



(51) International Patent Classification:

C07C 31/125 (2006.01) C11D 1/66 (2006.01)
C07C 309/04 (2006.01) C08F 110/02 (2006.01)
C07C 2/30 (2006.01) C08F 4/659 (2006.01)
C07C 47/02 (2006.01)

(21) International Application Number:

PCT/US2014/042887

(22) International Filing Date:

18 June 2014 (18.06.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/840,765 28 June 2013 (28.06.2013) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR THE PREPARATION OF LIGHTLY-BRANCHED HYDROPHOBES AND THE CORRESPONDING SURFACTANTS AND APPLICATIONS THEREOF

(57) Abstract: Processes to prepare lightly branched surfactant products comprise combining at least one olefin and a coordination-insertion catalyst under conditions such that at least one oligomer product is formed. The surfactant products comprise a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches, wherein the branches are located more than one carbon away from each end of the main carbon chain in more than 20% of surfactant product molecules



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PROCESS FOR THE PREPARATION OF LIGHTLY-BRANCHED HYDROPHOBES
AND THE CORRESPONDING SURFACTANTS AND APPLICATIONS THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

5 This application claims priority to U.S. Provisional Application No. 61/840,765,
filed June 28, 2013, which is hereby incorporated by reference in its entirety.

FIELD

The invention relates to processes for the manufacture of lightly-branched
hydrophobes, and their corresponding nonionic and anionic surfactants.

10

BACKGROUND

Surfactant molecules generally comprise a water-soluble moiety (hydrophile) and
an oil-soluble moiety (hydrophobe). Various hydrophilic groups, such as
polyoxyethylene, polysaccharide, quaternary ammonium, amine oxide, sulfate, sulfonate,
sulfosuccinate, carboxylic, and the like, are attached to an alkyl, alkenyl, or alkaryl
15 hydrophobe that usually contains 8 to 20 carbon atoms through different linkage
chemistries. The hydrophobe structure affects the properties, performance,
biodegradability, toxicity, and therefore the application of the surfactants. Hydrophobes
may be derived from natural oils and fats, which are typically linear. Linear hydrophobes
are favorable in affording ready biodegradability of surfactants. However, they are
20 limited in providing key performance features of surfactants, such as high solubility, easy
handling and good wetting.

Hydrophobes can also be synthesized from petrochemical or coal-derived raw
materials. Synthetic hydrophobes include the linear versions that are functionally
equivalent to the linear hydrophobes derived from natural oils and fats. One advantage of
25 synthetic hydrophobes is the flexibility of creating various branching structures by using
different chemistries and processes. In general, branched hydrophobes help afford
surfactants with better handling properties, less stable foam, and enhanced wettability,
which are highly desirable features in many applications. The highly branched structure
of the hydrophobe however may cause poor surfactant biodegradability. It is believed
30 that a lightly branched hydrophobe may provide a favorable balance between high
performance and ready biodegradability for the corresponding surfactant.

Current processes for generating lightly branched surfactants require multiple
steps to obtain the desired branching. In addition, such processes typically require the use
of more than one starting monomer. Thus, there is a need for a process for preparing
35 surfactants with the same ability to reduce surface tension as the surfactants produced by

the current processes, but in fewer steps. Furthermore, there is a need for a process for preparing surfactants from only one starting monomer.

BRIEF SUMMARY

5 In one aspect, a process is provided comprising combining at least one olefin and at least one coordination-insertion catalyst and, optionally, an alpha-olefin, wherein the coordination-insertion catalyst is a metal-ligand complex wherein the metal is selected from zirconium, hafnium and titanium, and has an ethylene/octene reactivity ratio up to 20 at an operating reactor temperature, and a kinetic chain length up to 20 monomer units;
10 under conditions such that at least one oligomer product is formed. The oligomer product includes a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches, wherein the branches are located on average more than one carbon away from each end of the main carbon chain in more than 20% of oligomer product molecules, wherein the branches are situated at a
15 second carbon relative to an unsaturated end of the main carbon chain in less than 40% of the oligomer product molecules, and wherein the oligomer product contains greater than 50% vinyl olefin. The process further comprises fractionating the oligomer product to produce a fractionated oligomer product, such that the average carbon number of the fractionated oligomer product is between 8 and 28; and hydroformylating the fractionated
20 oligomer product to produce an aldehyde product or sulfonating the fractionated oligomer product to produce a sulfonated surfactant product.

 In another aspect, a process comprises combining at least one olefin and at least one coordination-insertion catalyst and, optionally, an alpha-olefin, wherein the coordination-insertion catalyst is a metal-ligand complex wherein the metal is selected
25 from zirconium, hafnium and titanium, and has an ethylene/octene reactivity ratio up to 20 at an operating reactor temperature, and a kinetic chain length up to 20 monomer units; under conditions such that at least one oligomer product is formed. The oligomer product includes a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches, wherein the branches are
30 located on average more than one carbon away from each end of the main carbon chain in more than 20% of oligomer product molecules, wherein the branches are situated at a second carbon relative to an unsaturated end of the main carbon chain in less than 40% of the oligomer product molecules, and wherein the oligomer product contains greater than 50% vinyl olefin. The process further comprises fractionating the oligomer product to

produce a fractionated oligomer product, such that the average carbon number of the fractionated oligomer product is between 8 and 28; hydroformylating the fractionated oligomer product to produce an aldehyde product; and hydrogenating the aldehyde product to produce an alcohol product.

5 In another aspect, an alcohol product is provided, comprising a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches, wherein the branches are located more than one carbon away from each end of the main carbon chain in more than 20% of alcohol product molecules.

10 In yet another aspect, a lightly branched surfactant product is provided, comprising a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches, wherein the branches are located more than one carbon away from each end of the main carbon chain in more than 20% of surfactant product molecules.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Figure 1 is a formula drawing of a coordination-insertion catalyst of the formula 2',2'''-(ethane-1,2-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)-zirconiumdimethyl.

20 Figure 2 is a formula drawing of a coordination-insertion catalyst of the formula 3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-2'-(2-(((3'-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5-fluoro-2'-hydroxy-5'-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-yl)oxy)ethoxy)-3',5'-difluoro-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)-zirconiumdimethyl.

25 Figure 3 is a formula drawing of a coordination-insertion catalyst of the formula 3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-2'-(2-(((3'-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3,5-difluoro-2'-hydroxy-5'-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-yl)oxy)ethoxy)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)-zirconiumdimethyl.

Figure 4 is a formula drawing of a coordination-insertion catalyst of the formula 2',2'''-(ethane-1,2-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3',5'-difluoro-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)-hafniumdimethyl.

30 Figure 5 is a formula drawing of a coordination-insertion catalyst of the formula 2',2'''-(ethane-1,2-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)-hafniumdimethyl.

Figure 6 is a formula drawing of a coordination-insertion catalyst of the formula 6',6'''-(ethane-1,2-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-fluoro-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)-hafniumdimethyl.

Figure 7 is a formula drawing of a coordination-insertion catalyst of the formula 2',2'''-(ethane-1,2-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3',5'-difluoro-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)-zirconiumdimethyl.

Figure 8 is formula drawing of an organophosphorus ligand, tris(2,4-di-tert-butylphenyl) phosphite (L).

Figure 9 is a reaction scheme for the preparation of 2-(2-bromoethoxy)-1,5-difluoro-3-iodobenzene.

Figure 10 is a reaction scheme for the preparation of 2-(2-(2,4-difluoro-6-iodophenoxy)ethoxy)-5-fluoro-1-iodo-3-methylbenzene.

Figure 11 is a reaction scheme for the preparation of 3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-2'-(2-((3'-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3,5-difluoro-2'-hydroxy-5'-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-yl)oxy)ethoxy)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol.

Figure 12 is a reaction scheme for the preparation of (3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-2'-(2-((3'-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3,5-difluoro-2'-hydroxy-5'-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-yl)oxy)ethoxy)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)dimethyl-zirconium.

DETAILED DESCRIPTION

This invention provides a new process to produce lightly mid-branched olefins and alcohols as hydrophobes for surfactants, in which majority of the mid-branched groups is ethyl or higher alkyl, at least 50% of the branches are ethyl or higher alkyl, and there is no (< 1%) terminal isopropyl type of branch.

The present process is advantageous in that it generates lightly branched surfactants for improved performance while maintaining ready biodegradability. Furthermore, the process provides significant cost advantage since (1) it generates the desired branching structure in one step to the oligomer, without further processing, and (2) can be prepared from only one monomer, such as ethylene.

The process comprises several steps: (1) formation of a lightly branched ethylene oligomer, (2) formation of a hydrophobe (in some embodiments, the hydrophobe is the ethylene oligomer itself), and (3) formation of a surfactant product. The lightly branched hydrophobes may be prepared first via ethylene oligomerization, generating a mixture of lightly branched olefins, which are then (1) converted to alcohols, then (2a) alkoxyated to generate nonionic surfactants, (2b) first ethoxylated or alkoxyated then sulfated to

generate anionic ethoxysulfate or alkoxysulfate surfactants or (2c) sulfated to generate sulfated surfactants. The lightly branched hydrophobe may also comprise the oligomeric lightly branched olefin which is then (3) directly converted to anionic sulfonated surfactants via sulfonation, respectively.

5 The preparation of the oligomer involves (1) oligomerization of the olefin using a catalyst and appropriate process conditions to make oligomeric products that approximate a Schulz-Flory distribution of oligomeric products, and (2) fractionation to obtain the desired fraction to generate the hydrophobe or fractionated oligomer product, such that the average carbon number of the fraction is between C8 and C28. Preferably, the
10 average carbon number of the fractionated oligomer product may be between C8 and C10, between C8 and C12, between C8 and C14, between C10 and C12, between C10 and C14, between C10 and C16, between C12 and C14, between C12 and C16, between C14 and C16, between C14 and C18, or between C16 and C18. When a carbon number is given, it means a distribution of molecules averaging that carbon number. For example
15 C12 means a distribution of molecules averaging twelve carbon atoms.

 The starting olefin may be ethylene alone, or a proportion of an alpha-olefin comonomer may be included along with ethylene. The starting olefin may also be any terminal olefin, for example, linear olefins. If an alpha-olefin is to be included, it may be selected from, in non-limiting example, linear alpha-olefins having from 3 to 12 carbons,
20 such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, and combinations thereof.

 The starting olefin mixture may contain three types of olefins: olefins with vinyl groups, olefins with vinylidene groups, and olefins with vinylene groups. The olefin mixture may comprise greater than 50% olefins with vinyl groups, preferably between
25 about 70% and 80% olefins with vinyl groups. The olefin mixture may also comprise about 20% olefins with vinylidene groups and about 5% olefins with vinylene groups. Preferably vinylidene group is 1,1-ethenediyl.

 Notwithstanding the above, it is preferred that only a minor amount of alpha-olefin is included, if any. That amount preferably ranges from 0 to 30 mol%; more preferably from 0 to 25 mol%; still more preferably from 0 to 20 mol%; yet more preferably from 0 to 10 mol%; and most preferably from 0 to 5 mol%. The amount of added alpha-olefin is most commonly preferred to be 0 mol% because added alpha-olefins tend to be more costly than the spectrum of alpha-olefins that are created *in-situ*.
30 While ethylene feed streams often have a small fraction (less than 1 mol%) of alpha-

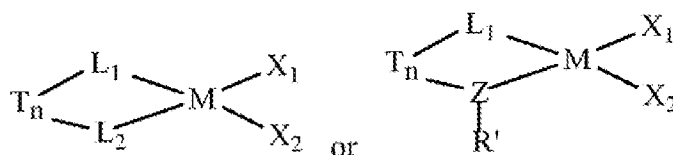
olefin monomer impurities such as propylene, it is expected that such would have no significant detrimental effect on process operation or oligomer properties.

In the inventive process the selected starting olefin or olefins, is/are contacted with a suitable coordination-insertion catalyst. As the term is used here, “coordination-
 5 insertion” means that the catalysts are capable of consecutively inserting unsaturated monomers, with the result that previously unsaturated carbons in the monomers and the oligomer become the backbone of a new oligomer. This catalyst may be selected, in one
 10 embodiment, from a wide variety of metal-ligand complexes. Those skilled in the art will be aware that catalyst performance varies with process temperature and also may vary with reaction mixture composition and conversion. Preferred catalysts are those
 15 exhibiting an activity level of 100,000 grams of oligomer per gram of catalyst metal (g/g cat). Also preferred are catalysts capable of producing a chain termination rate that results in product oligomer of a desired molecular weight and having a high fraction, preferably at least 25 %, more preferably at least 50 %, and most preferably at least 75 %, of vinyl groups.

Kinetic chain length is also important in identifying particularly suitable catalysts for the present invention. Kinetic chain length is defined as the average number of monomeric repeat units incorporated by a catalyst before a chain transfer or chain growth terminating reaction.

