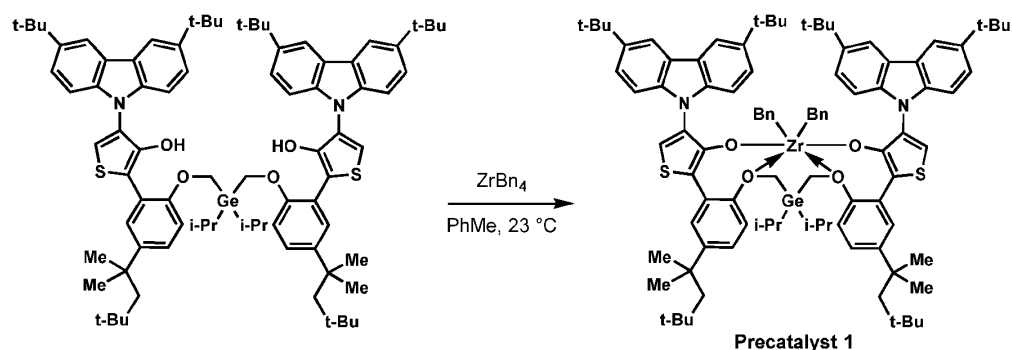


[00224] A mixture of the thiophene boropinacolate ester (1.602 g, 2.077 mmol, 4.00 eq, 72% pure by NMR), K_3PO_4 (1.323 g, 6.230 mmol, 12.0 eq), $\text{Pd}(\text{AmPhos})\text{Cl}_2$ (74.0 mg, 0.1038 mmol, 0.20 eq), and the bisphenyliodide (0.294 g, 0.5192 mmol, 1.00 eq). The mixture was evacuated, then back-filled with nitrogen, this process was repeated 3x more, then deoxygenated 1,4-dioxane (10.0 mL) and deoxygenated water (1.0 mL) were added sequentially via syringe. The mixture was then placed in a mantle heated to 50 °C. After stirring vigorously (1000 rpm) for 40 hrs, the black mixture was removed from the mantle, allowed to cool gradually to 23 °C, suction filtered over a pad of silica gel, washed with CH_2Cl_2 (4 x 20 mL), the clear black filtrate was concentrated, residual 1,4-dioxane was azeotropically

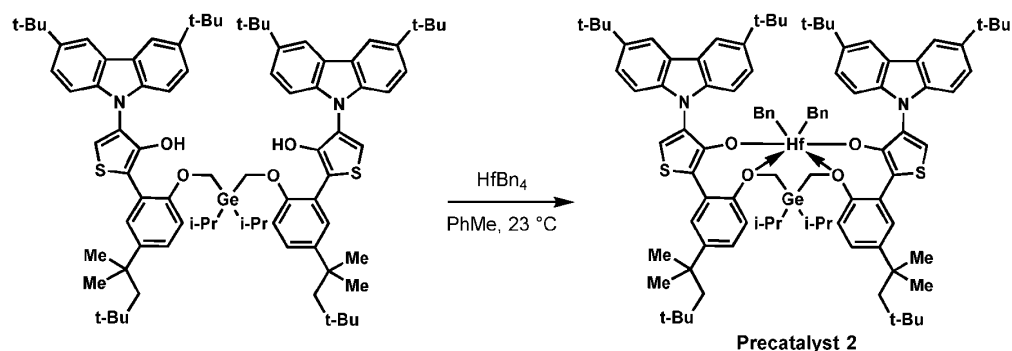
removed using toluene (2 x 10 mL) via rotary evaporation, the black mixture was then suspended in CH₂Cl₂ (20 mL), suction filtered over a pad of silica gel, rinsed with CH₂Cl₂ (4 x 20 mL), the black filtrate was then concentrated onto diatomaceous earth, and purified via silica gel chromatography via an ISCO chromatography purification system; 10% - 55% CH₂Cl₂ in hexanes to afford the impure bisthiophene as a pale yellow foam (0.220 g). NMR indicated product which contained impurities. The impure material was used in the subsequent reaction.

[00225] To a solution of the impure coupled product in CH₂Cl₂-1,4-dioxane (6 mL, 1:1) under nitrogen at 23 °C was added conc. HCl (3 mL). The golden brown solution was stirred (500 rpm) for 20 hrs, diluted with 1N HCl (10 mL) and CH₂Cl₂ (10 mL), poured into separatory funnel, partitioned, organics were washed with 1 N HCl (1 x 10 mL), residual organics were extracted from the aqueous using CH₂Cl₂ (2 x 10 mL), combined, dried over solid Na₂SO₄, decanted, concentrated onto diatomaceous earth, and purified via silica gel chromatography via an ISCO chromatography purification system; 10% - 75% CH₂Cl₂ in hexanes to afford the bisthiophene as a clear amorphous foam (0.100 g, 0.08617 mmol, 17% two steps). NMR indicated pure product. **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.16 (dd, *J* = 1.9, 0.6 Hz, 4H), 7.42 (dd, *J* = 8.6, 1.9 Hz, 4H), 7.35 (s, 2H), 7.17 (dd, *J* = 8.6, 0.7 Hz, 4H), 7.12 (dd, *J* = 9.2, 3.1 Hz, 2H), 6.71 (s, 2H), 6.56 (ddd, *J* = 9.0, 7.7, 3.1 Hz, 2H), 6.34 (dd, *J* = 9.2, 4.6 Hz, 2H), 3.94 (s, 4H), 1.47 (s, 36H), 1.39 – 1.29 (m, 2H), 0.94 (d, *J* = 7.5 Hz, 12H). **¹⁹F NMR** (470 MHz, Chloroform-*d*) δ -121.59 (td, *J* = 8.4, 4.6 Hz). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 157.50 (d, *J* = 240.5 Hz), 152.50, 146.74, 142.85, 139.78, 127.26, 123.55, 123.25 (d, *J* = 9.3 Hz), 123.21, 120.73, 116.49 (d, *J* = 24.6 Hz), 116.08, 115.02 (d, *J* = 22.9 Hz), 114.50 (d, *J* = 8.9 Hz), 114.22 (m), 109.59, 60.00, 34.73, 32.04, 19.34, 13.91.

[00226] *Examples 21 and 22: synthesis of Precatalyst 1: a precatalyst of formula (II) wherein R¹, R², and R⁵ to R⁹ are H, R³ and R⁴ are each (CH₃)₃CCH₂C(CH₃)₂- ("t-Octyl"), each R¹⁰ is tertiary-butyl, R¹¹ and R¹² are each isopropyl, M is Zr, each X is benzyl, and subscript n is 2; and synthesis of Precatalyst 2: a precatalyst of formula (II) wherein R¹, R², and R⁵ to R⁹ are H, R³ and R⁴ are each (CH₃)₃CCH₂C(CH₃)₂- ("t-Octyl"), each R¹⁰ is tertiary-butyl, R¹¹ and R¹² are each isopropyl, M is Hf, each X is benzyl, and subscript n is 2.*

