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(54) Title: METALLOCENE SYNTHESIS PROCESS

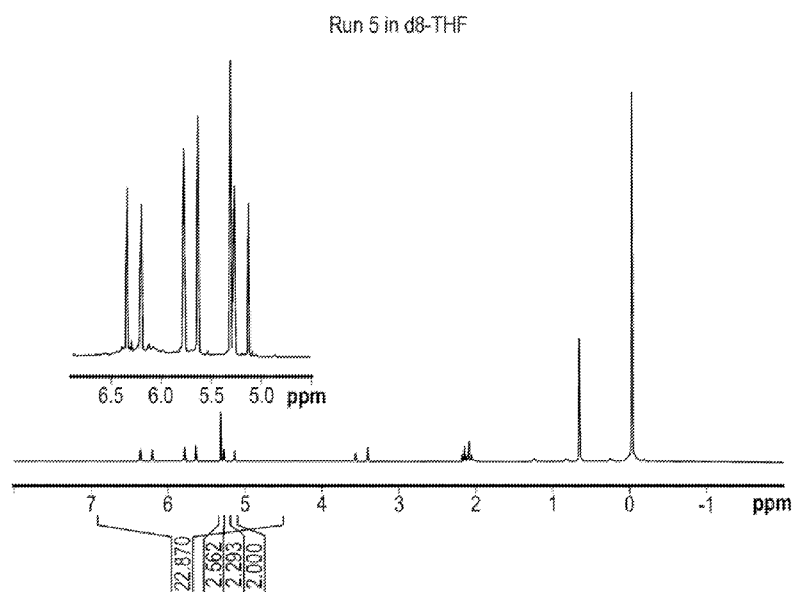


FIG. 1
(Prior Art)

(57) Abstract: A process to synthesize a Group 4 ansa-metallocene. The process includes reacting an alkaline earth metal dianion dicyclopentadiene ligand-Lewis base complex with a Group 4 metal tetrahalide in the presence of an alkali metal halide, and forming the Group 4 ansa-metallocene dihalide with high yield and purity.



TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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2018EM183 PCT

Title: METALLOCENE SYNTHESIS PROCESS

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Priority Claim

- 5 [0001] This application claims priority to and the benefit of USSN 62/693,504, filed July 3, 2018 and EP 18191970.5, filed August 31, 2018, which are incorporated by reference herein.

Field of the Invention

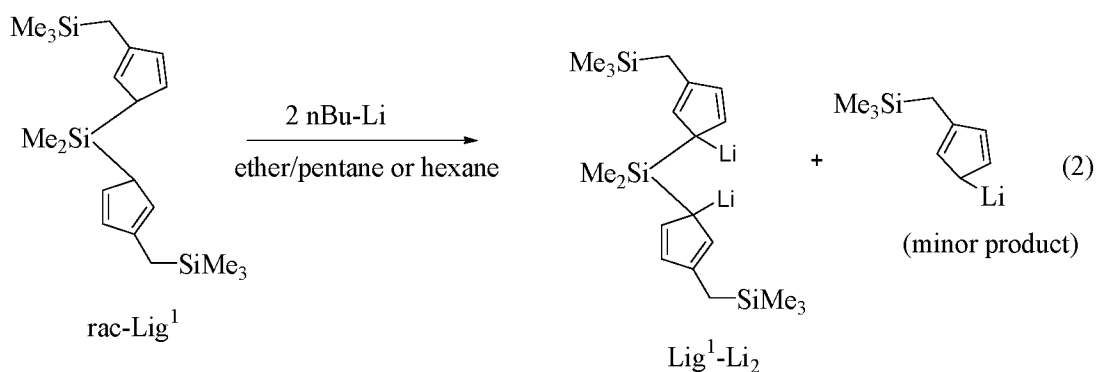
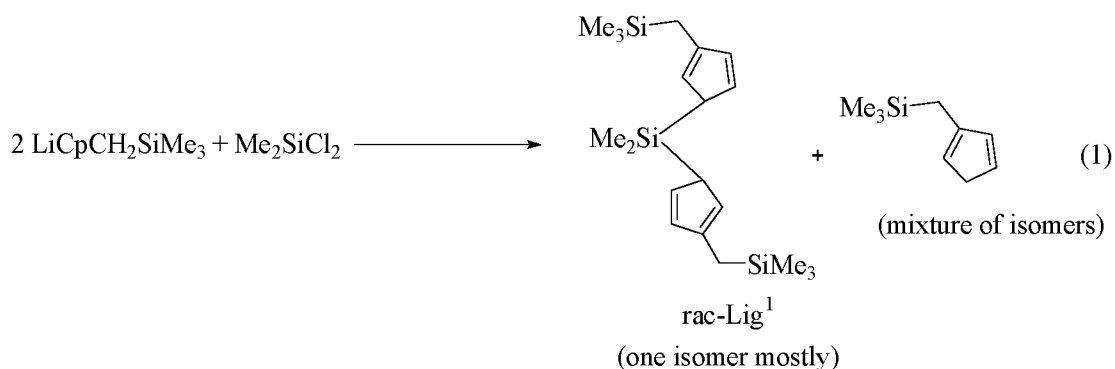
[0002] The present disclosure relates to processes for synthesis of *ansa*-metallocenes.