20 Examples of suitable coordination-insertion catalysts may generally include, in certain non-limiting embodiments, metal-ligand complexes including any of the metals zirconium, hafnium, or titanium, and preferably zirconium or hafnium. Among these catalysts may be certain metallocene catalysts, including certain constrained geometry catalysts, and bis-phenylphenoxy catalysts, provided that the selected catalyst meets the
 25 ethylene/octene reactivity ratio and kinetic chain length requirements as defined hereinabove.

The metallocene compounds useful herein are cyclopentadienyl derivatives of titanium, zirconium, and hafnium. These metallocenes (e.g., titanocenes, zirconocenes and hafnocenes) may be represented by the following formula:



formula (I)

formula (II)

wherein M is the metal center, and is a Group 4 metal, preferably titanium, zirconium or hafnium;

5 T is an optional bridging group which, if present, in preferred embodiments is selected from dialkylsilyl, diarylsilyl, dialkylmethyl, ethylenyl (-CH₂-CH₂-) or hydrocarbylethylenyl wherein one, two, three or four of the hydrogen atoms in ethylenyl are substituted by hydrocarbyl, where hydrocarbyl can be independently C₁ to C₁₆ alkyl or phenyl, tolyl, xylyl and the like, and when T is present, the catalyst represented can be in a racemic or a meso form;

10 L₁ and L₂ are the same or different cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl rings, optionally substituted, that are each bonded to M, or L₁ and L₂ are the same or different cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, which are optionally substituted, in which any two adjacent R groups on these rings are optionally joined to form a substituted or unsubstituted, saturated, partially unsaturated, or aromatic
15 cyclic or polycyclic substituent;

Z is nitrogen, oxygen or phosphorus;

R' is a cyclic linear or branched C₁ to C₄₀ alkyl or substituted alkyl group; and

X₁ and X₂ are, independently, hydrogen, halogen, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl
20 radicals, silylcarbyl radicals, substituted silylcarbyl radicals, germylcarbyl radicals, or substituted germylcarbyl radicals; or both X are joined and bound to the metal atom to form a metallocycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand.

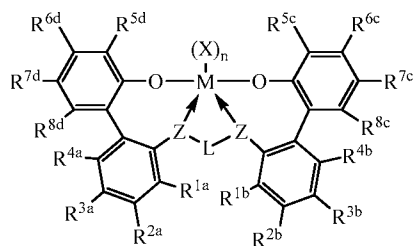
Among the metallocene compounds which can be used in this invention are
25 stereorigid, chiral or asymmetric, bridged or non-bridged, or so-called "constrained geometry" metallocenes. See, for example and methods for preparation, U.S. Patent No. 4,892,851; U.S. Patent No. 5,017,714; U.S. Patent No. 5,132,281; U.S. Patent No. 5,155,080; U.S. Patent No. 5,296,434; U.S. Patent No. 5,278,264; U.S. Patent No. 5,318,935; U.S. Patent No. 5,969,070; U.S. Patent No. 6,376,409; U.S. Patent No.
30 6,380,120; U.S. Patent No. 6,376,412; WO-A- (PCT/US92/10066); WO 99/07788; WO-A-93/19103; WO 01/48034; EP-A2-0 577 581; EP-A1-0 578 838; WO 99/29743, and also the academic literature, e.g., "The Influence of Aromatic Substituents on the Polymerization Behavior of Bridged Zirconocene Catalysts," Spaleck, W., *et al.*, *Organometallics* 1994, Vol. 13, pp. 954-963; "ansa-Zirconocene Polymerization Catalysts

with Annelated Ring Ligands—Effects on Catalytic Activity and Polymer Chain Lengths," Brintzinger, H., *et al.*, *Organometallics* 1994, Vol. 13, pp. 964-970; "Constrained geometry complexes—Synthesis and applications," Braunschweig, H., *et al.*, *Coordination Chemistry Reviews* 2006, 250, 2691–2720; and documents referred to
5 therein.

The process uses as catalysts a particular subset of the bis-phenylphenoxy compounds described in US20110282018. These are termed metal-ligand complex catalysts that combine a transition metal center and any of a wide variety of bis-phenylphenoxy-containing ligands conforming to formula (III), provided that the
10 following limitations are met. First, the bridge, L, between the Z moieties is from 2 atoms to 8 atoms in length. Second, the Z moieties may be selected independently from oxygen, sulfur, phosphorus(C₁₋₄₀)hydrocarbylene, and nitrogen(C₁₋₄₀)hydrocarbylene. Third, the ligand has a halogen atom located in at least one of the positions on the benzene rings in the R^{1a} and/or R^{1b} position of formula (III), i.e., at a position, or
15 positions, that is/are ortho to the bridged Z moieties. The term "halogen atom" means a fluorine atom radical (F), chlorine atom radical (Cl), bromine atom radical (Br), or iodine atom radical (I). Preferably each halogen atom independently is a Br, F, or Cl radical, and more preferably a F or Cl radical. Fourth, the metal M is preferably selected from zirconium (Zr), hafnium (Hf), and titanium (Ti), and more preferably is either Zr or Hf.

The members of the catalyst family defined are generally convenient to prepare and may operate efficiently and over a wide thermal operating range, in some non-limiting embodiments withstanding temperatures exceeding 200 °C. Such catalysts may, themselves, be of effectively any molecular weight (M_w), but in certain non-limiting embodiments preferably range from 200 Daltons (Da) to 5,000 Da. Preparation
25 may include, in non-limiting embodiments, construction of a suitable ligand structure followed by its reaction with a salt of the desired transition metal, which effects the desired metal-ligand complexation. Additional and highly detailed preparation information may be found in, e.g., the previously referenced US20110282018; US Serial Number PCT/US2012/0667700, filed November 28, 2012, claiming priority to
30 US Provisional Application 61/581,418, filed December 29, 2011; and US Serial Number 13/105,018, filed May 11, 2011, Publication Number 20110282018, claiming priority to US Provisional Application 61/487,627, filed March 25, 2011. Those skilled in the art will recognize that similar and analogous processes may be used to prepare other useful bis-phenylphenoxy compounds falling within the given general definition.

In certain embodiments, such suitable catalysts may generally include, in more specific but non-limiting embodiments, metal-ligand complexes of formula (III)



formula (III)

- 5 wherein M is titanium, zirconium, or hafnium, each independently being in a formal oxidation state of +2, +3, or +4; n is an integer of from 0 to 3, wherein when n is 0, X is absent; each X independently is a monodentate ligand that is neutral, monoanionic, or dianionic, or two X are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic; X and n are selected such that the metal-ligand complex is, overall, neutral; each Z is independently O, S, N(C₁-C₄₀)hydrocarbyl, or P(C₁-C₄₀)hydrocarbyl; L is (C₁-C₄₀)hydrocarbylene or (C₁-C₄₀)heterohydrocarbylene, wherein the (C₁-C₄₀)hydrocarbylene has a portion that comprises a 2- to 8-atom linker backbone linking the Z moieties and the (C₁-C₄₀)heterohydrocarbylene has a portion that comprises a 2- to 8-atom linker backbone linking the Z moieties, wherein each atom of
- 10 the 2- to 8-atom linker of the (C₁-C₄₀)heterohydrocarbylene independently is a carbon atom or a heteroatom, wherein each heteroatom independently is O, S, S(O), S(O)₂, Si(R^C)₂, Ge(R^C)₂, P(R^P), or N(R^N), wherein independently each R^C is unsubstituted (C₁-C₁₈)hydrocarbyl or the two R^C are taken together to form a (C₂-C₁₉)alkylene, each R^P is unsubstituted (C₁-C₁₈)hydrocarbyl; and each R^N is unsubstituted (C₁-C₁₈)hydrocarbyl, a
- 15 hydrogen atom or absent; R^{1a}, R^{1b}, or both is a halogen atom; R^{2a} and R^{2b} independently is a hydrogen, (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, N(R^N)₂, NO₂, OR^C, SR^C, Si(R^C)₃, Ge(R^C)₃, CN, CF₃, F₃CO, halogen atom; and each of the others of R^{1a}, R^{2a}, R^{1b}, and R^{2b} independently is a hydrogen, (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, N(R^N)₂, NO₂, OR^C, SR^C, Si(R^C)₃, CN, CF₃, F₃CO or halogen atom; each of R^{3a}, R^{4a}, R^{3b},
- 20 R^{4b}, R^{6c}, R^{7c}, R^{8c}, R^{6d}, R^{7d}, and R^{8d} independently is a hydrogen atom; (C₁-C₄₀)hydrocarbyl; (C₁-C₄₀)heterohydrocarbyl; Si(R^C)₃, Ge(R^C)₃, P(R^P)₂, N(R^N)₂, OR^C, SR^C, NO₂, CN, CF₃, RCS(O)-, RCS(O)₂-, (RC)₂C=N-, RCC(O)O-, RCOC(O)-, RCC(O)N(R)-, (RC)₂NC(O)- or halogen atom; each of R^{5c} and R^{5d} is independently a
- 25 (C₆-C₄₀)aryl or (C₁-C₄₀)heteroaryl; and each of the aforementioned aryl, heteroaryl, hydrocarbyl, heterohydrocarbyl, hydrocarbylene, and heterohydrocarbylene groups is
- 30

independently unsubstituted or substituted with one or 5 more substituents R^S; and each R^S is independently a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C₁-C₁₈)alkyl, F₃C-, FCH₂O-, F₂HCO-, F₃CO-, R₃Si-, R₃Ge-, RO-, RS-, RS(O)-, RS(O)₂-, R₂P-, R₂N-, R₂C=N-, NC-, RC(O)O-, ROC(O)-, RC(O)N(R)-, or R₂NC(O)-, or two of the R^S are taken together to form an unsubstituted (C₁-C₁₈)alkylene, wherein each R independently is an unsubstituted (C₁-C₁₈)alkyl.

A wide variety of additional substitution may be present at all other carbons of the at least four phenyl rings included within the catalyst of formula (III) or such may have simply hydrogen. Some examples of preferred R^{5c} and R^{5d} substituents include 3,5-di(tertiary-butyl)phenyl; 3,5-diphenylphenyl; 1-naphthyl, 2-methyl-1-naphthyl; 2-naphthyl; 1,2,3,4-tetrahydronaphthyl; 1,2,3,4-tetrahydro-naphth-5-yl; 1,2,3,4-tetrahydronaphth-6-yl; 1,2,3,4-tetrahydroanthracenyl; 1,2,3,4-tetrahydroanthracen-9-yl; 1,2,3,4,5,6,7,8-octahydroanthracenyl; 1,2,3,4,5,6,7,8-octahydroanthracen-9-yl; phenanthren-9-yl; 1,2,3,4,5,6,7,8-octahydrophenanthren-9-yl; 2,3-dihydro-1*H*-inden-6-yl; naphthalene-2-yl; 1,2,3,4-tetrahydronaphthalen-6-yl; 1,2,3,4-tetrahydronaphthalen-5-yl; anthracen-9-yl; 1,2,3,4-tetrahydroanthracen-9-yl; 1,2,3,4,5,6,7,8-octahydro-anthracen-9-yl; 2,6-dimethylphenyl; 2,6-diethylphenyl; 2,6-bis(1-methylethyl)phenyl; 2,6-diphenyl-phenyl; 3,5-dimethylphenyl; 3,5-bis(tri-fluoromethyl)phenyl; 3,5-bis(1-methylethyl)phenyl; 3,5-bis(1,1-dimethylethyl)phenyl; 3,5-diphenyl-phenyl); 2,4,6-trimethylphenyl; and 2,4,6-tris(1-methylethyl)phenyl); 1-methyl-2,3-dihydro-1*H*-inden-6-yl; 1,1-dimethyl-2,3-dihydro-1*H*-inden-6-yl; 1-methyl-1,2,3,4-tetrahydro-naphthalen-5-yl; 1,1-dimethyl-1,2,3,4-tetrahydronaphthalen-5-yl. 1,2,3,4-tetrahydroquinolinyl; isoquinolinyl; 1,2,3,4-tetrahydroisoquinolinyl; carbazolyl; 1,2,3,4-tetrahydrocarbazolyl; 1,2,3,4,5,6,7,8-octahydrocarbazolyl; 3,6-di(tertiary-butyl)-carbazolyl; 3,6-di(tertiary-octyl)-carbazolyl; 3,6-diphenylcarbazolyl; 3,6-bis(2,4,6-trimethylphenyl)-carbazolyl; 3,6-di(tertiary-butyl)-carbazol-9-yl; 3,6-di(tertiary-octyl)-carbazol-9-yl; 3,6-diphenylcarbazol-9-yl; 3,6-bis(2,4,6-trimethylphenyl)-carbazol-9-yl; quin-olin-4-yl; quinolin-5-yl; quinolin-8-yl; 1,2,3,4-tetrahydroquinolin-1-yl; isoquinolin-1-yl; isoquinolin-4-yl; iso-quinolin-5-yl; isoquinolin-8-yl; 1,2,3,4-tetrahydroisoquinolin-2-yl; 1*H*-indol-1-yl; 1*H*-indolin-1-yl; 9*H*-carbazol-9-yl; 1,2,3,4-tetrahydrocarbazolyl-9-yl; 1,2,3,4,5,6,7,8-octahydrocarbazolyl-9-yl; 4,6-bis(1,1-dimethylethyl)pyridine-2-yl; 4,6-diphenylpyridin-2-yl; 3-phenyl-1*H*-indol-1-yl; 3-(1,1-dimethylethyl)-1*H*-indol-1-yl; 3,6-diphenyl-9*H*-carbazol-9-yl; 3,6-

bis[2',4',6'-tris(1,1-dimethylphenyl)]-9*H*-carbazol-9-yl; 3,6-bis(1,1-dimethyl-ethyl)-9*H*-carba- zol-9-yl.