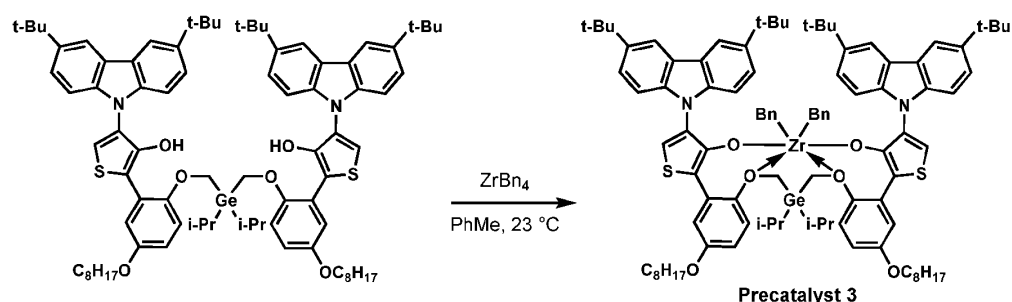


[00227] The thiophene ligand was azeotropically dried using PhMe (4 x 10 mL) prior to use. To a clear pale golden yellow solution of the thiophene (0.150 g, 0.1112 mmol, 1.00 eq) in PhMe (35.5 mL) in a continuous purge, nitrogen filled glovebox at 23 °C was added a solution of ZrBn_4 (55.8 mg, 0.1223 mmol, 1.10 eq) in PhMe (4.46 mL) in a dropwise manner. After stirring (500 rpm) for 20 mins the pale golden yellow solution was filtered using a 0.45 μm PTFE submicron filter connected to a 0.20 μm PTFE submicron filter, rinsed with PhMe (3 x 3 mL), and concentrated to afford the zirconium complex (precatalyst 1) as a golden yellow foam (0.178 g, 0.1100 mmol, 99%). NMR indicated product. **^1H NMR** (400 MHz, C_6D_6) δ 8.60 (d, J = 1.9 Hz, 2H), 8.22 (d, J = 1.8 Hz, 2H), 7.60 – 7.50 (m, 6H), 7.47 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H), 7.14 – 7.08 (m, 4H), 7.08 – 6.99 (m, 2H), 6.90 (s, 2H), 6.88 – 6.81 (m, 2H), 6.35 – 6.30 (m, 4H), 5.53 (d, J = 8.6 Hz, 2H), 4.52 (d, J = 13.0 Hz, 2H), 3.56 (d, J = 13.1 Hz, 2H), 1.79 (d, J = 14.6 Hz, 2H), 1.60 (d, J = 14.6 Hz, 2H), 1.58 (s, 18H), 1.28 (s, 18H), 1.28 (s, 6H), 1.23 (s, 6H), 1.21 (d, J = 12.5 Hz, 2H), 0.93 (dt, J = 14.8, 7.4 Hz, 2H), 0.75 (s, 18H), 0.74 (d, J = 7.5 Hz, 6H), 0.65 (d, J = 7.5 Hz, 6H), 0.55 (d, J = 12.5 Hz, 2H). **^{13}C NMR** (101 MHz, C_6D_6) δ 156.48, 152.38, 147.32, 143.05, 142.67, 139.77, 139.59, 130.59, 128.47, 128.34, 127.30, 126.40, 125.33, 125.15, 124.70, 122.84, 122.44, 120.90, 120.71, 118.22, 117.69, 116.25, 115.64, 112.46, 109.16, 75.85, 71.81, 56.72, 38.08, 34.69, 34.40, 32.45, 32.16, 32.07, 31.71, 30.15, 19.34, 19.29, 13.65.



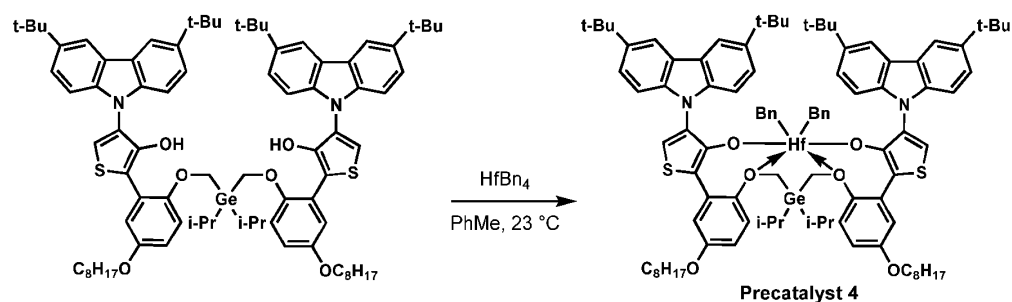
[00228] The thiophene ligand was azeotropically dried using PhMe (4 x 10 mL) prior to use. To a clear pale golden yellow solution of the thiophene (34.0 mg, 0.02521 mmol, 1.00 eq) in PhMe (16.0 mL) in a continuous purge, nitrogen filled glovebox at 23 °C was added a solution of HfBn₄ (15.8 mg, 0.02899 mmol, 1.15 eq) in PhMe (1.27 mL) in a dropwise manner. After stirring (500 rpm) for 20 mins the pale golden yellow solution was filtered using a 0.45 µm PTFE submicron filter connected to a 0.20 µm PTFE submicron filter, rinsed with PhMe (3 x 3 mL), and concentrated to afford the hafnium complex (precatalyst 2) as a pale golden yellow foam (42.5 mg, 0.02493 mmol, 99%). NMR indicated product. **¹H NMR** (400 MHz, C₆D₆) δ 8.57 (d, *J* = 1.9 Hz, 2H), 8.19 (d, *J* = 1.8 Hz, 2H), 7.55 – 7.45 (m, 6H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.13 – 7.06 (m, 6H), 7.06 – 7.00 (m, 2H), 6.83 (s, 2H), 6.77 (t, *J* = 7.3 Hz, 2H), 6.29 – 6.23 (m, 4H), 5.49 (d, *J* = 8.6 Hz, 2H), 4.53 (d, *J* = 13.1 Hz, 2H), 3.54 (d, *J* = 13.2 Hz, 2H), 1.75 (d, *J* = 14.7 Hz, 2H), 1.53 (s, 18H), 1.23 (s, 18H), 1.23 (s, 6H), 1.18 (s, 6H), 0.96 (d, *J* = 13.3 Hz, 2H), 0.87 (p, *J* = 7.5 Hz, 2H), 0.71 (s, 18H), 0.67 (d, *J* = 7.4 Hz, 6H), 0.58 (d, *J* = 7.4 Hz, 6H), 0.23 (d, *J* = 12.9 Hz, 2H). **¹³C NMR** (101 MHz, C₆D₆) δ 156.17, 152.42, 147.79, 147.52, 143.04, 142.61, 139.71, 139.50, 128.79, 128.27, 126.99, 125.26, 124.65, 122.79, 122.32, 121.19, 120.75, 117.80, 117.46, 116.22, 115.58, 112.48, 109.10, 78.51, 72.32, 56.67, 38.04, 34.66, 34.37, 32.14, 32.06, 31.68, 30.09, 19.29, 19.20, 13.67.

[00229] Examples 23 and 24: synthesis of Precatalyst 3: a precatalyst of formula (II) wherein R¹, R², and R⁵ to R⁹ are H, R³ and R⁴ are each CH₃(CH₂)₇O- (octyloxy), each R¹⁰ is tertiary-butyl, R¹¹ and R¹² are each isopropyl, M is Zr, each X is benzyl, and subscript n is 2; and synthesis of Precatalyst 4: a precatalyst of formula (II) wherein R¹, R², and R⁵ to R⁹ are H, R³ and R⁴ are each CH₃(CH₂)₇O- (octyloxy), each R¹⁰ is tertiary-butyl, R¹¹ and R¹² are each isopropyl, M is Hf, each X is benzyl, and subscript n is 2.



[00230] The thiophene ligand was azeotropically dried using PhMe (4 x 10 mL) prior to use. To a clear pale golden yellow solution of the thiophene (40.4 mg, 0.02926 mmol, 1.00 eq) in PhMe (16.8 mL) in a continuous purge, nitrogen filled glovebox at 23 °C was added a solution of ZrBn₄ (15.3 mg, 0.03365 mmol, 1.15 eq) in PhMe (1.22 mL) in a dropwise manner. After stirring (500 rpm) for 20 mins the golden yellow solution was filtered using a 0.45 µm PTFE

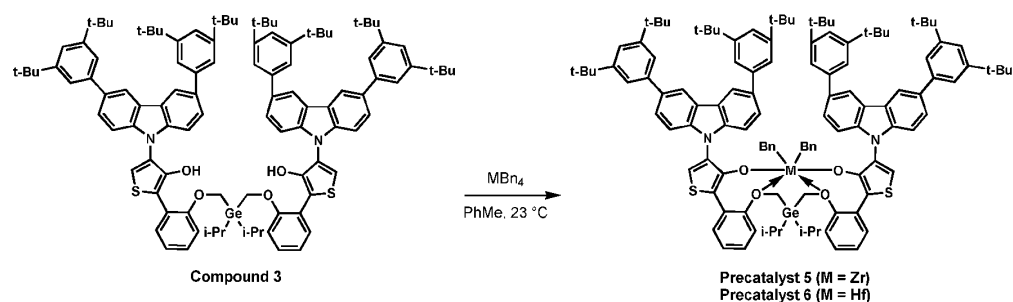
submicron filter connected to a 0.20 μm PTFE submicron filter, rinsed with PhMe (3 x 3 mL), and concentrated to afford the zirconium complex (precatalyst 3) as a pale golden brown foam (48.0 mg, 0.02905 mmol, 99%). NMR indicated product. **¹H NMR** (400 MHz, C_6D_6) δ 8.58 – 8.54 (m, 2H), 8.31 (dd, J = 1.9, 0.6 Hz, 2H), 7.60 – 7.56 (m, 4H), 7.47 – 7.39 (m, 4H), 7.14 – 7.10 (m, 4H), 7.03 (d, J = 3.0 Hz, 2H), 6.91 (s, 2H), 6.83 (tt, J = 7.3, 1.2 Hz, 2H), 6.67 (dd, J = 9.0, 3.1 Hz, 2H), 6.48 – 6.44 (m, 4H), 5.55 (d, J = 9.0 Hz, 2H), 4.47 (d, J = 13.0 Hz, 2H), 3.67 (dt, J = 8.9, 6.5 Hz, 2H), 3.58 (dt, J = 9.0, 6.4 Hz, 2H), 3.51 (d, J = 13.0 Hz, 2H), 1.63 – 1.53 (m, 4H), 1.51 (s, 18H), 1.30 (s, 18H), 1.36 – 1.14 (m, 20H), 0.93 (t, J = 7.0 Hz, 6H), 0.94 – 0.82 (m, 4H), 0.73 (d, J = 7.4 Hz, 6H), 0.70 (d, J = 12.5 Hz, 2H), 0.63 (d, J = 7.4 Hz, 6H). **¹³C NMR** (101 MHz, C_6D_6) δ 156.66, 152.62, 152.02, 147.57, 143.25, 142.80, 139.89, 139.66, 128.40, 128.36, 128.31, 127.01, 126.59, 126.41, 125.27, 124.70, 122.81, 122.53, 122.50, 120.71, 118.02, 117.71, 116.35, 116.12, 115.60, 114.81, 112.49, 109.12, 75.91, 71.67, 68.14, 34.62, 34.46, 32.01, 31.85, 31.75, 29.85, 29.34, 29.28, 29.18, 25.97, 22.73, 19.36, 14.02, 13.79.