Background of the Invention

- 10 [0003] Group 4 *ansa*-metallocenes such as substituted hafnocenes used in olefin polymerization processes, are described in U.S. Patent Nos. 6,242,545; 6,248,845; 6,528,597; 6,936,675; 6,956,088; 7,172,816; 7,179,876; 7,381,783; 8,247,065; 8,378,043; 8,476,392; 9,290,593; and U.S. Patent Application Publication No. 2015/0291748.

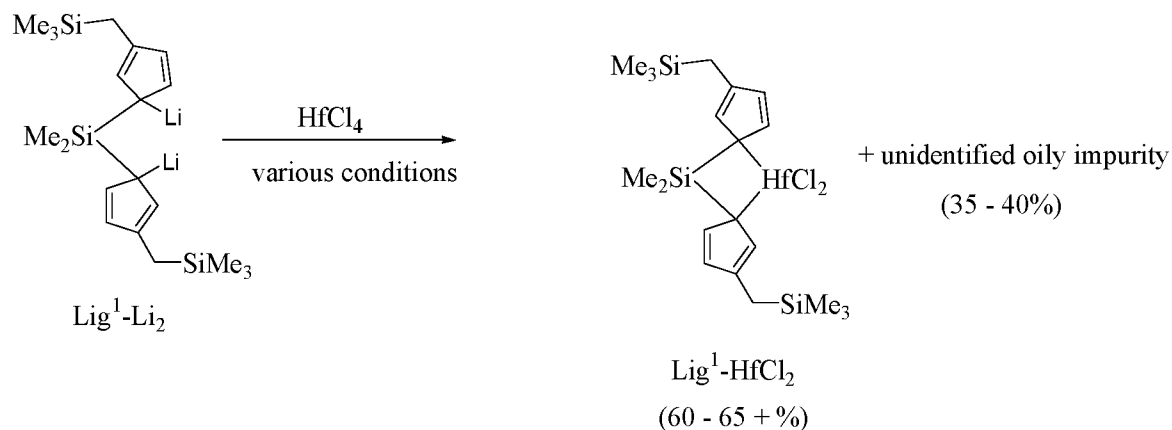
- [0004] *Ansa*-metallocenes have typically been synthesized by formation of a neutral
15 bridged ligand, deprotonation to form the ligand dianion, reaction with transition metal tetrahalide, and then alkylation. However, in some cases this procedure gives a product of 60 to 65% purity and usually contaminated with a mixture of organic species derived from the ligand dianion. In an example, with the ligand dimethylsilyl-bis((trimethylsilyl)methylcyclopentadiene) ("Lig¹"), synthesis of Lig¹-HfMe₂ may start with the reaction of
20 LiCpCH₂SiMe₃ with Me₂SiCl₂ in THF, followed by deprotonation with n-BuLi, and isolation of the ligand dianion. See Scheme 1:

2018EM183 PCT



Scheme 1

[0005] The dilithium salt of the ligand may contain greater than 7 mol% of the mono-Cp anion. The impurity might result from deprotonation of the neutral bridged species by reaction with the unreacted starting LiCpCH₂SiMe₃, present following the first step, to form the neutral H-CpCH₂SiMe₃, which is then deprotonated back to the LiCpCH₂SiMe₃ anion in the second step. Moreover, the reaction of the dilithium salt of the ligand with HfCl₄ is not clean and yields Me₂Si-bis(CpCH₂SiMe₃)HfCl₂ on the order of 60 to 65%. See Scheme 2:



Scheme 2

2018EM183 PCT

[0006] The use of different solvents, temperatures, and hafnium compounds, as well as starting with the purified dilithium salt of the ligand, have all obtained similarly poor results. Attempts to remove the impurities by recrystallization of the Lig¹-HfCl₂ compound tend to lose about half of the yield due to its high solubility in aliphatic hydrocarbons. In addition, the
5 rac/meso ratio is sensitive to slight differences in the initial conditions of the recrystallization, and the rac/meso ratio is not usefully reproducible in this method. Moreover, a separate purification step is required to obtain the metallocene dihalide prior to alkylation to the corresponding catalyst compound, complicating the synthesis procedure, and requiring additional time and separate purification and alkylation vessels.

10 [0007] U.S. Patent No. 5,831,106 similarly discloses that the Scheme 2 type of reaction forms undesirable compounds (such as LiCl) that can be difficult to remove, and discloses another synthesis route said to have improved yield and purity, namely, the reaction of a magnesocene such as dimethylsilanediy-bis(2-methylbenzindenyl)-Mg*2THF with a bis-acetylacetonato Group 4 metal halide compound such as bis(acetylacetonato)ZrCl₂, as reported
15 in U.S. Patent No. 5,831,106. Reacting a diamine adduct of the desired metal halide with an alkali metal or a magnesium halide salt of a cyclopentadiene ligand was similarly disclosed in WO 1996/034002A1 and U.S. Patent No. 5,760,262. However, these require the additional step of preparing the intermediate acetylacetonato complex such as by reacting ZrCl₄ with acetylacetonate, or preparing the diamine adduct by treatment with the diamine. Applicant also
20 found that the reaction of a magnesocene directly with a transition metal tetrahalide such as HfCl₄ did not provide a reaction product mixture having the improved yield and purity to the extent desired.

[0008] WO 1996/019488A1 discloses a method of preparing high purity racemic metallocene alkyls substantially free of alkali metal salts and meso isomer comprising forming
25 a reaction product in the presence of a solvent of a cyclopentadienyl ligand Group 1 or Group 2 metal salt and a perhalogenated Group 4-6 transition metal compound or its etherate complex, combining the crude reaction product with an alkylating agent such as an alkali metal alkyl or Grignard reagent, separating the resulting solution, and then removing the solvent and washing to recover the metallocene alkyl. This document also discloses when the alkylating reagent
30 used in the alkylating step is a Grignard reagent, the addition of 1,4-dioxane may facilitate precipitation of magnesium salts.

[0009] U.S. Patent No. 5,359,105 discloses deprotonation of cyclopentadienyl derivatives by reaction with a Grignard reagent in an inert solvent which contains 0.5-1.5 equivalents per

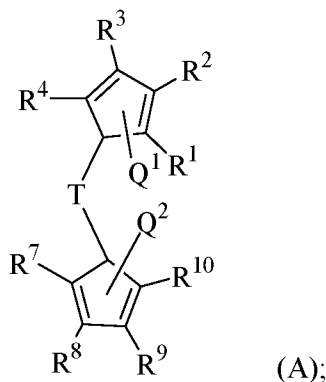
2018EM183 PCT

cyclopentadienyl equivalent of a cyclic ether or acyclic polyether so as to form the dianionic salt. Conducting the Grignard reaction in the absence of ether followed by ether addition resulted in gel formation, whereas excess ether produced the mono-MgCl salt and other impurities contaminating the product, reduction of yield, and slowing of the reaction rate.