In more particular embodiments, the catalyst may be selected from the compounds represented by formulas (IV) to (X), shown in Figures 1-7. Additional moieties denoted
5 by abbreviations include Me (methyl) and t-Bu (*tert*-butyl).

In carrying out the process of the invention it is desirable that the contact between the olefin(s) and the coordination-insertion catalyst occur in a continuously-fed backmixed reactor zone. As the term is used herein, "backmixed reactor zone" refers to an environment wherein a reaction product is intermingled with unconverted reactor
10 feeds. A continuous stirred tank reactor is preferred for this purpose, while it is noted that plug-flow reactors are specifically designed to prevent back-mixing. However, a loop reactor can accomplish a variable degree of backmixing by recycling a portion of reactor effluent to the feed of a plug-flow zone, with the recycle ratio moderating the degree of backmixing. Thus, plug-flow reactors are non-preferred, while a loop reactor with a plug
15 flow zone is preferred. In the inventive process backmixing ensures reaction of already-produced oligomers with new feedstock, e.g., ethylene. It is this continuous contact that enables the oligomers to become branched via repeated olefin insertion.

Conditions under which the contact occurs in the continuously-fed, backmixed reactor zone may include a temperature desirably ranging from 0 °C to 250 °C, more
20 desirably from 25 °C to 200 °C, and most desirably from 50 °C to 180 °C; an ethylene partial pressure desirably ranging from 15 psi (pounds per square inch, 103 kilopascals, kPa) to 500 psi (3450 kPa), more desirably from 30 psi (207 kPa) to 300 psi (2070 kPa), and most desirably from 50 psi (345 kPa) to 200 psi (1380 kPa); and a residence time desirably ranging from 1 minute (min) to 120 min, more desirably from 5 min to 60 min,
25 and most desirably from 10 min to 30 min. A reactor system may be comprised of many low residence time reaction zones or a few high residence time reaction zones. Nonetheless, those skilled in the art will easily understand that alteration of parameters may be employed for reasons of convenience, alteration of yield, avoidance of undesirable side products or degradation, and the like.

In order to prepare the homo-oligomers or co-oligomers of the invention, the
30 starting olefin and/or the selected alpha-olefin monomer(s) is/are fed into a suitable reactor, for batch, semi-continuous, or continuous production, wherein such olefin(s) will come into contact with the catalyst. In the case of preparation of co-oligomers, it is noted that the ethylene/alpha-olefin reactivity ratio is distinct for any given catalyst and

provides a methodology to determine the amount of alpha-olefin that will be required to attain a targeted co-oligomer composition. Reactivity ratios may be determined using well known theoretical techniques or empirically derived from actual polymerization data. Suitable theoretical techniques are disclosed, for example, in B. G. Kyle, *Chemical and*
5 *Process Thermodynamics*, 3rd ed., Prentice-Hall (1999) and in Soave, Giorgio. "Equilibrium constants from a modified Redlich-Kwong equation of state", *Chemical Engineering Science*, Vol. 27, Issue 6, June 1972, pp. 1197-1203. Commercially available software programs may be used to assist in deriving reactivity ratios from experimentally derived data. One example of such software is *Aspen Plus* from Aspen Technology, Inc.,
10 Ten Canal Park, Cambridge, Massachusetts 02141-2201, USA.

The metal-ligand complex discussed above is rendered catalytically active by contacting it to, or combining it with, the activating co-catalyst or by using an activating technique such as those that are known in the art for use with metal-based olefin polymerization reactions. Suitable activating co-catalysts for use herein include alkyl
15 aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds, including but not limited to the use of such compounds under oxidizing conditions. A suitable activating technique may be bulk electrolysis. Combinations of one or more of the foregoing activating co-catalysts and/or techniques are also contemplated. The term
20 "alkyl aluminum" means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Alumoxanes and their preparations are described in, for additional understanding, US 6,103,657. Examples of preferred polymeric or oligomeric alumoxanes are methylalumoxane, triisobutylaluminum-modified methylalumoxane, and
25 isobutylalumoxane. Such may be employed such that the ratio of total number of moles of the one or more metal-ligand complexes of formula (III) to total number of moles of activating co-catalyst is preferably from 1:10,000 to 100:1.

A variety of homo-oligomerization or co-oligomerization conditions and combinations thereof may be employed, according to the starting materials, nature of the
30 reaction (batch, semi-continuous, or continuous), apparatus set-up, desired products, and so forth. However, in general, suitable oligomers or co-oligomers of the invention may be produced using one or more of the specified catalyst selections at a temperature ranging from 20 degrees Celsius (°C) to 220 °C, and preferably 100 °C to 200 °C, for a time preferably ranging from 10 minutes (min) to 300 min. Other parameters, such as

pressure, may be controlled within ranges known to those skilled in the art and are not generally considered to be critical to practice of the present invention, but may be varied according to the desires and needs of the practitioner. It is usually preferred to carry out the process as a continuous process, using at least one continuous stir tank reactor
5 (CSTR) or other suitable vessel(s).

The oligomerization process generates an oligomer (in some embodiments the hydrophobe) with a specific structure. In the desired fraction, the main carbon chain contains an average of preferably between 0.5 and 2.5 branches. The branches are predominantly (greater than 50%) ethyl branches, preferably greater than 80% ethyl
10 branches. Finally, the branches are located more than one carbon away from each end of the main chain in more than 20% of the molecules on average, preferentially in more than 40% on average. Furthermore, the branches (on the oligomer) are situated at the C2 carbon (relative to the unsaturated chain end) in less than 40% of the molecules on average, preferably in less than 25% on average. Finally, the oligomer may contain a
15 vinyl olefin, a vinylidene olefin, or a vinylene olefin. The oligomer product contains greater than 50% vinyl olefin, preferably greater than 70% vinyl olefin.

The preparation of the alcohol is carried out via hydroformylation followed by hydrogenation. Hydroformylation/hydrogenation to generate a primary alcohol may add more branching (i.e., a methyl branch at the C2 position relative to the alcohol) to the
20 olefins oligomer with vinyl groups depending on the selectivity of the hydroformylation catalyst (i.e. whether hydroformylation occurs mostly at the C1 position of the olefin (little added branches relative to the corresponding olefin oligomer) or at the C2 position of the olefin (methyl branch introduced)). A rhodium catalyst with an organophosphorus ligand may be used for hydroformylation of the oligomer product. The
25 organophosphorus ligand may be, for example, the one shown in Figure 8 for tris(2,4-di-*tert*-butylphenyl) phosphite (L).

During hydroformylation, different types of olefins lead to various structures for related aldehydes. The aldehydes contain one carbon atom more than the starting olefins.

Subsequent hydrogenation of the aldehydes to the corresponding alcohols may be
30 performed with hydrogen in the presence of a hydrogenation catalyst. For example, hydrogenation can be performed using platinum group metal catalysts or a nickel catalyst. The catalysts can be supported on activated carbon, silica or alumina or unsupported.

The alcohol product may comprise a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches,

wherein the branches are located more than one carbon away from each end of the main carbon chain in more than 20% of alcohol product molecules.

The process may further include the reaction of the alcohol with an alkylene oxide in the presence of a catalyst to generate nonionic alkoxyated surfactants. The alkylene oxide may be any epoxide with carbon numbers ranging from C2-C12. Preferably, the
5 alkylene oxide is ethylene oxide, 1,2-epoxypropane, or 1,2-epoxybutane. Further, the alkoxylation step may involve alkoxylation of more than one type of alkylene oxide, as is known in the art. Also, each initiator may be alkoxyated by 1 to 100 alkylene oxide molecules, preferably by 1 to 20 alkylene oxide molecules, which may be all the same or
10 a mixture of different alkylene oxides in a random or block configuration. The alkoxylation catalyst or catalyst precursor may be any catalyst known for alkoxylation reactions (as described in Alkylene Oxides and Their Polymers, Surfactant Science Series, Vol. 35, Ed. by F. E. Bailey, Jr. and Joseph V. Koleske, Marcel Dekker, Inc., New York, 1990). Preferred examples are alkali metal hydroxides, like sodium hydroxide,
15 potassium hydroxide, alkali earth metal hydroxide, alkali metals, like sodium or potassium, potassium hydride, and DMC (double metal cyanide) catalysts. The alkoxylation reaction may be conducted in a solvent or without solvent. The solvent can be any solvent suitable for use in alkoxylation reactions. It is preferable that the solvent be capable of dissolving the reactants. Examples of solvents include dimethoxyethane,
20 THF, 1,4-dioxane, diglyme, and tetraglyme.

The nonionic alkoxyated surfactants may further be sulfated to produce an anionic ether sulfate surfactant product. In an alternative embodiment, the alcohol may be sulfated to produce an anionic sulfate surfactant product.

In an alternative embodiment, instead of hydroformylating the oligomer olefin, the
25 oligomer olefin may instead be sulfonated to generate anionic sulfonated surfactants. Due to the composition of the oligomer (i.e. vinyl, vinylidene and vinylene olefins), the product is a mixture of lightly branched alpha olefin sulfonates (AOS) and internal olefin sulfonates (IOS).

The final lightly branched surfactant product may comprise a main carbon chain
30 containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches, wherein the branches are located more than one carbon away from each end of the main carbon chain in more than 20% of surfactant product molecules.

The final nonionic products (nonionic surfactants) should be able to reduce the surface tension of water. For a 0.1 wt% aqueous solution, the equilibrium surface tension should be less than 50 mN/m and the contact angle on a PTFE film should be less than 75 degrees. Further surfactant performance requirements may be obtained in other similar applications for nonionic and anionic surfactants.

Possible applications of the nonionic and anionic surfactants generated include household and industrial cleaning, personal care, paints & coatings, emulsion polymerization, agriculture, oil & gas, textile process, food processing, lubricant and fuel additives, leather processing and mining.

10 EXAMPLES

Various examples are demonstrated.

Example 1: Ethylene Oligomerization Catalyst Preparation

Analytical Measurements

For ^{13}C NMR experiments, samples are dissolved in 10 mm NMR tubes in chloroform-d with 0.02 M $\text{Cr}(\text{acac})_3$ added. The typical concentration is 0.50 g/2.4 mL. The tubes are then heated in a heating block set at 50 °C. The sample tubes are repeatedly vortexed and heated to achieve a homogeneous flowing fluid. For samples with visible wax present, tetrachloroethane- d_2 is used as the solvent instead of chloroform-d, and the sample preparation temperature is 90 °C.

^{13}C NMR spectra are taken on a Bruker Avance 400 MHz spectrometer equipped with a 10 mm cryoprobe. The following acquisition parameters are used: 5 seconds relaxation delay, 90 degree pulse of 13.1 μs , 256 scans. The spectra are centered at 80 ppm with a spectral width of 250 ppm. All measurements are taken without sample spinning at either 50 °C (for chloroform solutions) or 90 °C (for tetrachloroethane solutions). The ^{13}C NMR spectra are referenced to 77.3 ppm for chloroform or 74.5 ppm for tetrachloroethane.

Catalyst Synthesis

Preparation of 2-(2-bromoethoxy)-1,5-difluoro-3-iodobenzene

16.55g (64.65 mmol) of 2-iodo-4,6-difluorophenol, 86.232g (459.02 mmol) of 1,2-dibromoethane, 29.5g (213.35 mmol) of potassium carbonate and acetonitrile (85mL) is placed in a 250mL round bottom flask. The reaction is shown in Figure 9. The suspension is stirred at 60 °C under nitrogen overnight. The reaction is filtered and the organic solution is concentrated. The residue is run through a 220g ISCO column

eliminating one impurity and the remaining 1,2-dibromoethane. The product is 18.22g of a colorless oil (77.6% Yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 (ddd, *J* = 7.4, 3.0, 2.0 Hz, 1H), 6.89 (ddd, *J* = 10.7, 8.1, 2.9 Hz, 1H), 4.34 – 4.29 (m, 2H), 3.70 – 3.65 (m, 2H). ¹³C NMR (101 MHz, cdcl₃) δ 159.63, 159.52, 157.03, 152.62, 121.06, 105.73, 91.48, 73.44, 73.40, 28.97. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -114.47 (tt, *J* = 7.6, 3.4 Hz), -122.18 (dd, *J* = 10.7, 3.0 Hz).