[00231] The thiophene ligand was azeotropically dried using PhMe (4 x 10 mL) prior to use. To a clear pale golden yellow solution of the thiophene (50.5 mg, 0.03658 mmol, 1.00 eq) in PhMe (18.2 mL) in a continuous purge, nitrogen filled glovebox at 23 °C was added a solution of HfBn_4 (22.9 mg, 0.04207 mmol, 1.15 eq) in PhMe (1.83 mL) in a dropwise manner. After stirring (500 rpm) for 20 mins the pale golden yellow solution was filtered using a 0.45 μm PTFE submicron filter connected to a 0.20 μm PTFE submicron filter, rinsed with PhMe (3 x 3 mL), and concentrated to afford the hafnium complex (precatalyst 4) as a pale golden yellow foam (63.2 mg, 0.03631 mmol, 99%). NMR indicated product. **¹H NMR** (400 MHz, C_6D_6) δ 8.59 – 8.55 (m, 2H), 8.34 – 8.30 (m, 2H), 7.57 (dd, J = 8.6, 1.9 Hz, 4H), 7.44 (d, J = 8.5 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.18 – 7.12 (m, 4H), 7.02 (d, J = 3.0 Hz, 2H), 6.91 (s, 2H), 6.81 (dt, J = 7.3, 1.2 Hz, 2H), 6.70 (dd, J = 9.0, 3.1 Hz, 2H), 6.48 – 6.44 (m, 4H), 5.57 (d, J = 9.0 Hz, 2H), 4.52 (d, J = 13.1 Hz, 2H), 3.68 (dt, J = 9.0, 6.5 Hz, 2H), 3.58 (dt, J = 8.9, 6.4 Hz, 2H), 3.53 (d, J = 13.1 Hz, 2H), 1.58 (dd, J = 8.3, 6.2 Hz, 4H), 1.51 (s, 18H), 1.31 (s, 18H), 1.36 – 1.16 (m, 20H), 1.09 (d, J = 13.3 Hz, 2H), 0.93 (t, J = 7.0 Hz, 6H), 0.94 – 0.81 (m, 2H), 0.72 (d, J = 7.4 Hz, 6H), 0.62 (d, J = 7.4 Hz, 6H), 0.40 (d, J = 13.4 Hz, 2H). **¹³C NMR** (101 MHz, C_6D_6)

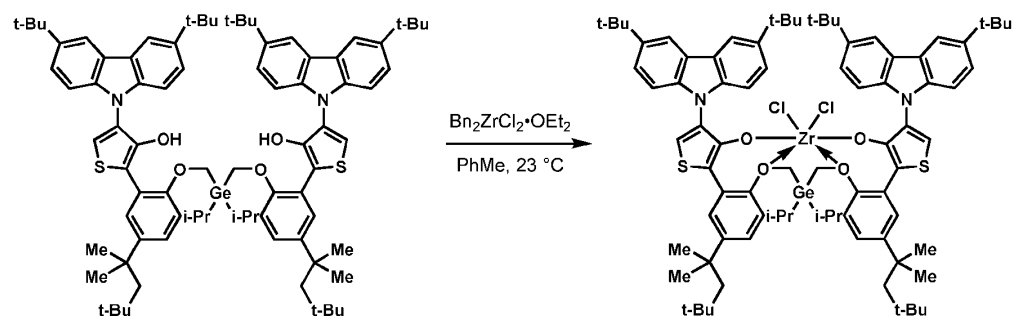
δ 156.82, 152.74, 151.73, 148.07, 143.31, 142.81, 139.91, 139.65, 128.82, 128.31, 127.05, 126.91, 126.76, 125.33, 124.73, 122.80, 122.77, 122.48, 120.81, 118.16, 117.01, 116.33, 116.12, 115.54, 114.71, 112.51, 109.10, 78.89, 72.10, 68.15, 34.62, 34.46, 32.01, 31.86, 31.76, 29.34, 29.28, 29.18, 25.97, 22.73, 19.32, 14.02, 13.88.

[00232] Examples 25 and 26 (prophetic): synthesis of Precatalyst 5: a precatalyst of formula (II) wherein R^1 to R^9 are H, each R^{10} is tertiary-butyl, R^{11} and R^{12} are each isopropyl, M is Zr, each X is benzyl, and subscript n is 2; and synthesis of Precatalyst 6: a precatalyst of formula (II) wherein R^1 to R^9 are H, each R^{10} is tertiary-butyl, R^{11} and R^{12} are each isopropyl, M is Hf, each X is benzyl, and subscript n is 2.



[00233] Precatalysts 5 and 6 are made in a manner similar to the procedures Precatalysts 3 and 4.

[00234] Examples 27: synthesis of Precatalyst 7: a precatalyst of formula (II) wherein R^1 , R^2 , and R^5 to R^9 are H, R^3 and R^4 are each $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2$ ("t-Octyl"), each R^{10} is tertiary-butyl, R^{11} and R^{12} are each isopropyl, M is Zr, each X is chloro, and subscript n is 2.

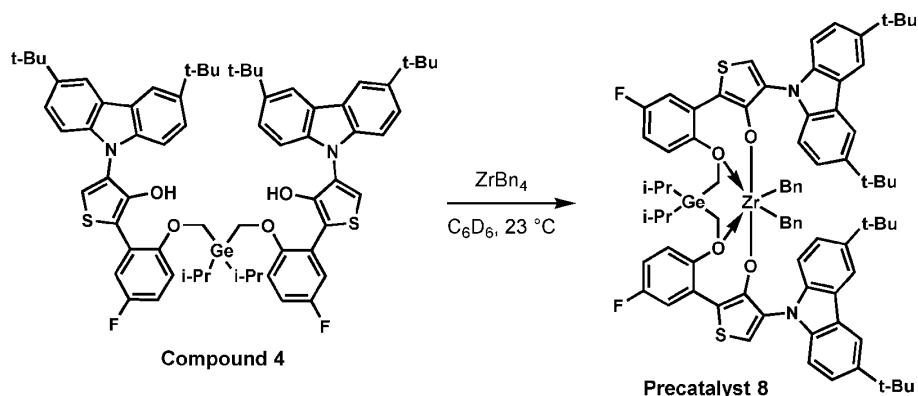


[00235] The thiophene ligand was azeotropically dried using PhMe (4 x 10 mL) prior to use. To a clear pale golden yellow solution of the thiophene (48.8 mg, 0.03618 mmol, 1.00 eq) in PhMe (16.8 mL) in a continuous purge, nitrogen filled glovebox at 23 °C was added a solution of ZrBn_2Cl_2 (16.7 mg, 0.03980 mmol, 1.10 eq) in PhMe (1.34 mL) in a dropwise manner. After stirring (500 rpm) for 15 mins the pale golden yellow solution was filtered using a 0.45 μm PTFE submicron filter connected to a 0.20 μm PTFE submicron filter, rinsed with PhMe (3 x 3

mL), and concentrated to afford the zirconium complex as a white foam (53.9 mg, 0.0357 mmol, 99%). NMR indicated product. **¹H NMR** (400 MHz, C₆D₆) δ 8.57 (d, *J* = 1.9 Hz, 2H), 8.37 (t, *J* = 1.3 Hz, 2H), 7.54 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.45 (d, *J* = 2.1 Hz, 4H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.09 (dd, *J* = 8.8, 2.4 Hz, 2H), 6.87 (s, 2H), 5.82 (d, *J* = 8.7 Hz, 2H), 4.65 (d, *J* = 13.0 Hz, 2H), 3.50 (d, *J* = 13.1 Hz, 2H), 1.72 (d, *J* = 14.6 Hz, 2H), 1.59 (d, *J* = 14.6 Hz, 2H), 1.48 (s, 18H), 1.38 (s, 18H), 1.24 (s, 6H), 1.17 (s, 6H), 0.98 – 0.86 (m, 2H), 0.73 (s, 18H), 0.68 (d, *J* = 5.9 Hz, 6H), 0.60 (d, *J* = 6.5 Hz, 6H). **¹³C NMR** (101 MHz, C₆D₆) δ 157.52, 152.22, 148.12, 143.27, 142.90, 139.90, 139.77, 128.61, 125.93, 125.07, 124.16, 122.50, 122.33, 121.32, 119.13, 117.74, 116.28, 115.03, 112.60, 109.23, 73.02, 56.78, 38.06, 34.58, 34.45, 32.18, 31.98, 31.94, 31.78, 31.74, 30.42, 29.84, 19.31, 18.99, 13.81.