- 5 [0010] Thus, there is a need for a metallocene synthesis process that improves purity and/or yield of the metallocene, facilitates purification of the metallocene, and/or facilitates control and/or reproducibility of the rac/meso isomer ratio, and/or that simplifies the synthesis process.

Summary of the Invention

- [0011] In a class of embodiments, the invention provides a process for synthesizing a
 10 Group 4 *ansa*-metallocene comprising (i) reacting a bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex with a Group 4 metal tetrahalide in the presence of an alkali metal halide; and (ii) forming the Group 4 *ansa*-metallocene dihalide. Preferably, the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex is represented by formula (A), the Group 4 metal tetrahalide is represented by formula (B), and the alkali metal
 15 halide is represented by formula (C), wherein the alkaline earth metal dianion ligand complex comprises an alkaline earth metal metallocene, the corresponding diGrignard complex, or a combination thereof, wherein the formula (A) is:



- where each R^1 to R^4 and R^7 to R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;
 T is a bridging group; and
 25 together Q^1 and Q^2 are a divalent complex of an alkaline earth metal complexed with a Lewis base, preferably according to the formula (D1), or each Q^1 and Q^2 is independently an anion of

2018EM183 PCT

a monovalent complex of an alkaline earth metal complexed with a Lewis base, preferably according to the formula (D2), wherein the formulae (D1) and (D2) are:



5 where “>” indicates a divalent complex and “-” indicates a monovalent complex;

M^1 is an alkaline earth metal, such as a Group 2 metal, such as magnesium;

X^1 is a halogen such as chlorine; and

together L^1 and L^2 are a difunctional Lewis base, or each L^1 and L^2 is independently a monofunctional Lewis base;

10 wherein the formula (B) is:



where M^2 is a Group 4 transition metal such as hafnium, zirconium, or titanium; and

each X^2 is independently halogen; and

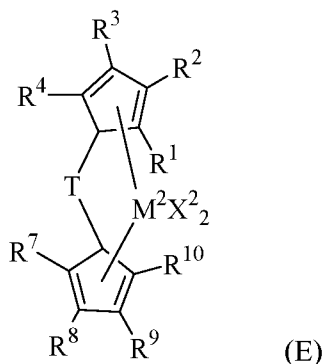
wherein the formula (C) is:



where M^3 is an alkali metal, such as a Group 1 metal, such as lithium and X^3 is independently halogen such as chlorine.

[0012] Preferably, the process comprises the reaction of the alkaline earth metal dianion ligand complex with the Group 4 metal tetrahalide in the presence of the alkali metal halide at
20 a molar ratio of the alkali metal halide to the alkaline earth metal dianion ligand complex equal to or preferably greater than 1, more preferably wherein the molar ratio is greater than 1.5 or equal to or greater than 2. Where the alkaline earth metal dianion ligand complex comprises the diGrignard, the alkali metal is preferably combined with the diGrignard prior to the reaction with the Group 4 transition metal tetrahalide.

25 [0013] Preferably, the reaction produces a Group 4 *ansa*-metallocene dihalide represented by the formula (E):



2018EM183 PCT

where R^1 to R^4 , R^7 to R^{10} , T, M^2 , and X^2 are as defined above.

[0014] The process may optionally further comprise alkylation of the Group 4 *ansa*-metallocene dihalide product with an alkylation reagent. Other embodiments of the invention are described and claimed herein and are apparent by the following disclosure.

5 **Brief Description of the Drawings**

[0015] FIG. 1 is a ^1H NMR analysis of the reaction mixture from the prior art synthesis of HfCl_2 from $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{Li}_2$ and HfCl_4 as described in Run 5 of the examples below.

[0016] FIG. 2 is a comparison of the ^1H NMR analyses of the impurity isolated from the reaction mixture from synthesis of HfCl_2 from $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{Mg}(\text{DME})$ and HfCl_4 in
10 toluene, and the reaction mixture from $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2$ and a Grignard reagent, as described in Runs 23 and 24, respectively, of the examples below.

[0017] FIG. 3 is a ^1H NMR analysis of the reaction mixture from the synthesis of $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{HfCl}_2$ from the $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{diGrignard}$ and HfCl_4 in the presence of LiCl according to the present invention in Run 25 of the examples below.