Preparation of 2-(2-(2,4-difluoro-6-iodophenoxy)ethoxy)-5-fluoro-1-iodo-3-methylbenzene

150mL of acetone, 3.768g (27.261 mmol) of potassium carbonate, 6.00g (16.036 mmol) of 1-(2-bromoethoxy)-2,4-difluorobenzene, and 4.041g (16.036 mmol) of 2-iodo-4-fluoro-6-methylphenol is added to a 250mL round bottom flask under nitrogen. The reaction is shown in Figure 10. The solution is heated to reflux overnight. Gas chromatography (GC) confirms full conversion to product, so the reaction mixture is cooled, filtered and the filtrate was concentrated. The residue is dissolved in methylene chloride, washed with brine, dried over magnesium sulfate, and recrystallized from acetonitrile. The solid is then run through a 330g ISCO column using a hexanes:ethyl acetate gradient. The oil is then recrystallized to yield 4.23g of the product (49.4% Yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 (ddt, *J* = 7.4, 3.0, 2.2 Hz, 2H), 6.93 – 6.86 (m, 2H), 4.44 (ddd, *J* = 6.0, 3.9, 1.0 Hz, 2H), 4.23 (ddd, *J* = 5.5, 4.2, 0.6 Hz, 2H), 2.40 (s, 3H).

¹³C NMR (101 MHz, cdcl₃) δ 159.80, 159.44, 159.33, 157.34, 156.96, 156.84, 155.30, 155.18, 153.20, 153.17, 152.78, 152.65, 143.73, 143.69, 143.61, 143.57, 133.59, 133.50, 123.51, 123.27, 121.27, 121.23, 121.03, 120.99, 118.08, 117.85, 91.47, 91.44, 91.36, 91.34, 91.14, 91.05, 72.90, 72.86, 71.53, 17.45, 17.44.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -115.24 (td, *J* = 7.7, 3.7 Hz), -117.55 – -117.74 (m), -122.11 (dt, *J* = 10.8, 2.7 Hz).

Preparation of 3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-2'-(2-((3'-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3,5-difluoro-2'-hydroxy-5'-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-yl)oxy)ethoxy)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol.

1,2-dimethoxyethane (67 mL) is added to 4.00g (5.725 mmol) of 3,6-di-tert-butyl-9-(2-((tetrahydro-2H-pyran-2-yl)oxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(2,4,4-trimethylpentan-2-yl)phenyl)-9H-carbazole, 1.482g (2.719 mmol) of 2-(2-(2,4-

5 difluoro-6-iodophenoxy)ethoxy)-5-fluoro-1-iodo-3-methylbenzene, a solution of NaOH (.6870g) in water (16mL) and THF (40 mL) in a three neck 250mL round bottom flask. The reaction is shown in Figure 11. The reaction mixture is sparged with N₂ for 15 minutes then .1322g (.1145 mmol) of Pd(PPh₃)₄ is added. Upon addition the reaction mixture is heated to 85 °C overnight. The reaction mixture is then concentrated with the residue being taken up in methylene chloride (200 mL), washed with brine (200 mL), dried over anhydrous magnesium sulfate, filtered through a pad of silica gel, and concentrated to afford crude protected ligand. THF (50mL), methanol (50mL) and PTSA is added to the crude protected ligand until the solution is acidic. The solution is heated to 60 °C overnight, then cooled and concentrated. The crude ligand is taken up in methylene chloride (100mL), washed with brine (100mL), dried with anhydrous magnesium sulfate, filtered through a pad of silica gel then concentrated to afford ligand as an off white crystalline powder. Thin layer chromatography (TLC) shows impurities, so the ligand is run through a 330g column using solid phase loading and a ethyl acetate: hexanes gradient. The appropriate fractions are concentrated and placed under vacuum overnight to afford 2.7g of white crystals (79.7% Yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.7 Hz, 4H), 7.43 – 7.16 (m, 9H), 7.06 – 6.79 (m, 8H), 6.06 (d, *J* = 1.7 Hz, 1H), 5.58 (d, *J* = 1.9 Hz, 1H), 4.04 (t, *J* = 4.8 Hz, 2H), 3.78 (t, *J* = 4.8 Hz, 2H), 2.04 (d, *J* = 1.8 Hz, 3H), 1.70 – 1.63 (m, 4H), 1.44 (dd, *J* = 8.6, 1.7 Hz, 36H), 1.28 (d, *J* = 27.3 Hz, 12H), 0.75 (s, 16H).

¹³C NMR (101 MHz, CDCl₃) δ 160.25, 159.14, 157.83, 156.82, 156.75, 156.70, 156.62, 149.78, 149.76, 147.60, 147.42, 143.33, 143.30, 143.13, 143.03, 142.55, 140.46, 140.43, 140.35, 140.31, 139.68, 139.43, 139.40, 134.36, 134.33, 134.26, 134.23, 133.94, 133.86, 133.04, 132.95, 128.78, 128.74, 127.52, 127.28, 126.17, 126.15, 125.42, 124.96, 124.93, 124.91, 124.68, 124.05, 123.74, 123.60, 123.56, 123.53, 123.40, 117.39, 117.17, 116.43, 116.35, 116.10, 115.87, 113.65, 113.62, 113.41, 109.32, 109.26, 104.73, 104.47, 104.24, 72.74, 72.70, 72.26, 57.03, 56.95, 38.22, 38.20, 34.74, 32.44, 32.42, 32.14, 32.10, 32.05, 31.93, 31.87, 31.69, 31.62, 31.52, 31.46, 30.38, 16.39.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -115.26 (dt, *J* = 8.7, 4.1 Hz), -117.94 (t, *J* = 8.7 Hz), -124.48 (dd, *J* = 11.1, 4.2 Hz).

Preparation of (3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-2'-(2-((3'-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3,5-difluoro-2'-hydroxy-5'-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-yl)oxy)ethoxy)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol)dimethyl-zirconium.

5

A 20 mL vial is charged with $ZrCl_4$ (0.119 g, 0.509 mmol) and toluene (10 mL) and cooled to $-35\text{ }^\circ\text{C}$. MeMgBr (3M solution in ether, 0.66 mL, 1.98 mmol) is added to the solution. The reaction is shown in Figure 12. The solution quickly turns to a dark color. After 5 min of stirring the solution is treated with a $-35\text{ }^\circ\text{C}$ toluene (7 mL) solution of 3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-2'-(2-((3'-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3,5-difluoro-2'-hydroxy-5'-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-yl)oxy)ethoxy)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol (0.615 g, 0.494 mmol). The solution is allowed to stir for 3 hours, then the solution is passed through a filter frit. The solids are washed with toluene and all volatiles are removed in vacuo leaving a white solid. The white solid is dissolved in hexanes and passed through a 0.45 micron frit. All volatiles are removed and the crude solid is checked by ^1H NMR and used without further purification. Yield 91% (0.610 g).

^1H NMR (400 MHz, C_6D_6) δ 8.21-8.40 (m, 4H), 7.96-8.00 (m, 1H), 7.85 (d, 1H), 7.61-7.72 (m, 3H), 7.48-7.50 (m, 2H), 7.28-7.34 (m, 3H), 7.17 (d, 1H), 6.86-7.10 (m, 3H), 6.65-6.68 (m, 1H), 6.19-6.22 (m, 1H), 3.76-3.77 (m, 2H), 2.65-2.73 (m, 2H), 1.54-1.62 (m, 4H), 1.50 (s, 9H), 1.49 (s, 9H), 1.35 (s, 9H), 1.31 (s, 9H), 1.18-1.29 (m, 12H), 0.99 (s, 3H), 0.80 (s, 9H), 0.76 (s, 9H), -0.76 (s, 3H), -0.96 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6) δ 155.9, 155.6 (d), 153.4, 153.1 (d), 148.5 (d), 148.1, 147.1, 142.1 (d), 137.4, 137.1, 136.9, 136.6, 135.7, 135.6, 134.6, 134.2, 134.1 (d), 134.0, 131.1 (dd), 130.9 (d), 123.9, 123.8, 123.0, 122.9, 121.5, 121.3, 120.1, 119.4, 119.3, 119.2, 118.3, 118.2, 117.0, 117.1, 112.6, 112.3, 111.5, 111.5, 111.2, 111.0, 110.5 (d), 108.7, 108.5, 107.6 (d), 105.5 (d), 103.9, 97.9 (d), 97.6 (d), 64.7, 64.6, 52.0, 51.7, 37.4, 36.4, 36.3, 32.9, 32.8, 29.5, 29.5, 29.4, 29.3, 27.1, 27.1, 27.0, 26.9, 26.9, 26.8, 26.7, 26.6, 26.5, 25.7 (br m), 17.5, 10.4, 8.9.

^{19}F NMR (376 MHz, C_6D_6) δ -110.55 (m), -115.33 (m), -119.54 (m).

Example 2: Ethylene Oligomerization

Semi-Batch Oligomerizations

Oligomerizations are conducted in a 2 L ParrTM batch reactor. The reactor is heated by an electrical heating mantle, and is cooled by an internal serpentine cooling coil containing cooling water. Both the reactor and the heating/cooling system are controlled

and monitored by a Camile™ TG process computer. The bottom of the reactor is fitted with a dump valve, which empties the reactor contents into a stainless steel dump pot, which is prefilled with a catalyst kill solution (typically 5 mL of an Irgafos™/Irganox™/toluene mixture).

5 The dump pot is vented to a 30 gallon blowdown tank, with both the pot and the tank N₂ purged. All chemicals used for oligomerization or catalyst makeup are run through purification columns to remove any impurities that may affect oligomerization. Liquid feeds such as alpha-olefin and solvents are passed through two columns, the first containing Al₂O₃ alumina, the second containing Q5, which is a copper reactant to scrub oxygen. Ethylene feed is passed through two columns, the first containing Al₂O₃ alumina and 4 Angstroms (Å) average pore size molecular sieves to remove water, the second containing Q5 reactant. The N₂, used for transfers, is passed through a single column containing Al₂O₃ alumina, 4 Å average pore size molecular sieves, and Q5 reactant.

10 The reactor is loaded first from the shot tank containing toluene. The shot tank is filled to the load set points by use of a lab scale to which the shot tank is mounted. After liquid feed addition, the reactor is heated up to the polymerization temperature set point. Ethylene is added to the reactor when at reaction temperature to maintain reaction pressure set point. Ethylene addition amounts are monitored by a micro-motion flow meter and integrated to give overall ethylene uptake after catalyst injection.

15 The catalyst and bis (octadecyl)methylammonium tetrakis(pentafluorophenyl) borate ([HNMe(C₁₈H₃₇)₂][B(C₆F₅)₄]) (BOMATPB) activator are mixed with the appropriate amount of purified toluene to achieve a desired molarity solution. The catalyst and activator are handled in an inert glove box, drawn into a syringe and pressure transferred into the catalyst shot tank. This is followed by three rinses of toluene, 5 mL each. Immediately after catalyst addition the run timer begins. Ethylene is then added continuously by the Camile™ to maintain reaction pressure set point in the reactor. If the ethylene uptake rate is low, then the headspace is purged, more catalyst and activator are added, and the ethylene pressure is re-established. After a designated time or ethylene uptake the agitator is stopped and the bottom dump valve opened to empty reactor contents to the dump pot. The dump pot contents are poured into a round bottom flask and all C8 and below volatiles were removed via rotary evaporation (80 °C/20 Torr).

Example 3: Fractionation

A Vigreux column and short path distillation head are equipped onto the round bottom flask and the crude product is first distilled at 50 °C/500 mTorr to remove the

~C10 components. Next, the heating bath is raised to 100 °C (300 mTorr) and the ~C12 fractions are collected, followed by the ~C14 fractions at 135 °C (200 mTorr). The Vigreux column is then removed and the ~C16 fractions can be collected at 100 °C/100 mTorr. Distillation of the desired products may be done at various temperature/pressures and those skilled in the art will recognize the importance of theoretical plates on the degree of separation.

A series of semibatch oligomerizations are performed with 3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-2'-(2-((3'-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3,5-difluoro-2'-hydroxy-5'-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-yl)oxy)ethoxy)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)-[1,1'-biphenyl]-2-ol-zirconiumdimethyl (Formula (VI)) catalyst at 60° using toluene as a reaction solvent (Table 1 below). The semibatch nature of the reaction is due to the continuous feeding of ethylene gas to maintain a constant pressure, and excess butene is purged out to allow the continued consumption of ethylene. No alpha-olefin comonomers are added to the reaction. The average number of carbons per product oligomer is calculated assuming all molecules have a single unsaturation group.