[00236] Examples 28 and 29: synthesis of Precatalyst 8: a precatalyst of formula (II) wherein *R*¹, *R*², and *R*⁵ to *R*⁹ are H, *R*³ and *R*⁴ are each F (Fluoro), each *R*¹⁰ is tertiary-butyl, *R*¹¹ and *R*¹² are each isopropyl, M is Zr, each X is benzyl, and subscript n is 2; and synthesis of Precatalyst 9: a precatalyst of formula (II) wherein *R*¹, *R*², and *R*⁵ to *R*⁹ are H, *R*³ and *R*⁴ are each F (fluoro), each *R*¹⁰ is tertiary-butyl, *R*¹¹ and *R*¹² are each isopropyl, M is Hf, each X is benzyl, and subscript n is 2.

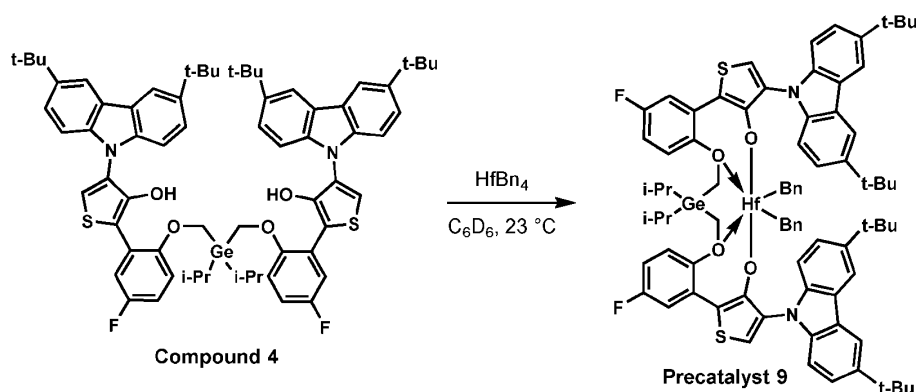
[00237] Synthesis of Precatalyst 8:



[00238] The thiophene ligand was azeotropically dried using PhMe (4 x 10 mL) prior to use. To a clear colorless solution of the thiophene (5.0 mg, 4.31 μmol, 1.00 eq) in anhydrous C₆D₆ (1.54 mL) in a nitrogen filled glovebox at 23 °C was added a solution of ZrBn₄ (2.2 mg, 4.74 μmol, 1.10 eq) in C₆D₆ (0.18 mL) in a dropwise manner. After stirring (500 rpm) for 30 mins the pale golden yellow solution was filtered using a 0.20 μm PTFE submicron filter to afford the zirconium complex as a solution in C₆D₆. NMR indicated product. The same procedure can be used with PhMe as the solvent to prepare the precatalyst solution (0.0025 M or 0.0042 M) which is used directly after filtration for the slurry polymerization experiments. **¹H NMR** (500 MHz, Benzene-*d*₆) δ 8.45 (dd, *J* = 1.9, 0.6 Hz, 2H), 8.30 (dd, *J* = 2.0, 0.6 Hz, 2H), 7.54 (dd, *J*

= 8.7, 1.9 Hz, 2H), 7.49 (dd, J = 8.5, 1.9 Hz, 2H), 7.38 (dd, J = 8.7, 0.6 Hz, 2H), 7.31 (dd, J = 8.5, 0.6 Hz, 2H), 7.07 – 7.02 (m, 2H), 6.99 – 6.95 (m, 4H), 6.83 (s, 2H), 6.77 (tt, J = 7.3, 1.2 Hz, 2H), 6.61 (ddd, J = 9.0, 7.3, 3.2 Hz, 2H), 6.37 – 6.34 (m, 4H), 5.42 (dd, J = 9.0, 4.7 Hz, 2H), 4.32 (d, J = 13.0 Hz, 2H), 3.33 (d, J = 13.0 Hz, 2H), 1.40 (s, 18H), 1.28 (s, 18H), 1.17 (d, J = 12.5 Hz, 2H), 0.71 (dp, J = 14.1, 6.9 Hz, 2H), 0.60 (d, J = 7.2 Hz, 6H), 0.57 (d, J = 12.5 Hz, 2H), 0.51 (d, J = 7.3 Hz, 6H). **^{19}F NMR** (470 MHz, Benzene- d_6) δ -115.87 (td, J = 8.0, 4.8 Hz). **^{13}C NMR** (126 MHz, Benzene- d_6) δ 159.44 (d, J = 245.5 Hz), 154.21, 154.19, 152.80, 146.62, 143.27 (d, J = 53.0 Hz), 139.67 (d, J = 30.0 Hz), 130.56, 128.33, 128.16, 126.33, 125.24, 124.59, 122.81, 122.51, 121.20, 119.01, 116.58 (m), 116.35, 116.19 (d, J = 17.8 Hz), 116.01 (d, J = 16.9 Hz), 115.62, 112.27, 108.98, 76.05, 71.65, 34.53, 34.45, 31.89, 31.70, 19.18, 19.13, 13.59.

[00239] Synthesis of Precatalyst 9:



[00240] The thiophene ligand was azeotropically dried using PhMe (4 x 10 mL) prior to use. To a clear colorless solution of the thiophene (5.2 mg, 4.48 μmol , 1.00 eq) in anhydrous C_6D_6 (1.58 mL) in a nitrogen filled glovebox at 23 $^\circ\text{C}$ was added a solution of HfBn_4 (2.7 mg, 4.93 μmol , 1.10 eq) in C_6D_6 (0.22 mL) in a dropwise manner. After stirring (500 rpm) for 30 mins the pale golden yellow solution was filtered using a 0.20 μm PTFE submicron filter to afford the hafnium complex as a 0.0025 M solution in C_6D_6 . NMR indicated product. The same procedure can be used with PhMe as the solvent to prepare the precatalyst solution (0.0025 M) which is used directly after filtration for the slurry polymerization experiments. **^1H NMR** (500 MHz, Benzene- d_6) δ 8.46 (dd, J = 2.0, 0.6 Hz, 2H), 8.31 (dd, J = 1.9, 0.6 Hz, 2H), 7.53 (dd, J = 8.7, 1.9 Hz, 2H), 7.48 (dd, J = 8.5, 1.9 Hz, 2H), 7.30 (ddd, J = 11.7, 8.6, 0.6 Hz, 4H), 6.99 – 6.94 (m, 4H), 6.82 (s, 2H), 6.78 – 6.73 (m, 2H), 6.65 (ddd, J = 9.0, 7.2, 3.1 Hz, 2H), 6.52 – 6.48 (m, 2H), 6.40 – 6.35 (m, 4H), 5.44 (dd, J = 9.0, 4.8 Hz, 2H), 4.36 (d, J = 13.0 Hz, 2H), 3.33 (d, J = 13.1 Hz, 2H), 1.40 (s, 18H), 1.28 (s, 18H), 1.03 (d, J = 13.5 Hz, 2H), 0.68 (dq, J = 14.1, 7.2 Hz, 2H), 0.58 (d, J = 7.3 Hz, 6H), 0.49 (d, J = 7.3 Hz, 6H), 0.28 (d, J = 13.7 Hz, 2H). **^{19}F NMR** (470 MHz, Benzene- d_6) δ -114.35 – -117.32 (m). **^{13}C NMR** (126 MHz, Benzene- d_6)

δ 159.63 (d, J = 246.1 Hz), 153.86 (d, J = 2.5 Hz), 152.93, 147.26, 143.32 (d, J = 61.1 Hz), 139.67 (d, J = 33.6 Hz), 129.89, 128.58, 128.18, 127.17, 126.70, 125.31, 124.49 (d, J = 34.8 Hz), 123.03 (d, J = 9.2 Hz), 122.78, 122.45, 121.24, 119.15, 116.32, 116.16 (d, J = 13.5 Hz), 115.98 (d, J = 13.4 Hz), 115.90, 115.88, 115.53, 112.32, 108.97, 83.00, 72.10, 34.53, 34.45, 31.88, 31.70, 19.13, 19.07, 13.67.