15 [0018] FIG. 4 is a ^1H NMR analysis of the reaction mixture from the synthesis of $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{HfCl}_2$ from $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{Mg}(\text{DME})$ and HfCl_4 in the presence of LiCl according to the present invention in Run 30 of the examples below.

[0019] FIG. 5 is a ^1H NMR analysis of the reaction mixture from the synthesis of $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{HfCl}_2$ from $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{Mg}(\text{DME})$ and HfCl_4 without
20 LiCl , as described in Run 34 of the examples below.

[0020] FIG. 6 is a ^1H NMR analysis of the $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{HfMe}_2$ product from $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2\text{Mg}(\text{DME})$ and HfCl_4 in the presence of LiCl followed by *in-situ* methylation according to the present invention, as described in Run 36 of the examples below.

Detailed Description

25 [0021] Before the present compounds, components, compositions, and/or methods are disclosed and described, it is to be understood that unless otherwise indicated this invention is not limited to specific compounds, components, compositions, reactants, reaction conditions, ligands, metallocene structures, catalyst structures, or the like, as such may vary, unless otherwise specified. It is also to be understood that the terminology used herein is for the
30 purpose of describing particular embodiments only and is not intended to be limiting.

[0022] In several classes of embodiments of the invention, the present disclosure is directed to the synthesis of Group 4 *ansa*-metallocene compounds.

2018EM183 PCT

[0023] For purposes of this invention and the claims hereto, the numbering scheme for the Periodic Table Groups is according to the new notation of the IUPAC Periodic Table of Elements. Alkaline earth metal means a Group 2 metal, such as beryllium, magnesium, calcium, strontium, or barium. Alkali metal means a Group 1 metal, such as lithium, sodium, potassium, rubidium, and cesium.

[0024] The terms "substituent," "radical," "group," and "moiety" may be used interchangeably.

[0025] As used herein, and unless otherwise specified, the term "C_n" means hydrocarbon(s) having n carbon atom(s) per molecule, wherein n is a positive integer.

[0026] As used herein, and unless otherwise specified, the term "hydrocarbon" means a class of compounds containing hydrogen bound to carbon, and encompasses (i) saturated hydrocarbon compounds, (ii) unsaturated hydrocarbon compounds, and (iii) mixtures of hydrocarbon compounds (saturated and/or unsaturated), including mixtures of hydrocarbon compounds having different values of n.

[0027] The terms "hydrocarbyl radical," "hydrocarbyl," and "hydrocarbyl group" are used interchangeably throughout this document. For purposes of this disclosure, "hydrocarbyl radical" is defined to be C₁-C₁₀₀ radicals, that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such radicals include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like including their substituted analogues. Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom of the hydrocarbyl radical has been substituted with at least one heteroatom or heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as NR*₂, OR*, SeR*, TeR*, PR*₂, AsR*₂, SbR*₂, SR*, BR*₂, SiR*₃, GeR*₃, SnR*₃, PbR*₃, and the like where each R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure, or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0028] Except with respect to the term "substituted hydrocarbyl," the term "substituted" means that at least one hydrogen atom has been replaced with at least one non-hydrogen group, such as a hydrocarbyl group, a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as -NR*₂, -OR*, -SeR*, -TeR*, -PR*₂, -AsR*₂, -SbR*₂, -SR*, -BR*₂, -SiR*₃, -GeR*₃, -SnR*₃, -PbR*₃, and the like, where

2018EM183 PCT

each R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure, or where at least one heteroatom has been inserted within a hydrocarbyl ring. As examples, methyl cyclopentadiene (Cp) is a Cp group substituted with a methyl group, and ethyl alcohol is an ethyl group substituted with an —OH group.