Table 1

Run	Temp	Toluene	Press	Run Time	Catalyst			RIBS-2	MMAO-3A	Exo-	Ethylene	
#	(°C)	(g)	(psi)	(min)	Name	μmoles	Metal	μmoles	μmoles	Therm (°C)	(g) Initial	(g) Added
1	60	300	116	164.6	Formula VI	16.9	Zr	20.28	10	7.6	21.6	120
2	60	300	116	226.9	Formula VI	39.9	Zr	39.9	10	2.2	19.4	220.6

Table 2

	Average MW	Average # of branches	Detailed Degree of branching				Conc. of unsaturation				Branching position	
			(Including chain ends)				Vinylene	Vinyl		Vinylidene	(relative to unsat. Chain ends)	
	Mn	(per chain)	Hexyl	Butyl	Ethyl	Methyl		V1	V3		C2	C4
C12 fraction – Run #1	167	0.80	0.66	0.29	0.86	0.01	0.03	0.39	0.43	0.17	17%	42%
C14 fraction – Run #1	185	0.91	0.66	0.33	0.96	0.01	0.03	0.35	0.45	0.17	17%	45%
C16 fraction – Run #1	216	1.12	0.70	0.39	1.12	0.01	0.04	0.30	0.46	0.17	17%	48%
C12 fraction – Run #2	164	0.82	0.63	0.31	0.88	0.01	0.03	0.37	0.43	0.19	18%	42%
C14 fraction – Run #2	180	0.91	0.63	0.33	0.98	0.01	0.03	0.33	0.45	0.19	19%	45%
C16 fraction – Run #2	210	1.10	0.70	0.38	1.08	0.01	0.04	0.31	0.46	0.19	19%	46%

Determination of the characterizing properties listed above in Table 2 may be accomplished as follows:

For ^{13}C NMR measurement, product samples are dissolved in 10 millimeter (mm) nuclear magnetic resonance (NMR) tubes in chloroform- d_1 (deuterated chloroform) to which 0.02 molar (M) chromium acetylacetonate, $\text{Cr}(\text{acac})_3$, is added. The typical concentration is 5 0.50 grams per 2.4 milliliter (g/mL). The tubes are then heated in a heating block set at 50 °C. The sample tubes are repeatedly vortexed and heated to achieve a homogeneous flowing fluid. For samples with visible wax present, tetrachloroethane- d_2 (deuterated tetrachloroethane) is used as the solvent instead of chloroform- d_1 , and the sample 10 preparation temperature is 90 °C. ^{13}C NMR spectra are taken on a Bruker Avance 400 megahertz (MHz) spectrophotometer equipped with a 10 mm cryoprobe. The following acquisition parameters are used: 5 seconds relaxation delay, 90 degree pulse of 13.1 milliseconds, 256 scans. The spectra are centered at 80 parts per million (ppm) with a spectral width of 250 ppm. All measurements are taken without sample spinning at either 15 50 °C (for chloroform- d_1 solutions) or 90 °C (for tetrachloroethane- d_2 solutions). The ^{13}C NMR spectra are referenced to 77.3 ppm for chloroform- d_1 or 74.5 ppm for tetrachloroethane- d_2 .

Example 4: Hydroformylation of C12 olefins to C13 aldehydes

$\text{Rh}(\text{CO})_2(\text{acac})$ (15.1 mg; 0.0585 mmol), tris(2,4-di-*tert*-butylphenyl)phosphite 20 (757 mg; 1.17 mmol) and toluene (20 g) are placed in a 50 mL nitrogen purged bottle with a septum. The mixture is stirred until the components dissolved to form a yellow solution. The solution is transferred by syringe into a 150 mL Parr reactor under nitrogen, then purged three times with syngas (1:1) at 100 psi with stirring and activated at 90 °C and 100 psi of syngas (1:1) for about 1 h. Then the syngas is vented and the 25 starting C12 olefin feedstock (9.39 g) is quickly added to the reactor via syringe. The reaction is carried out for two hours at 100 °C and then analyzed by ^1H NMR. The olefin signals at about 2 ppm and 4.5-6 ppm disappeared and new signals of aldehyde protons appeared at 9.5-10 ppm, suggesting that the reaction is complete. Toluene is removed under reduced pressure and the aldehydes are separated from the catalyst and the ligand 30 by vacuum distillation at 57 °C/127 mm Hg to give 7.46 g of the aldehyde product.

Example 5: Hydrogenation of the C13 aldehydes

A distilled aldehyde product from the previous example (7.46 g) is dissolved in 20 mL of anhydrous THF and hydrogenated in a 150 mL Parr reactor at 500 psi and 100 °C using 0.75 g of 5%Ru/C catalyst from Strem Chemical. The reaction is followed by

hydrogen pressure drop. ¹H NMR analysis indicates in four hours that no residual aldehyde remains. The mixture is filtered, the catalyst washed with 5 mL x 2 of THF and the combined solutions are evaporated in vacuum to give 7.18 g of the alcohol product.

5 Example 6: Hydroformylation of C14 olefins to C15 aldehydes

Rh(CO)₂(acac) (25.0 mg; 0.0969 mmol), tris(2,4-di-*tert*-butylphenyl)phosphite (1.161 g; 1.79 mmol) and toluene (20 g) are placed in a 50 mL nitrogen purged bottle with a septum. The mixture is stirred until the components dissolved to form a yellow solution. The solution is transferred by syringe into a 150 mL Parr reactor under nitrogen, then purged three times with syngas (1:1) at 100 psi with stirring and activated at 90 °C and 100 psi of syngas (1:1) for about one hour. Then the syngas is vented and the starting C14 olefin feedstock (15.03 g) is quickly added to the reactor via syringe. The reaction is carried out for two hours at 100 °C and then analyzed by ¹H NMR. The olefin signals at about 2 ppm and 4.5-6 ppm disappear and new signals of aldehyde protons appear at 9.5-10 ppm, suggesting that the reaction is complete. Toluene is removed under reduced pressure and the aldehydes are separated from the catalyst and the ligand by vacuum distillation at 68 °C/202 mm Hg to give 11.99 g of the aldehyde product.

Example 7: Hydrogenation of the C15 aldehydes

A distilled aldehyde product from the previous example (11.99 g) is dissolved in 50 mL of anhydrous THF and hydrogenated in a 150 mL Parr reactor at 500 psi and 100 °C using 1.2 g of 5%Ru/C catalyst from Strem Chemical. The reaction is followed by hydrogen pressure drop. ¹H NMR analysis indicates in four hours that no residual aldehyde remains. The mixture is filtered, the catalyst washed with 10 mL x 2 of THF and the combined solutions are evaporated in vacuum to give 11.80 g of the alcohol product. The characterizing properties of the C13 and C15 alcohol products are listed below in Table 3.

Table 3

	Average MW	Average # of branches	Detailed Degree of branching (Including chain ends)						Branching position (relative to hydroxyl group)				
			Methyl	Ethyl	Propyl	Butyl	Longer	Quarter-nary	>=C4	C3	C2		
	Mn	(per chain)	(per chain)								Methyl	Ethyl	Longer
C13 Alcohol	175	1.27	0.17	0.32	0.05	0.21	0.26	0.0	41%	6%	36%	6%	12%
C15 Alcohol	203	1.58	0.14	0.29	0.08	0.22	0.27	0.0	38%	4%	33%	6%	19%

Example 8: Ethoxylation of the C13 and C15 alcohols

The reactions are carried out in a Symyx PPR[®] (Parallel Pressure Reactor) setup using twelve small reactors. The MFRM-331448 library involves ethoxylation of the alcohols with ethylene oxide (EO). The library layout was designed using Library Studio[®].

Ethylene oxide (EO) is delivered via an Isco syringe pump equipped with a robotically controlled needle and compressed gas micro-valve connected to the Symyx PPR[®]. Glass inserts along with removable PEEK stir paddles for each of twelve cells are dried in a vacuum oven at 125°C overnight. The starter solutions after dissolution of potassium (1 wt%) are charged manually into the glass inserts under nitrogen using a pipette. The amounts of starting alcohols are 4 mmol for all cases (Table 3).

All reagents are delivered by pipette into glass inserts and the mass of material in each inset is recorded. The inserts with reagents are loaded into the corresponding PPR wells, the reactor modules are sealed, heated to 60 °C, and pressurized with 50 psi nitrogen. The corresponding twelve cells are charged with calculated amounts of EO. The temperature is then increased to 150°C and the reaction mixtures are stirred for three hours at that temperature. The reactors are then cooled, and the cells are vented and purged with nitrogen to remove residual EO. After cooling to room temperature, the glass inserts are removed from the reactors, the weights of the glass inserts are taken, and the product yields are calculated. The materials are analyzed by ¹H NMR and the number of EO equivalents for each product are determined (Table 4).

Table 4

Sample	Average Number of carbons in ROH	ROH weight (g)	EO added (g)	Product yield (g)	EO equiv by ¹ H NMR
1	C13	0.813	0.805	1.616	4.9
2	C13	0.813	1.283	2.094	6.8
3	C13	0.813	2.289	3.100	14.6
4	C15	0.925	1.098	2.023	7.0
5	C15	0.925	1.710	2.635	10.1
6	C15	0.925	2.332	3.257	14.3

Example 9: Surface Properties of SurfactantsSurface Tension

The surface tension of a surfactant solution is measured using Kruss K100 Surface Tensiometer fitted with a Wilhelmy platinum plate at ambient temperature (21-22 °C).
5 Deionized water is used to make the solutions and the surface tension of the water is measured to be between 72 and 73 mN/m. The result is reported as a mean of five repeated testing values with the standard deviation < 0.1 mN/m.

Ross-Miles Foam Test

Ross-Miles Foam test is conducted as described by ASTM method D1173
10 “Standard Test Method for Foaming properties of Surface Active Agents.” A glass pipet (“foam pipet”) is charged with 200 ml of the 0.1% aqueous surfactant solution, while the graduated glass tube (“foam receiver”) with ID=5.0 cm is filled with 50 ml of the same solution. After centering the pipet above the foam receiver, the aqueous solution in the pipet is allowed to drain 90 cm through air and splash into the solution in the foam
15 receiver, thereby forming foam. The height of the foam layer, a measure of the volume of air which is incorporated into the foam, was recorded at zero seconds, and at five minutes. Two measurements are made for each system at the ambient temperature and result is reported as the mean.

Draves Wetting Time

20 Draves Wetting time is tested following the procedures of ASTM D 2281-68 (Standard Test Method for Evaluation of Wetting Agents by the Skein Test). All the tests are carried out at 0.1 weight percent concentration of surfactant and at room temperature.

Contact Angle

Contact angle measurements are performed at ambient temperature utilizing Kruss
25 DSA-100 Drop Shape Analyzer. The instrument has a movable sample stage. Kruss software, DSA3.exe, controlled operation of the instrument and performed data analysis. The contact angle measurements is performed on a static sessile (*i.e.* sitting) drop. Teflon® tape (pink thread seal tape purchased from Lowes) or parafilm is carefully placed on glass microscope slide, using a small amount of adhesive on the each edge of
30 the microscope slide to hold the Teflon tape on the surface. Variability in surface composition and uniformity can significantly affect the contact angle measurement, thus, extreme care is used when placing tape on a slide so that the tape, film, or paper is not stretched or touched. The substrate was placed on a sample stage, and five liquid drops are deposited on the substrate programmatically, using the procedure predefined via DSA

software. An automated procedure is utilized, as the drop volume, dispense rate, and needle height can affect the drop shape, and thus, the contact angle measurement. In this study, drop volume was 5 μL , rate of drop deposition was 6 $\mu\text{L}/\text{min}$, and measurement was made immediately after drop placement. Once the drop image is taken, the baseline is determined, left and right contact angles are determined by software, and the arithmetic mean of left and right contact angles is calculated for each drop. The result is reported as mean of the values from three groups of testing total fifteen drops.

The test results are summarized in Table 5 below. Two commercial products, Lutensol AO-7 (7 EO adduct of C13-C15 oxo alcohol) and Lutensol TO-7 (7EO adduct of iso-tridecanol) from BASF are included for comparison. The experimental samples demonstrate good surfactancy, reducing surface tension to about 30 mN/m with cmc lower than 100 ppm. Sample 1, which has similar amount EO adduction as the two commercial products, shows almost identical surface tension as the two commercial products, and demonstrates better wetting than Lutensol AO-7 and similar to Lutensol TO-7, a highly branched alcohol with low biodegradability.