[00241] *Examples 30 to 36: spray-drying precatalysts to make spray-dried supported catalyst systems.*

[00242] Supported catalyst systems described in TABLE 3 above were made and spray-dried in a nitrogen-purged glove box. In an oven-dried jar, Cabosil™ TS-610 fumed silica was slurried in toluene until well dispersed, then a 10 % solution by weight of MAO in toluene was added. The mixture was stirred magnetically for approximately 15 minutes at ambient temperature, then the metal-ligand complex was added to the resulting slurry, and the mixture was stirred for 30 to 60 minutes at ambient temperature. The mixture was spray-dried using a Büchi Mini Spray Dryer B-290 with the following parameters to yield the dried sample: Set Temperature: 140 °C, Outlet Temperature: 75 °C (min.), aspirator setting of 95 rotations per minute (rpm), and pump speed of 150 rpm. TABLE 4 contains the amounts of the metal-ligand complex, fumed silica, 10% MAO solution, and toluene used to make each of the spray-dried supported catalyst systems 1 to 7. Quantities of reagents used are listed below in TABLE 4.

[00243] TABLE 4: SCS 4 to 6 are prophetic examples.

Ex. No.	Spray-dried SCS No.	Precatalyst No.	Precatalyst Weight, Actual [expected] (g)	Fumed Silica, Actual [expected] (g)	10% MAO solution, Actual [expected] (g)	Toluene, Actual [expected] (g)
30a	SCS 1a	1	0.076	0.556	4.84	37.5
30b	SCS 1b	1	0.043	0.710	5.75	37.5
31	SCS 2	2	0.075	0.518	4.53	37.5
32	SCS 3	3	0.039	0.680	5.50	37.5
33	SCS 4	4	0.063	0.426	3.73	37.5
34	P-SCS 5	5	[0.08]	[0.8]	[5]	[37.5]
35	P-SCS 6	6	[0.08]	[0.8]	[5]	[37.5]
36	SCS 7	7	0.018	1.36	10.55	37.5

[00244] *Gas-Phase Polymerizations Making ethylene/1-hexene copolymers.*

[00245] The spray dried catalysts described in TABLE 4 were used to catalyze gas phase polymerizations of ethylene monomer and 1-hexene comonomer to give ethylene/1-hexene copolymers (also called poly(ethylene-co-1-hexene) copolymers). The gas phase

polymerizations conducted in a 2 liter (L), semi-batch, stainless steel autoclave gas phase polymerization reactor equipped with a mechanical agitator. For each polymerization run, the reactor was first dried ("baked out") for 1 hour by charging the reactor with 200 grams (g) of NaCl, and heating the reactor contents at 100 °C under dry nitrogen for 30 minutes. Then 5 g of spray-dried methylaluminoxane/fumed silica ("SDMAO") was added to the reactor under nitrogen pressure to scavenge any remaining water. The reactor was sealed, and the contents were stirred. The polymerizations were initiated by charging the reactor with hydrogen (H₂) and 1-hexene (C₆), then pressurizing the reactor with ethylene (C₂). The feed ratios of hydrogen, 1-hexene, and ethylene were set to achieve a predetermined H₂/C₂ molar ratio and C₆/C₂ molar ratio in the reactor. Once the reactor reached a steady state, the supported catalyst system was charged into the reactor at 80 °C to start polymerization. The reactor temperature was brought to a predetermined polymerization temperature, typically 90 °C or 100 °C is used for these experiments but any temperature from 75 to 115 °C may be used, and maintained at this polymerization temperature while keeping the ethylene, 1-hexene, and hydrogen feed ratios consistent for 1 hour. At the end of the 1-hour run, the feeds of hydrogen, 1-hexene, and ethylene were stopped, the reactor was cooled down, vented and opened. The resulting product mixture was washed with water and methanol, then dried to give the ethylene/1-hexene copolymer. The weight of the copolymer was recorded. Catalyst Productivity (grams copolymer/gram catalyst-hour) and catalyst efficiency (grams copolymer/gram catalyst metal (Zr or Hf)) were determined to compare the amount of copolymer produced, based on ethylene and hexene uptake/consumption, relative to the amount of supported catalyst system added to the reactor. The copolymer samples were characterized by DSC, GPC, and melt flow. The polymerization run conditions and results are listed in the following TABLES.

[00246] TABLE 5. Batch reactor conditions: Temp. = 100 °C, C₆/C₂ (molar ratio) = 0.00X, H₂/C₂ (molar ratio) = 0.00X, C₂PP = 220 psi, run time = 1 hr, catalyst injection temp. = 80 °C. NF = No Flow. N.D. = Not Determined.

Run	C ₆ /C ₂	H ₂ /C ₂	SCS No.	Charge (mg)	Yield (g)	Productivity (gPE/gCat/hr)	Efficiency (gPE/gM)	I21	C ₆ Uptake (%)
1	0.00	0.004	SCS 1a	4.9	128.7	25,200	6,575,400	NF	0.7
2	0.00	0.004	SCS 1a	5.5	152.2	32,000	8,342,700	NF	1.1

3	0.00	0.004	SCS 1b	5.8	109.	18,100	9,941,400	NF	0.7
1					5				
4	0.00	0.004	SCS 1b	5.9	112.	20,200	11,092,40	NF	1.3
2					7		0		
5	0.00	0.0068	SCS 1b	4.2	22.2	20,600	11,291,40	NF	3.9
4							0		
6	0.00	0.004	SCS 1b	4.4	43.4	23,900	13,100,20	NF	3.9
4							0		
7	0.00	0.004	SCS 2	5.0	83.7	16,000	2,128,700	NF	0.7
1									
8	0.00	0.004	SCS 2	5.5	106.	18,400	2,459,100	NF	1.4
2					7				
9	0.00	0.004	SCS 3	14.9	1.5	170	93,200	NF	N.D.
2									
10	0.00	0.004	SCS 3	15.4	1.7	90	55,400	NF	N.D.
3									
11	0.00	0.05	SCS 4	5.2	12.1	1,800	240,100	NF	1.3
4									
12	0.00	0.05	SCS 4	5.3	11.3	2,100	280,100	NF	0.8
2									
13	0.00	0.1	SCS 4	5.4	12.6	1,900	253,400	NF	0.8
2									
14	0.00	0.004	SCS 7	2.9	39.2	13,400	29,379,50	NF	4.8
4							0		
15	0.00	0.002	SCS 7	5.4	72.8	13,800	30,256,50	NF	4.4
4							0		
16	0.00	0.002	SCS 7	5.4	54.8	13,700	30,037,30	NF	3.0
3							0		

[00247] TABLE 6. Batch reactor conditions: Temp. = 90 °C, C₆/C₂ (molar ratio) = 0.00X, H₂/C₂ (molar ratio) = 0.00X, C₂PP = 220 psi, run time = 1 hr, catalyst injection temp. = 80 °C. NF = No Flow. N.D. = Not Determined.

Run	C ₆ /C ₂	H ₂ /C ₂	SCS	Charge	Yield	Productivity	Efficiency	I ₂ I	C ₆
			No.	(mg)	(g)	(gPE/gCat/hr)	(gPE/gM)		Uptake
									(% C ₆)

17	0.00 4	0.004	SCS 1b	4.2	35.5	21,300	11,620,30 0	NF	5.0
18	0.00 3	0.004	SCS 1b	3.3	79.0	26,100	14,306,10 0	NF	2.8
19	0.00 3	0.002	SCS 1b	4.8	42.1	14,900	8,167,100	NF	4.6
20	0.00 3	0.004	SCS 3	15.4	1.5	101	55,400	NF	N.D.

[00248] TABLE 7. Batch reactor conditions: Temp. = 100 °C, C6/C2 (molar ratio) = 0.00X, H2/C2 (molar ratio) = 0.00XX, C2PP = 220 psi, run time = 1 hr, catalyst injection temp. = 80 °C. NF = No Flow.