Table 5

Sample	cmc (ppm)	ST (0.1 wt%) mN/m	Ross Miles Foam (0.1 wt%)		Draves Wetting (0.1 wt%) (sec.)	Contact angle (degree) (0.1 wt%)	
			0 min.	5 min.		PTFE	Parafilm
1 - C13	36	28.2	30	30	26	59	50
2 - C13	35	27.8	110	110	18	55	49
3 - C13	96	31.4	128	120	188	83	71
4 - C15	10	28.8	80	80	56	63	61
5 - C15	10	30.4	110	110	70	70	64
6 - C15	17	33.4	120	120	228	77	72
Lutensol AO-7	6	27.9	85	85	47	62	58
Lutensol TO-7	19	27.3	65	60	13	53	46

Example 10: Biodegradability Test of the Surfactant Samples

The ready biodegradability of the Experimental surfactant samples is evaluated using the OECD guideline 301F: Manometric Respirometry test. Biodegradation of each material is determined at an initial concentration of approximately 50 mg/L, yielding approximately 100 mg/L theoretical oxygen demand (ThOD) in the test mixtures. The test chemicals are added to biodegradation test mixtures containing a defined mineral medium, which is inoculated with activated sludge (30 mg/L dry solids) from a municipal

wastewater treatment facility (Midland, Michigan USA). This facility treats an excess of 11 million L/day of a predominantly domestic (> 90% vol.) wastewater. Oxygen consumption and CO₂ evolution resulting from biodegradation of the test chemicals are measured over twenty-eight days using a Columbus Instruments MicroOxymax® respirometer system. In addition, removal of dissolved organic carbon (DOC) from the biodegradation test mixtures is determined after twenty-eight days. The results are reported as below.

Sample 6:

88 % Biodegradation by biological oxygen demand (BOD), 72% biodegradation by CO₂ evolution, 95% by dissolved organic carbon (DOC) removal

Conclusion: Readily biodegradable

Sample 1:

60% by BOD, 46% by CO₂, and 97% by DOC

Conclusion: Readily biodegradable

Sample 3:

100% by BOD, 81% by CO₂, and 100% by DOC

Conclusion: Readily biodegradable

While the invention has been described above according to its preferred embodiments, it can be modified within the spirit and scope of this disclosure. This application is therefore intended to cover any variations, uses, or adaptations of the invention using the general principles disclosed herein. Further, the application is intended to cover such departures from the present disclosure as come within the known or customary practice in the art to which this invention pertains and which fall within the limits of the following claims.

WHAT IS CLAIMED IS:

1. A process comprising:

(1) combining at least one olefin and at least one coordination-insertion catalyst and, optionally, an alpha-olefin,

5 wherein the coordination-insertion catalyst is a metal-ligand complex wherein the metal is selected from zirconium, hafnium and titanium,

and has an ethylene/octene reactivity ratio up to 20 at an operating reactor temperature, and a kinetic chain length up to 20 monomer units;

under conditions such that at least one oligomer product is formed,

10 wherein the oligomer product includes a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches, wherein the branches are located on average

more than one carbon away from each end of the main carbon chain in more than 20% of oligomer product molecules, wherein the branches are

15 situated at a second carbon relative to an unsaturated end of the main carbon chain in less than 40% of the oligomer product molecules, and

wherein the oligomer product contains greater than 50% vinyl olefin;

(2) fractionating the oligomer product to produce a fractionated oligomer product, such that the average carbon number of the fractionated oligomer

20 product is between 8 and 28; and

(3) hydroformylating the fractionated oligomer product to produce an aldehyde product or sulfonating the fractionated oligomer product to produce a sulfonated surfactant product.

25 2. A process comprising:

(1) combining at least one olefin and at least one coordination-insertion catalyst and, optionally, an alpha-olefin,

wherein the coordination-insertion catalyst is a metal-ligand complex wherein the metal is selected from zirconium, hafnium and titanium,

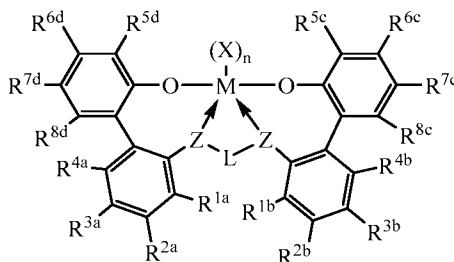
30 and has an ethylene/octene reactivity ratio up to 20 at an operating reactor temperature, and a kinetic chain length up to 20 monomer units;

under conditions such that at least one oligomer product is formed,

wherein the oligomer product includes a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the

- branches are ethyl branches, wherein the branches are located on average more than one carbon away from each end of the main carbon chain in more than 20% of oligomer product molecules, wherein the branches are situated at a second carbon relative to an unsaturated end of the main carbon chain in less than 40% of the oligomer product molecules, and wherein the oligomer product contains greater than 50% vinyl olefin;
- 5
- (2) fractionating the oligomer product to produce a fractionated oligomer product, such that the average carbon number of the fractionated oligomer product is between 8 and 28;
- 10
- (3) hydroformylating the fractionated oligomer product to produce an aldehyde product; and
- (4) hydrogenating the aldehyde product to produce an alcohol product.
3. A process according to claim 2, further comprising alkoxyating the alcohol product to produce an alkoxyate surfactant product.
- 15
4. A process according to claim 3, further comprising sulfating the alkoxyate surfactant product to produce an anionic ether sulfate surfactant product.
- 20
5. A process according to claim 2, further comprising sulfating the alcohol product to produce an anionic sulfate surfactant product.
6. A process according to any one of claims 1-5, wherein the at least one olefin is ethylene and an alpha-olefin is not used.
- 25
7. A process according to any one of claims 1-5, wherein the at least one olefin is an olefin mixture.
8. A process according to claim 7, wherein the olefin mixture includes olefins with vinyl groups, olefins with vinylidene groups, and olefins with vinylene groups.
- 30
9. A process according to any one of claims 1-8, further comprising use of a rhodium catalyst with an organophosphorus ligand in the hydroformylating step (3).

10. A process according to any one of claims 1-9, wherein the metal-ligand complex is a compound of the formula



5 wherein M is titanium, zirconium, or hafnium, each independently being in a formal oxidation state of +2, +3, or +4;

n is an integer of from 0 to 3, wherein when n is 0, X is absent;

each X independently is a monodentate ligand that is neutral, monoanionic, or dianionic, or two X are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic;

X and n are selected such that the metal-ligand complex of formula (I) is, overall, neutral;

each Z is independently O, S, N(C₁-C₄₀)hydrocarbyl, or P(C₁-C₄₀)hydrocarbyl;

L is (C₁-C₄₀)hydrocarbylene or (C₁-C₄₀)heterohydrocarbylene, wherein the (C₁-C₄₀)-hydrocarbylene has a portion that comprises a 2-carbon atom linker backbone linking the Z atoms in formula (I) and the (C₁-C₄₀)heterohydrocarbylene has a portion that comprises a 2-atom atom linker backbone linking the Z atoms in formula (I), wherein each atom of the 2-atom linker of the (C₁-C₄₀)-heterohydrocarbylene independently is a carbon atom or a heteroatom, wherein each heteroatom independently is O, S, S(O), S(O)₂, Si(R^C)₂, Ge(R^C)₂, P(R^P), or N(R^N), wherein independently each R^C is unsubstituted (C₁-C₁₈)hydrocarbyl or the two R^C are taken together to form a (C₂-C₁₉)alkylene, each R^P is unsubstituted (C₁-C₁₈)hydrocarbyl; and each R^N is unsubstituted (C₁-C₁₈)hydrocarbyl, a hydrogen atom or absent; R^{1a}, R^{2a}, R^{1b}, and R^{2b} independently is a hydrogen, (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)-heterohydrocarbyl, N(R^N)₂, NO₂, OR^C, SR^C, Si(R^C)₃, Ge(R^C)₃, CN, CF₃, F₃CO, halogen atom; and each of the others of R^{1a}, R^{2a}, R^{1b}, and R^{2b} independently is a hydrogen, (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)-heterohydrocarbyl, N(R^N)₂, NO₂, OR^C, SR^C, Si(R^C)₃, Ge(R^C)₃, CN, CF₃, F₃CO or halogen atom; each of R^{3a}, R^{4a}, R^{3b}, R^{4b}, R^{6c}, R^{7c}, R^{8c}, R^{6d}, R^{7d}, and R^{8d} independently is a hydrogen atom; (C₁-C₄₀)hydrocarbyl; (C₁-C₄₀)-heterohydrocarbyl; Si(R^C)₃, Ge(R^C)₃,

$P(R^P)_2$, $N(R^N)_2$, OR^C , SR^C , NO_2 , CN , CF_3 , $RCS(O)-$, $RCS(O)_2-$, $(RC)_2C=N-$, $RCC(O)O-$, $RCOC(O)-$, $RCC(O)N(R)-$, $(RC)_2NC(O)-$ or halogen atom;

each of R^{5c} and R^{5d} is independently a (C_6-C_{40}) aryl or (C_1-C_{40}) heteroaryl;

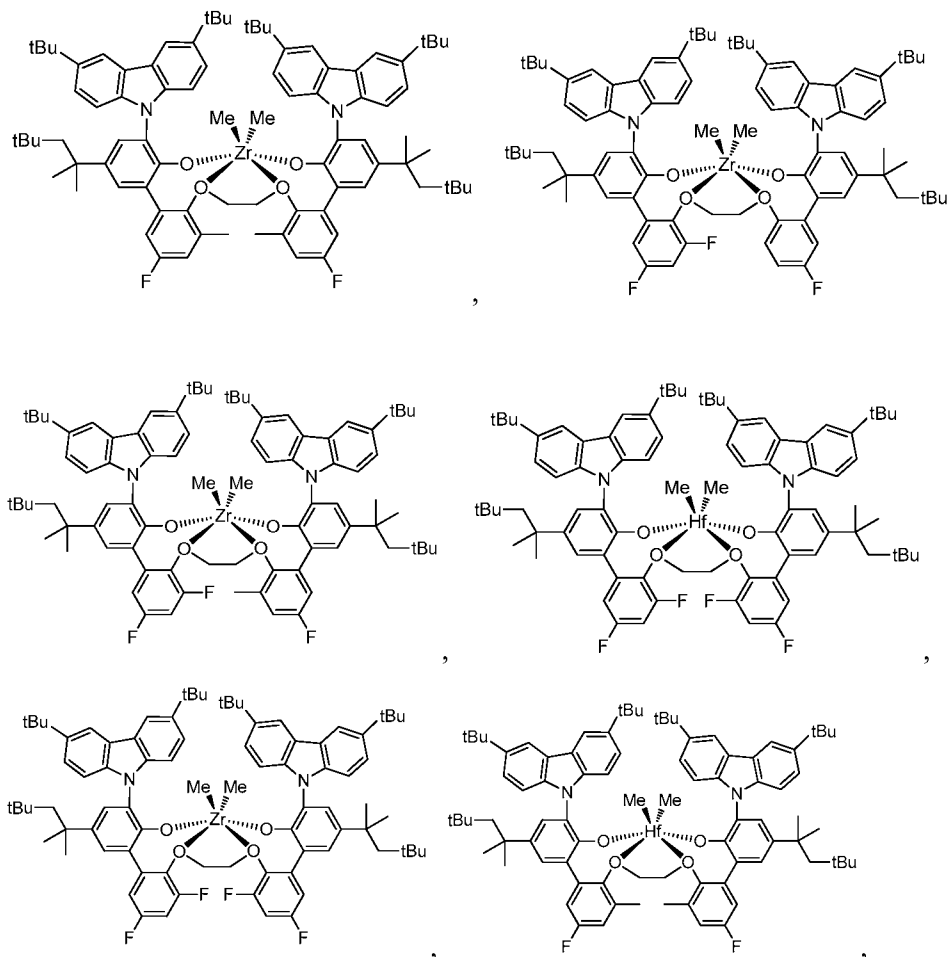
each of the aforementioned aryl, heteroaryl, hydrocarbyl, heterohydrocarbyl, hydrocarbylene, and heterohydrocarbylene groups is independently unsubstituted or substituted with 1 to 5 more substituents R^S ; and

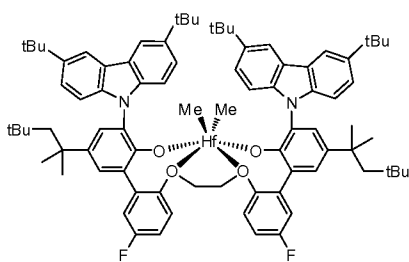
each R^S is independently a halogen atom, polyfluoro substitution, perfluoro substitution, unsubstituted (C_1-C_{18}) alkyl, F_3C- , FCH_2O- , F_2HCO- , F_3CO- , R_3Si- , R_3Ge- , $RO-$, $RS-$, $RS(O)-$, $RS(O)_2-$, R_2P- , R_2N- , $R_2C=N-$, $NC-$, $RC(O)O-$, $ROC(O)-$, $RC(O)N(R)-$, or $R_2NC(O)-$, or two of the R^S are taken together to form an unsubstituted (C_1-C_{18}) alkylene, wherein each R independently is an unsubstituted (C_1-C_{18}) alkyl.

11. The process according to any one of claims 1-10,

wherein the coordination-insertion catalyst is selected from the group consisting of

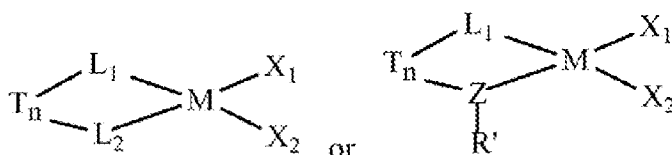
15





, and combinations thereof.

12. A process according to any one of claims 1-9, wherein the metal-ligand complex is a compound of the formula



5

wherein M is the metal center, and is a Group 4 metal selected from titanium, zirconium or hafnium;

T is an optional bridging group which, if present, is selected from dialkylsilyl, diarylsilyl, dialkylmethyl, ethylenyl (-CH₂-CH₂-) or hydrocarbylethylenyl wherein one, two, three or four of the hydrogen atoms in ethylenyl are substituted by hydrocarbyl, where hydrocarbyl can be independently C₁ to C₁₆ alkyl or phenyl, tolyl, or xylyl, and when T is present, the catalyst represented can be in a racemic or a meso form;

L₁ and L₂ are the same or different cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl rings, optionally substituted, that are each bonded to M, or L₁ and L₂ are the same or different cyclopentadienyl, indenyl, tetrahydroindenyl or fluorenyl, which are optionally substituted, in which any two adjacent R groups on these rings are optionally joined to form a substituted or unsubstituted, saturated, partially unsaturated, or aromatic cyclic or polycyclic substituent;

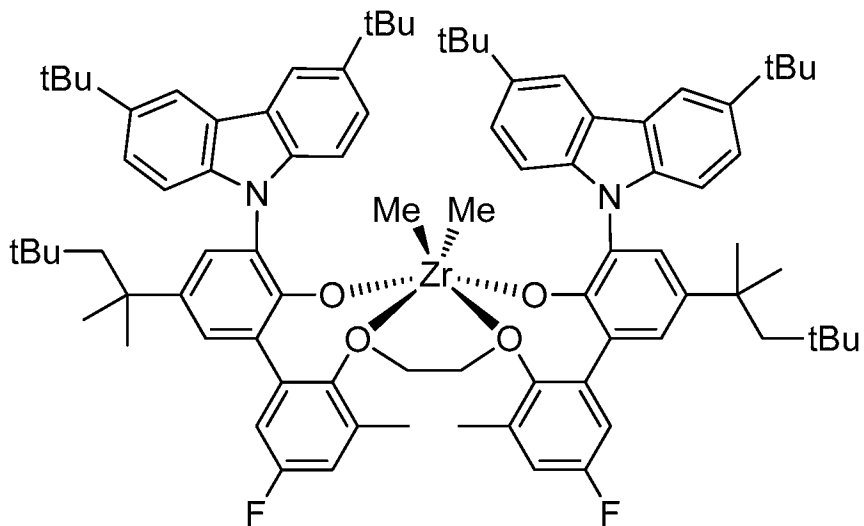
Z is nitrogen, oxygen or phosphorus;

R' is a cyclic linear or branched C₁ to C₄₀ alkyl or substituted alkyl group; and

X₁ and X₂ are, independently, hydrogen, halogen, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, silylcarbyl radicals, substituted silylcarbyl radicals, germylcarbyl radicals, or substituted germylcarbyl radicals; or both X are joined and bound to the metal atom to form a metallacycle ring containing from 3 to 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand.

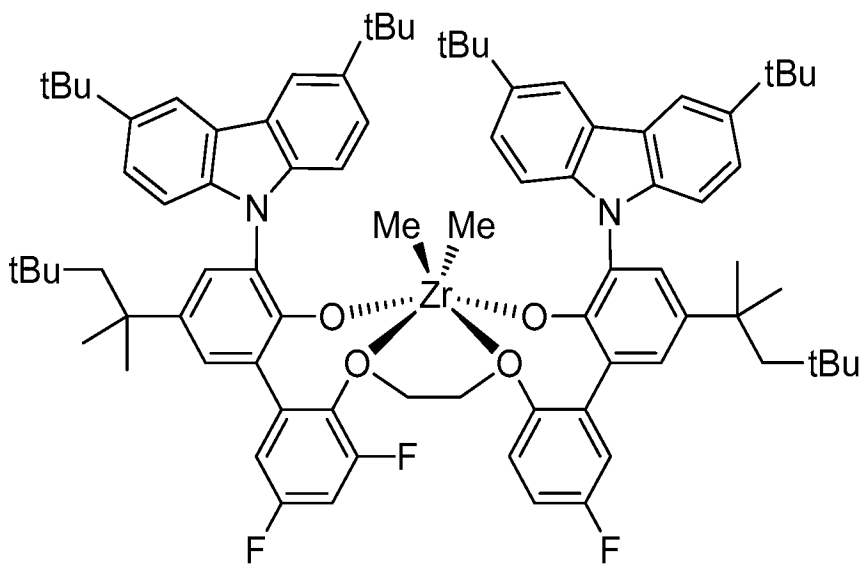
25

13. A surfactant product prepared by the process of any one of claims 1-12.
14. An alcohol product comprising a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are ethyl branches,
5 wherein the branches are located more than one carbon away from each end of the main carbon chain in more than 20% of alcohol product molecules.
15. A lightly branched surfactant product comprising a main carbon chain containing an average of between 0.5 and 2.5 branches, wherein more than 50% of the branches are
10 ethyl branches, wherein the branches are located more than one carbon away from each end of the main carbon chain in more than 20% of surfactant product molecules.



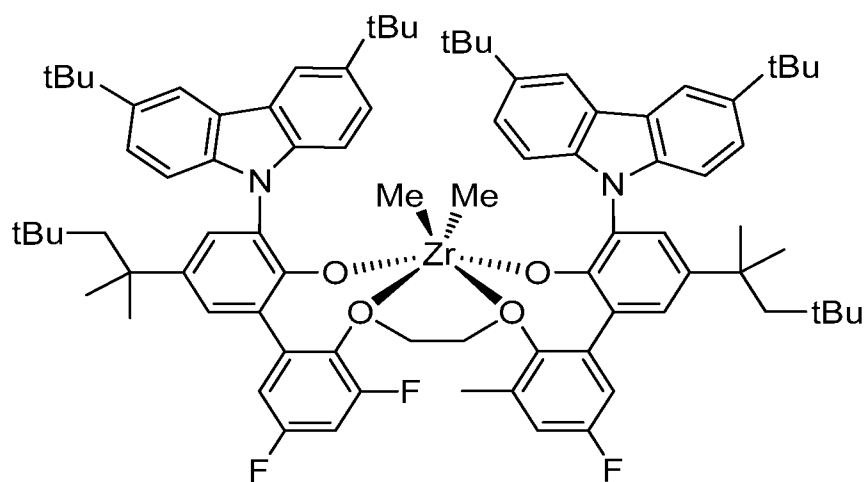
(formula IV)

Figure 1



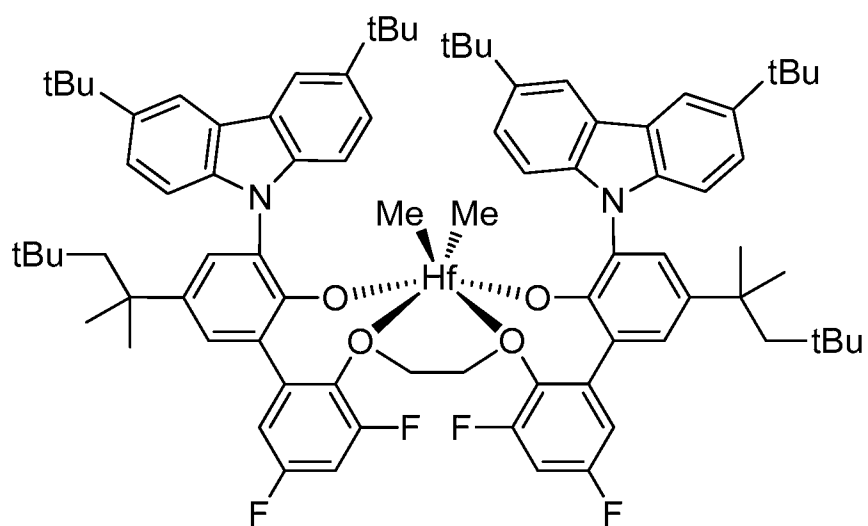
formula (V)

Figure 2



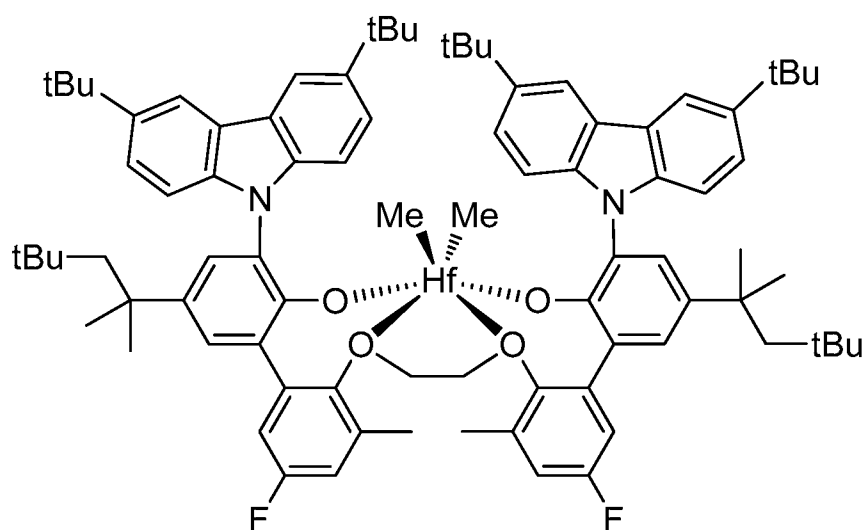
formula (VI)

Figure 3



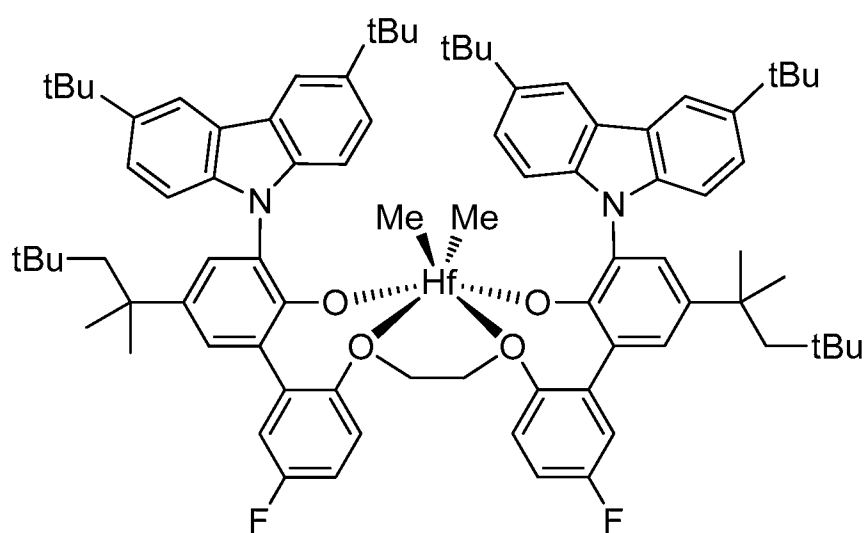
formula (VII)

Figure 4



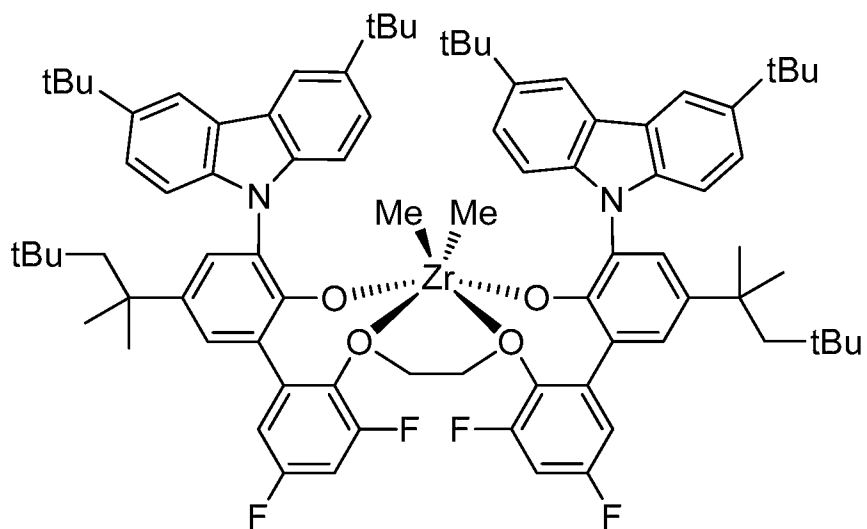
formula (VIII)