Run	C ₆ /C ₂	H ₂ /C ₂	SCS No.	C6 Wt%	Mw (g/mol)	PDI (Mw/Mn)	Mz (g/mol)	Mz/M w	T _M (°C)
1	0.001	0.004	SCS 1a	2.6	900,700	4.3	3,284,60 0	3.6	126. 7
2	0.002	0.004	SCS 1a	4.7	617,000	6.0	3,259,50 0	5.3	123. 9
3	0.001	0.004	SCS 1b	N.D.	N.D.	N.D.	N.D.	N.D.	126. 3
4	0.002	0.004	SCS 1b	N.D.	N.D.	N.D.	N.D.	N.D.	124. 0
5	0.004	0.0068	SCS 1b	6.1	388,300	3.6	1,500,20 0	3.9	113. 5
6	0.004	0.004	SCS 1b	5.4	603,100	3.7	1,948,40 0	3.2	114. 0
7	0.001	0.004	SCS 2	2.2	2,600,20 0	3.2	5,072,90 0	2.0	126. 8
8	0.002	0.004	SCS 2	4.6	2,729,30 0	3.4	5,286,70 0	1.9	124. 1
9	0.002	0.004	SCS 3	2.5	1,282,70 0	7.0	4,129,20 0	3.2	N.D.
10	0.003	0.004	SCS 3	2.7	1,205,40 0	7.6	4,120,60 0	3.4	N.D.
11	0.004	0.05	SCS 4	3.4	1,410,70 0	4.5	3,753,80 0	2.7	122. 3

12	0.002	0.05	SCS 4	2.6	1,456,400	4.2	3,895,600	2.7	125.7
13	0.002	0.1	SCS 4	3.1	1,100,100	5.0	3,373,900	3.1	126.4
14	0.004	0.004	SCS 7	6.3	807,400	3.5	1,991,100	2.5	112.2
15	0.004	0.002	SCS 7	6.9	460,800	4.4	1,989,000	4.3	115.5
16	0.003	0.002	SCS 7	5.6	710,300	5.5	2,669,000	5.6	118.3

[00249] TABLE 8. Batch reactor conditions: Temp. = 90 °C, C₆/C₂ (molar ratio) = 0.00X, H₂/C₂ (molar ratio) = 0.00XX, C₂PP = 220 psi, run time = 1 hr, catalyst injection temp. = 80 °C. NF = No Flow.

Run	C ₆ /C ₂	H ₂ /C ₂	SCS No.	C ₆ Wt%	Mw (g/mol)	PDI (Mw/Mn)	Mz (g/mol)	Mz/Mw	T _M (°C)
17	0.004	0.004	SCS 1b	6.5	554,100	3.9	2,456,700	4.4	113.9
18	0.003	0.004	SCS 1b	5.2	857,400	4.3	3,041,200	3.5	117.7
19	0.003	0.002	SCS 1b	6.2	655,500	4.0	3,127,000	4.8	117.3
20	0.003	0.004	SCS 3	2.6	1,499,800	8.9	4,503,500	3.0	N.D.

[00250] In TABLES 5 to 8, the results show that the inventive spray-dried supported catalyst system ("sd-SCS") comprising a substituted 2-hydroxythiophene compound, which contains a -CH₂Ge(i-Pr)₂CH₂- bridge between phenol rings, along with a variety of different substituent groups on the catalyst framework, successfully make ethylene/1-hexene copolymers under commercially-relevant gas phase polymerization process conditions. Unexpectedly, the inventive sd-SCS have high catalyst productivities—up to 32,000 gPE/gCat/hr—and high catalyst efficiencies—up to 30.3 MM gPE/gM. Based on the melt flow data (I₂, I₅, I₂₁) as well as GPC analysis under these, the inventive sd-SCS can produce polyethylene copolymers with high Mw—in these examples of up to 2,729,300 g/mol—and/or high Mz—in these examples up to 5,286,700 g/mol—as well as broad molecular weight distribution (MWD) or polydispersity index (PDI)—in these examples up to Mw/Mn of 8.9; and broad Mz/Mw—in these examples up to Mz/Mw 5.3. These Mw and Mz may be lowered by increasing the temperature as well as the H₂/C₂ or C₆/C₂ ratio used in the reactor. Lastly, based on

comonomer consumption in the reactor, GPC analysis and/or T_m , several of these inventive sd-SCS beneficially incorporate high levels 1-hexene comonomer under industrially relevant high density process conditions. This combination of high Mw and/or high Mz, broader Mw/Mn as well as broad Mz/Mw with higher alpha-olefin comonomer incorporation offers an ethylene/alpha-olefin copolymer resin with advantageous properties.

Slurry Phase Polymerization Experiments

[00251] Synthesis of Undried Supported Catalyst Systems for slurry phase polymerization. In a nitrogen filled continuous purge glovebox, a precatalyst of formula (II) is provided either in neat form, or as a solution thereof dissolved in toluene, or as a solid form wherein the precatalyst is already supported on spray-dried activator/hydrophobic fumed silica solids, wherein the activator is methylaluminoxane. This supported activator is called "SMAO" herein and is white in color. Unsupported precatalysts are diluted to 4.21 millimolar (mM) concentration in anhydrous deoxygenated toluene, and pipetted into oven-dried 4 mL or 8 mL scintillation vials containing a pre-weighed amount of the SMAO such that the resultant slurry has a catalyst charge of 45 micromoles (μmol) Zr atom or Hf atom, as the case may be, per 1.0 grams (g) SMAO, unless otherwise noted. The slurry is stirred at 300 rotations per minute (rpm) and heated to 50 °C for 30 minutes, then returned to room temperature to give a slurry of an undried supported catalyst system ("ud-SCS") in toluene. Colorization of the previously white SMAO indicates the precatalyst has been supported and activated. $^1\text{H-NMR}$ experiments of the slurry's liquid phase shows that there is no remaining precatalyst or unsupported active catalyst present in the liquid phase, which indicates the precatalyst has been fully converted to active catalyst in the ud-SCS. The slurries of ud-SCS at room temperature are vortexed and agitated at 700 rpm to produce a uniform dispersion thereof. The slurries of ud-SCS are agitated for at least one minute, and while vortexing is continued, aliquots are daughtered by positive displacement tip (PDT) into 8 mL vials. Daughtered aliquots of the ud-SCS will be diluted with isoparaffin solvent (Isopar E) to 50 millimoles (mmol) to 500 nmol per mL, depending on the expected catalytic activity. All catalyst materials and daughtered aliquots of ud-SCS are kept in a glovebox freezer at -30 °C until use in the slurry phase polymerization.

[00252] Preparation of slurry phase polymerization reactor cells in a drybox. A day prior to polymerization runs, 48 parallel pressure reactor cells having module heads and module bodies were prepared as follows. Oven-dried, pre-weighed glass tubes were manually inserted into the reactor wells, polyether ether ketone ("PEEK") stir paddles were attached to the module heads, and the module heads were attached to the module bodies. The reactor cells were heated to 190 °C, purged with nitrogen for 10 hours, and cooled to 50 °C. On the next day (day of the experiments), the reactors were purged twice with ethylene and vented completely to purge feed lines. The reactor cells were then pre-heated to 50 °C and the stir

paddles turned on to a stirring rate of 800 rotations per minute (rpm), thereby giving prepared reactor cells.

[00253] Running slurry phase polymerizations in the prepared reactor cells in the drybox. The prepared reactor cells were partially filled (to an appropriate solvent level) with an isoparaffin hydrocarbon ("solvent", Isopar-E from ExxonMobil), and olefin comonomer (for these experiments 1-hexene) using a robotic needle to later give a final total volume of 5 mL in each reactor cell (once all of the reagent solutions are added later). Following solvent injection, the reactor cells were heated to a target starting-the-polymerization temperature (in these experiments, 100 °C) and the stirring rate was increased. When the temperature of the reactor cells reached the starting the polymerization temperature, which required about 10-30 minutes of heating, the reactor cells were pressurized to a target starting-the-polymerization pressure with either pure ethylene, or a gas mixture of ethylene and hydrogen from a gas accumulator, and until the solvent was saturated with the pure ethylene or the gas mixture, respectively, (as observed by the gas uptake). If the gas mixture of ethylene and hydrogen was used, once the solvent was saturated in all cells, the gas feed line was switched from the accumulator to pure ethylene for the remainder of the polymerization run.

[00254] Then a robotic synthesis protocol was initiated whereby activator (a slurry of SMAO in solvent) was injected first, followed by injection of a slurry of the conventionally-dried supported catalyst system. Both injections for a given reactor cell were completed before the robot started the injection into the next reactor cell in the sequence. Each reagent addition was chased with 500 microliters (μL) of the solvent to ensure all the reagent had been injected. After each reagent injection the needles were washed with the solvent both inside and outside the needle.