Figure 5



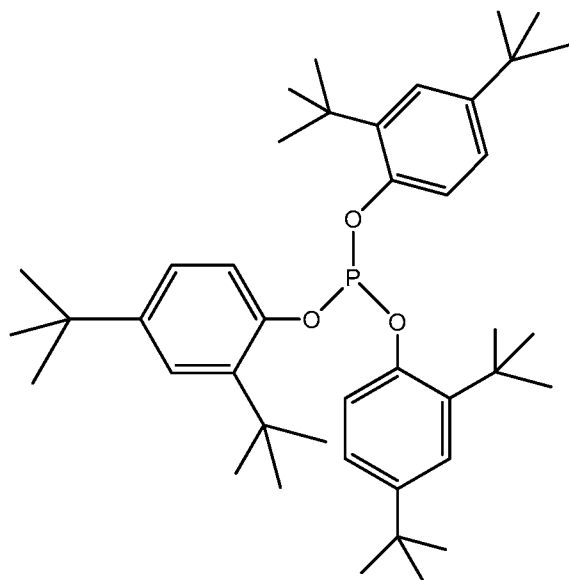
formula (IX)

Figure 6



formula
(X)

Figure 7



Formula (IX)

Figure 8

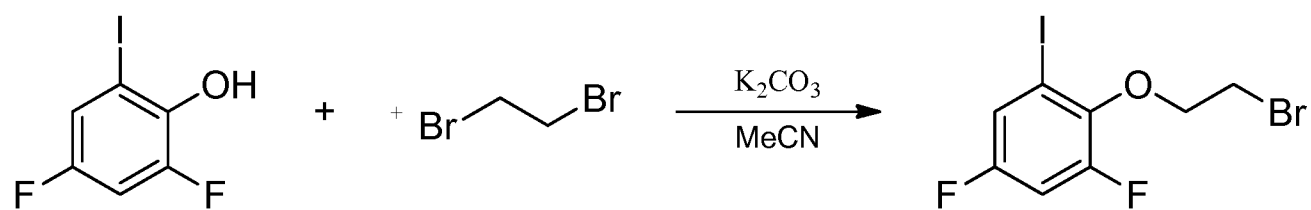


Figure 9

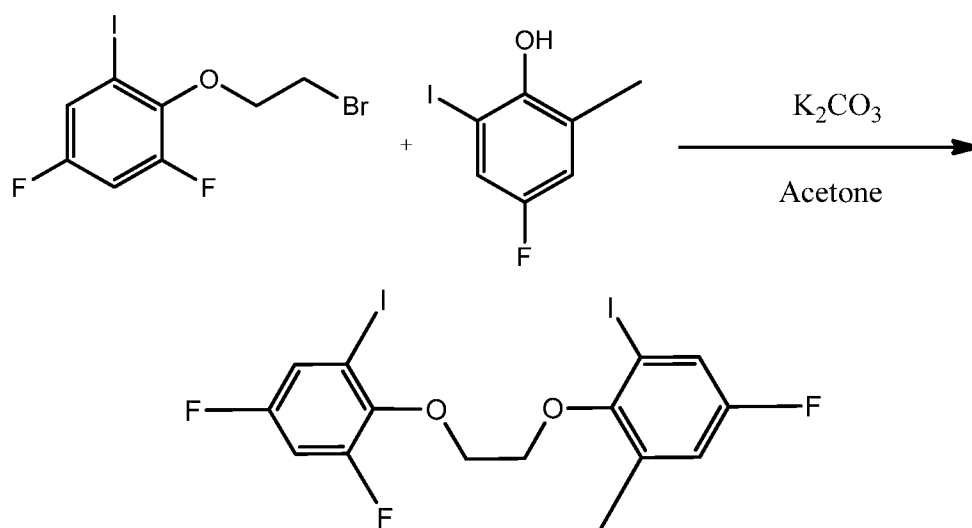


Figure 10

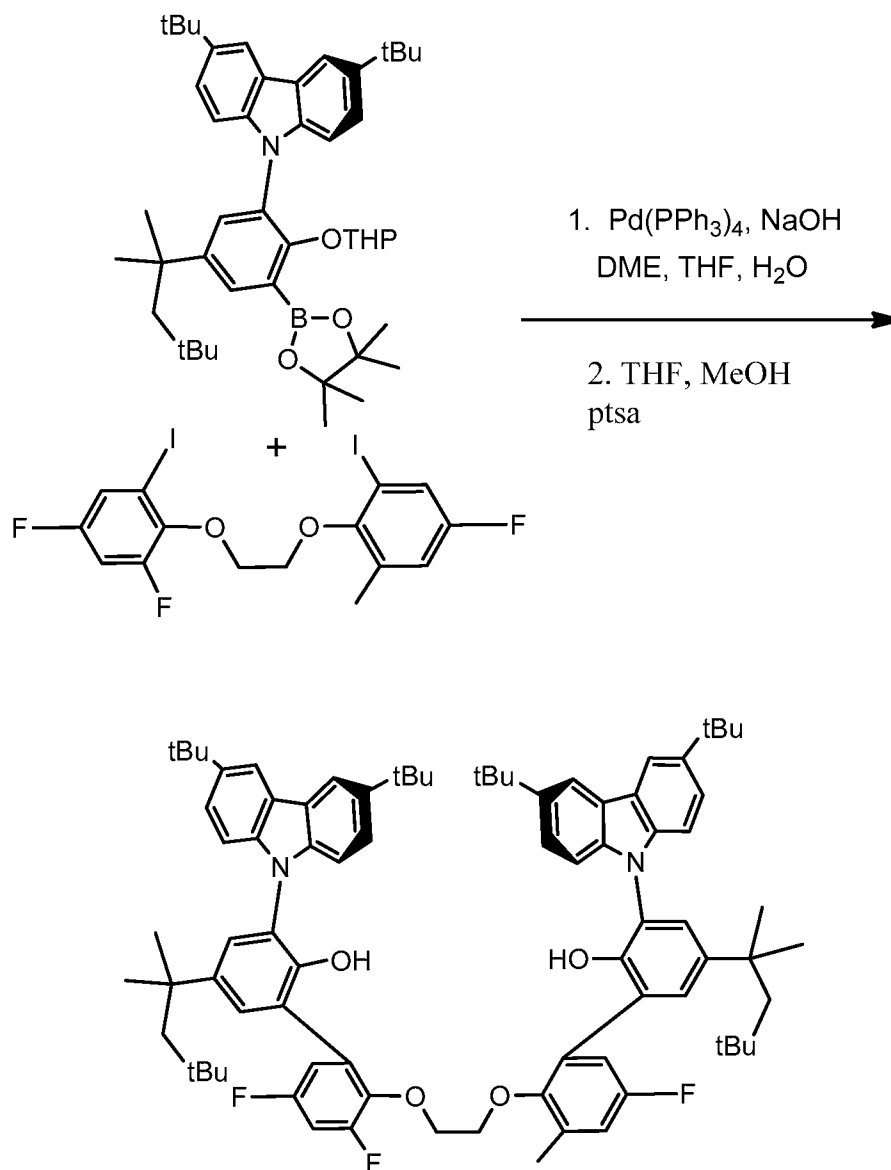


Figure 11

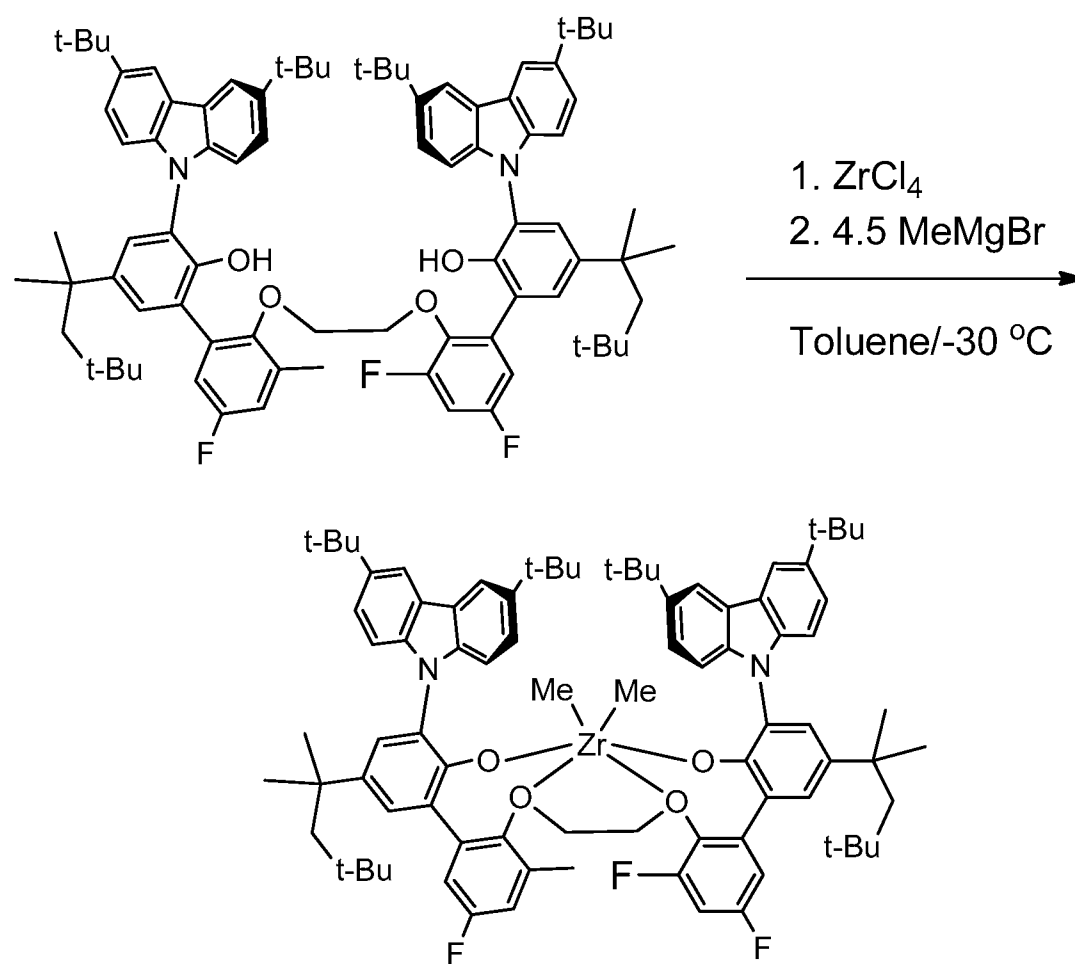


Figure 12

INTERNATIONAL SEARCH REPORT

International application No PCT/US2014/042887

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C31/125 C07C309/04 C07C2/30 C07C47/02 C11D1/66 C08F110/02 ADD. C08F4/659 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B01J C07C C11D C08F Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data, CHEM ABS Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
A, P	WO 2013/101376 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 4 July 2013 (2013-07-04) the whole document -----	1-15		
X	US 2005/107628 A1 (ROPER MICHAEL [DE] ET AL) 19 May 2005 (2005-05-19) paragraph [[0256]] ----- -/--	14, 15		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
22 August 2014	29/08/2014			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Balmer, J			

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>LIPSKA-QUINN A E ET AL: "CHAPTER 26: Thermal Degradation of Rice Straw and its Components", 1 January 1982 (1982-01-01), FUNDAMENTALS OF THERMOCHEMICAL BIOMASS CONVERSION : [INTERNATIONAL CONFERENCE ON FUNDAMENTALS OF THERMOCHEMICAL BIOMASS CONVERSION ; PROCEEDINGS OF A MEETING AT ESTES PARK IN COLORADO IN 1982]; 1982.10.18-22, ELSEVIER APPLIED SCIENCE PUBL, UK, PAGE(S, XP009179748, ISBN: 978-0-85334-306-6 table IX</p> <p align="center">-----</p>	14, 15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2014/042887

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013101376 A1	04-07-2013	TW 201337961 A WO 2013101376 A1	16-09-2013 04-07-2013
US 2005107628 A1	19-05-2005	AU 2003208874 A1 CN 1635984 A DE 10206845 A1 EP 1478609 A2 JP 2005517728 A KR 20040091634 A US 2005107628 A1 WO 03070669 A2	09-09-2003 06-07-2005 28-08-2003 24-11-2004 16-06-2005 28-10-2004 19-05-2005 28-08-2003