[00255] At the moment of the catalyst injection in each individual cell, a reaction timer and monitoring of each cell's pressure were started. The desired pressure (within approximately 2-6 psig) was maintained by adding supplemental amount of ethylene gas by opening the valve at the target pressure minus 2 psi and closing the valve when the pressure reached 2 psi above target pressure. All drops in reactor cell pressure were cumulatively recorded as uptake of ethylene for the duration of the run. The slurry phase polymerization reactions proceeded for 90 minutes or to an ethylene uptake of 90 psi, whichever occurred first, and then were quenched by adding a 60 psi overpressure of 10% (v/v) CO₂ in argon. Data collection of each cell continued for 5 minutes after the quench. After the last cell finished quenching, any potential gas leaks were identified from the cell pressure and ethylene uptake curves were noted. The reactors were cooled down to 50 °C, vented, and the glass tubes were removed from the module bodies. The glass tubes were removed from the drybox and the volatiles then removed using a rotary evaporator. The glass tubes were re-weighed to obtain

reaction yields, the obtained polyethylene homopolymer or ethylene/1-hexene copolymer products were analyzed by GPC using a High Throughput High Temperature Gel Permeation Chromatography (HT-HT-GPC) Test Method.

[00256] High Throughput High Temperature Gel Permeation Chromatography (HT-HT-GPC) Test Method was performed using a Robot Assisted Delivery (RAD) system equipped with a PolymerChar infrared detector (IR5) and Agilent PLgel Mixed A columns. Decane (10 μ L) was added to each sample for use as an internal flow marker. Samples were first diluted in 1,2,4-trichlorobenzene (TCB) stabilized with 300ppm butylated hydroxyl toluene (BHT) at a concentration of 10mg/mL and dissolved by stirring at 160°C for 120 minutes. Prior to injection samples were further diluted with TCB stabilized with BHT to a concentration of 2 mg/mL. Samples (250 μ L) were eluted through one PL-gel 20 μ m (50 x 7.5mm) guard column followed by two PL-gel 20 μ m (300 x 7.5mm) Mixed-A columns maintained at 160 °C with TCB stabilized with BHT at a flowrate of 1.0 mL/min. The total run time was 24 minutes. To calibrate for molecular weight (MW), Agilent EasiCal polystyrene standards (PS-1 and PS-2) were analyzed to create a 3rd order MW calibration curve. Molecular weight units were converted from polystyrene (PS) to polyethylene (PE) using a daily Q-factor calculated around 0.4 using the average of 5 reference samples of known MW.

[00257] The table below lists the slurry phase polymerization conditions: Temp. = 100 °C, Isopar E = 5 mL, C6/C2 (molar ratio) = 0.6/1 in liquid or 0.4/1 in liquid, H2/C2 (molar ratio) = 0.0016/1.0 in liquid, run time = 90 minutes maximum (5400 seconds), Quench time = time needed to uptake 90 psi of ethylene; the faster the quench time, the more active the catalyst is. SCS 8 is made to be 20 μ mol Zr /1 g SMAO, and SCS 9 and 10 are made to 45 μ mol Zr or Hf / 1 g SMAO. N.D. = not determined. The loading of SCS 8 in the slurry phase reactor was 5 nanomoles (nmol), and the loadings for SCS 9 and 10 are both 20 nmol. The “ud-SCS” means undried supported catalyst system, which is prepared according to the procedure of Synthesis of Undried Supported Catalyst Systems for slurry phase polymerization.

TABLE 17: slurry phase polymerization results.

Undried SCS No.	C6/C 2	Precat. No.	C2 Uptake (psi)	Quench Time (sec)	Mw (g/mol)	PDI Mw/Mn	C6 (wt %)	Yield (mg)
SCS 8	0.6	1	90	494	258,100	4.0	4.2	128
SCS 9	0.4	8	90	195	177,800	3.1	7.7	159
SCS 10	0.4	9	44	5,400	705,600	8.8	6.1	53

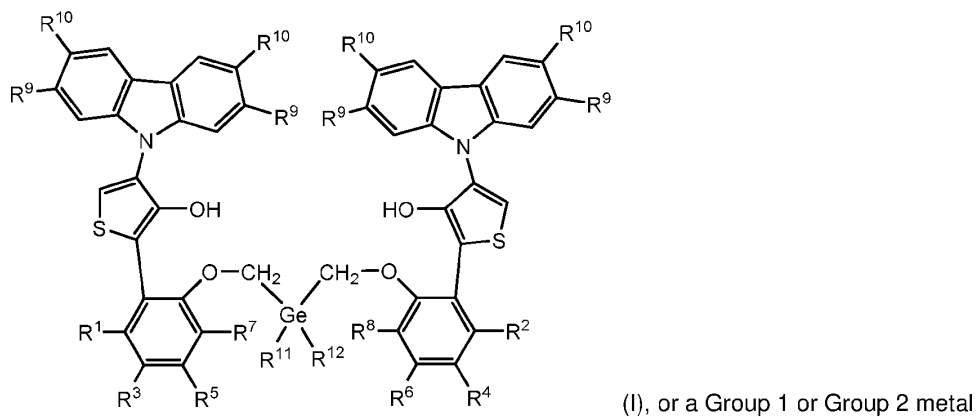
[00258] The slurry polymerization results for the undried supported catalyst systems (ud-SCS) are shown in TABLE 17. High activity is deemed as quench times of 1,000 seconds or faster at catalyst charges of 25 nanomoles (nmol) or lower at a loading of 45 μ mol of Zr or Hf or

lower per 1.0 g SMAO. The "quench time" is the time the polymerization reaction run takes to consume 90 psi of ethylene, where the shorter the time taken, the more active the ud-SCS. Under process relevant high density conditions, ud-SCS 8 and ud-SCS 9 have quench times of 494 seconds and 195 seconds, respectively, and therefore both catalysts exhibit high activity. Based on the GPC analysis of the polyethylene-hexene copolymers produced, under these slurry polymerization process conditions, the inventive ud-SCS produced polyethylene with a range of Mw and Mz, where several ud-SCS produced ethylene/hexene copolymers of above average ($> 100,000$ g/mol) to high Mw, average to broad polydispersity index (PDI, Mw/Mn), and higher 1-hexene incorporation polymers. The ud-SCS can make polyethylene polymers over a wide range of Mw and/or over a wide range of PDI and/or with high 1-hexene incorporation. These polyethylene polymers thus have advantageous properties for industrial uses.

[00259] Claimed embodiments follow.

CLAIMS

1. A substituted 2-hydroxythiophene compound of formula (I):



salt thereof, wherein:

R^1 and R^2 independently are H or a halogen;

R^3 and R^4 independently are H, a halogen, a (C₁-C₂₀)hydrocarbyl, a (C₁-C₁₀)alkoxy, or a Si((C₁-C₁₀)alkyl)₃;

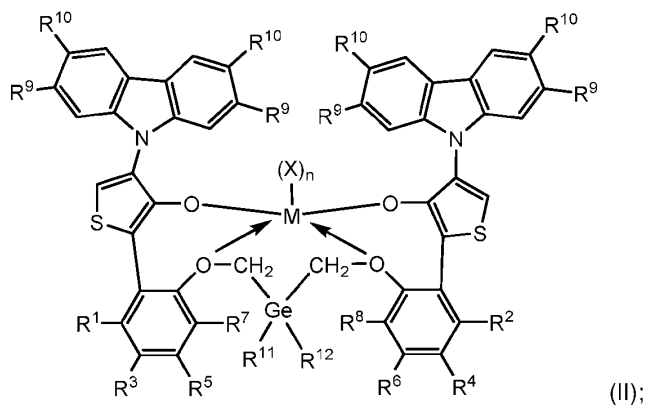
R^5 and R^6 independently are H or a halogen;

R^7 and R^8 independently are H or a halogen;

each R^9 is H and each R^{10} is a (C₁-C₂₀)hydrocarbyl; or each R^{10} is H and each R^9 is a (C₁-C₂₀)hydrocarbyl; and

R^{11} and R^{12} independently are a (C₁-C₁₀)alkyl.

2. A precatalyst of formula (II):



wherein:

M is Ti, Hf, or Zr;

subscript n is 1 or 2; and

each X independently is selected from a monodentate ligand independently chosen from a hydrogen atom, a (C₁–C₅₀)hydrocarbyl, a (C₁–C₅₀)heterohydrocarbyl, a (C₁–C₅₀)organoheteryl, a halogen atom, a dialkylamino, or a dialkyl carbamate;

R¹ and R² independently are H or a halogen;

R³ and R⁴ independently are H, a halogen, a (C₁–C₂₀)hydrocarbyl, a (C₁–C₁₀)alkoxy, or a Si((C₁–C₁₀)alkyl)₃;

R⁵ and R⁶ independently are H or a halogen;

R⁷ and R⁸ independently are H or a halogen;

each R⁹ is H and each R¹⁰ is a (C₁–C₂₀)hydrocarbyl; or each R¹⁰ is H and each R⁹ is a (C₁–C₂₀)hydrocarbyl; and

R¹¹ and R¹² independently are a (C₁–C₁₀)alkyl.

3. A supported catalyst system comprising the precatalyst of formula (II) of claim 2, a support material, and an activator.

4. A method of making the supported catalyst system of claim 3 comprising step (a) or comprising steps (b) and (c):

(a) spray drying a mixture of an inert hydrocarbon solvent, the precatalyst of formula (II), the support material, and the activator to make the supported catalyst system; or

(b) spray drying a mixture of an inert hydrocarbon solvent, the support material and the activator to make a spray-dried supported activator, and

(c) mixing the precatalyst of formula (II) with the spray-dried supported activator and an inert hydrocarbon solvent to make the supported catalyst system.

5. The invention of any one of claims 1 to 4 wherein:

R¹ and R² are different, or R¹ and R² are identical; or R¹ and R² are H; or R¹ and R² are F; or

R³ and R⁴ are different, or R³ and R⁴ are identical, or R³ and R⁴ are a halogen, a (C₁–C₂₀)hydrocarbyl, a (C₁–C₁₀)alkoxy, or a Si((C₁–C₁₀)alkyl)₃, or R³ and R⁴ are a (C₁–C₂₀)alkyl, a (C₁–C₁₀)alkoxy, or a fluoro; or

R⁵ and R⁶ are different, or R⁵ and R⁶ are identical, or R⁵ and R⁶ are H, or R⁵ and R⁶ are F; or

R⁷ and R⁸ are different, or R⁷ and R⁸ are identical, or R⁷ and R⁸ are H, or R⁷ and R⁸ are F; or

each R⁹ is H and each R¹⁰ is tertiary-butyl, 4-tert-butylphenyl, 4-triethylmethylphenyl, 3,5-dimethylphenyl, or 3,5-di-tert-butylphenyl; or each R¹⁰ is H and each R⁹ is 3,5-di-tert-butylphenyl; or

each R¹¹ and R¹² is identical; or each R¹¹ and R¹² is a (C₁-C₁₀)alkyl or a (C₁-C₅)alkyl; or each R¹¹ and R¹² is isopropyl; or

a combination of the foregoing definitions of R¹ to R¹².

6. The invention of any one of claims 2 to 5 wherein:

M is Hf or Zr; or

subscript n is 2; or

each X is benzyl or each X is Cl; or

M is Hf or Zr, subscript n is 2, and each X is benzyl; or

M is Hf or Zr, subscript n is 2, and X is chloro.

7. The substituted 2-hydroxythiophene compound of formula (I) of claim 1 selected from the group consisting of compounds 1 to 3 in TABLE 1:

TABLE 1:

Cmpd No.	R ¹ / R ² each is	R ³ / R ⁴ each is	R ⁵ / R ⁶ each is	R ⁷ / R ⁸ each is	R ⁹	R ¹⁰	R ¹¹ / R ¹² each is
1	H	t-Octyl	H	H	H	t-Bu	i-Pr
2	H	OctylO	H	H	H	t-Bu	i-Pr
3	H	H	H	H	H	3,5-dtBP	i-Pr
4	H	F	H	H	H	t-Bu	i-Pr

wherein "Cmpd No." is compound number, t-Bu is tertiary-butyl; t-Octyl is (CH₃)₃CCH₂C(CH₃)₂-; OctylO is CH₃(CH₂)₇O-; F is fluoro; 3,5-dtBP is 3,5-di-tert-butylphenyl; and i-Pr is isopropyl.

8. The precatalyst of formula (II) of claim 2 selected from the group consisting of precatalyst numbers 1 to 9 in TABLE 2:

TABLE 2:

Precatalyst No.	Made from Formula (I) Compound No.	M	X each is	n
1	1	Zr	Benzyl	2
2	1	Hf	Benzyl	2
3	2	Zr	Benzyl	2
4	2	Hf	Benzyl	2
5	3	Zr	Benzyl	2
6	3	Hf	Benzyl	2
7	1	Zr	Cl	2
8	4	Zr	Benzyl	2
9	4	Hf	Benzyl	2

9. The supported catalyst system of claim 3 selected from the group consisting of spray-dried supported catalyst system numbers SCS 1 to 7 and the undried supported catalyst system number SCS 8 to 10 in TABLE 3:

TABLE 3:

SCS No.	Made from Formula (II) Precatalyst No.	Support Material	Activator	Catalyst Drying Method
SCS 1	1	HPFS1	MAO	Spray
SCS 2	2	HPFS1	MAO	Spray
SCS 3	3	HPFS1	MAO	Spray
SCS 4	4	HPFS1	MAO	Spray
SCS 5	5	HPFS1	MAO	Spray
SCS 6	6	HPFS1	MAO	Spray
SCS 7	7	HPFS1	MAO	Spray
SCS 8	1	SMAO		None (undried)
SCS 9	8	SMAO		None (undried)
SCS 10	9	SMAO		None (undried)

wherein "HPFS1" is a hydrophobic fumed silica made from untreated fumed silica and a hydrophobing agent that is dichlorodimethylsilane; and "MAO" is methylaluminoxane; and wherein "SMAO" is spray dried methylaluminoxane/HPFS1, wherein HPFS1 is made from untreated fumed silica and a hydrophobing agent that is dichlorodimethylsilane.

10. The supported catalyst system of claim 3, 4, or 9 is that which has been shown to make by gas phase polymerization an ethylene/1-hexene copolymer having a weight-average

molecular weight greater than 500,000 grams per mole and/or a z-average molecular weight greater than 2,000,000 grams per mole.

11. A method of making a polyolefin in a gas phase polymerization process, the method comprising contacting one or more olefin monomers with the supported catalyst system, described above, in a gas phase polymerization reactor under gas phase polymerization conditions to make a polyolefin polymer.

12. The method of claim 11 having any one of limitations (i) to (v):

(i) wherein the one or more olefin monomers comprises ethylene or a combination of ethylene and propylene or a combination of ethylene and a (C₄-C₂₀)alpha-olefin and wherein the polyolefin polymer is an ethylene homopolymer or an ethylene/propylene copolymer or an ethylene/(C₄-C₂₀)alpha-olefin copolymer;

(ii) wherein the one or more olefin monomers comprises ethylene or a combination of ethylene and a (C₄-C₂₀)alpha-olefin and the polyolefin polymer is an ethylene homopolymer or an ethylene/(C₄-C₂₀)alpha-olefin copolymer; wherein the ethylene homopolymer or an ethylene/(C₄-C₂₀)alpha-olefin copolymer has a weight-average molecular weight 500,000 grams per mole or greater, or a z-average molecular weight of 2,000,000 grams per mole or greater, or both; or

(iii) wherein the one or more olefin monomers comprises a combination of ethylene and a (C₄-C₂₀)alpha-olefin and wherein the polyolefin polymer is an ethylene/(C₄-C₂₀)alpha-olefin copolymer having a polydispersity index (PDI) of a ratio of weight-average molecular weight to number-average molecular weight (M_w/M_n) of greater than or equal to 4.0, or a broad molecular weight distribution of a ratio of z-average molecular weight to weight-average molecular weight (M_z/M_w) greater than or equal to 3.5, or both;

(iv) any one of limitations (i) to (iii) wherein the (C₄-C₂₀)alpha-olefin is 1-hexene;

(v) a combination of limitations (ii) and (iii) or a combination of limitations (ii), (iii), and (iv).

13. A method of making a polyolefin in a slurry phase polymerization process, the method comprising contacting one or more olefin monomers with the supported catalyst system, described above, in a slurry phase polymerization reactor under slurry phase polymerization conditions to make a polyolefin polymer.

14. The method of claim 13 wherein the one or more olefin monomers comprises ethylene or a combination of ethylene and propylene or a combination of ethylene and a (C₄-C₂₀)alpha-olefin and the polyolefin polymer comprises an ethylene homopolymer or an ethylene/propylene copolymer or an ethylene/(C₄-C₂₀)alpha-olefin copolymer.