5 [0029] As used herein, and unless otherwise specified, the term “alkyl” refers to a saturated hydrocarbon radical having from 1 to 12 carbon atoms (*i.e.*, C₁–C₁₂ alkyl), particularly from 1 to 8 carbon atoms (*i.e.*, C₁–C₈ alkyl), particularly from 1 to 6 carbon atoms (*i.e.*, C₁–C₆ alkyl), and particularly from 1 to 4 carbon atoms (*i.e.*, C₁–C₄ alkyl). Examples of alkyl groups include, 10 but are not limited to, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, and so forth. The alkyl group may be linear, branched or cyclic. “Alkyl” is intended to embrace all structural isomeric forms of an alkyl group. For example, as used herein, propyl encompasses both n-propyl and isopropyl; butyl encompasses n-butyl, sec-butyl, isobutyl and tert-butyl and so forth. As used herein, “C₁ alkyl” refers to methyl (–CH₃), “C₂ alkyl” refers to ethyl 15 (–CH₂CH₃), “C₃ alkyl” refers to propyl (–CH₂CH₂CH₃) and “C₄ alkyl” refers to butyl (*e.g.*, –CH₂CH₂CH₂CH₃, –(CH₃)CHCH₂CH₃, –CH₂CH(CH₃)₂, etc.).

[0030] The following abbreviations may be used herein: Me is methyl, Et is ethyl, Pr is propyl, iPr is isopropyl, Bu is butyl, nBu is normal butyl, iBu is isobutyl, tBu is tert-butyl, Ph is phenyl, Np refers to neopentyl, dme, (also referred to as DME) is 1,2-dimethoxyethane, THF 20 (also referred to as thf) is tetrahydrofuran, and RT is room temperature (and is 23°C unless otherwise indicated).

[0031] As used herein, and unless otherwise specified, the term “alkenyl” refers to an unsaturated hydrocarbon radical having from 2 to 12 carbon atoms (*i.e.*, C₂–C₁₂ alkenyl), particularly from 2 to 8 carbon atoms (*i.e.*, C₂–C₈ alkenyl), particularly from 2 to 6 carbon 25 atoms (*i.e.*, C₂–C₆ alkenyl), and having one or more (*e.g.*, 2, 3, etc.) carbon-carbon double bonds. The alkenyl group may be linear, branched or cyclic. Examples of alkenyls include, but are not limited to ethenyl (vinyl), 2-propenyl, 3-propenyl, 1,4-pentadienyl, 1,4-butadienyl, 1-butenyl, 2-butenyl and 3-butenyl. “Alkenyl” is intended to embrace all structural isomeric forms of an alkenyl. For example, butenyl encompasses 1,4-butadienyl, 1-butenyl, 2-butenyl 30 and 3-butenyl, etc.

[0032] As used herein, and unless otherwise specified, the term “alkoxy” refers to –O-alkyl containing from 1 to about 10 carbon atoms. The alkoxy may be straight-chain or branched-chain. Non-limiting examples include methoxy, ethoxy, propoxy, butoxy, isobutoxy, tert-

2018EM183 PCT

butoxy, pentoxy, and hexoxy. “C₁ alkoxy” refers to methoxy, “C₂ alkoxy” refers to ethoxy, “C₃ alkoxy” refers to propoxy and “C₄ alkoxy” refers to butoxy. Further, as used herein, “OMe” refers to methoxy and “OEt” refers to ethoxy.

[0033] As used herein, and unless otherwise specified, the term “aromatic” refers to unsaturated cyclic hydrocarbons having a delocalized conjugated π system and having from 5 to 20 carbon atoms (aromatic C₅-C₂₀ hydrocarbon). Exemplary aromatics include, but are not limited to benzene, toluene, xylenes, mesitylene, ethylbenzenes, cumene, naphthalene, methylnaphthalene, dimethylnaphthalenes, ethylnaphthalenes, acenaphthalene, anthracene, phenanthrene, tetraphene, naphthacene, benzanthracenes, fluoranthrene, pyrene, chrysene, triphenylene, and the like, and combinations thereof.

[0034] Unless otherwise indicated, where isomers of a named alkyl, alkenyl, alkoxy, or aryl group exist (*e.g.*, n-butyl, iso-butyl, sec-butyl, and tert-butyl) reference to one member of the group (*e.g.*, n-butyl) shall expressly disclose the remaining isomers (*e.g.*, iso-butyl, sec-butyl, and tert-butyl) in the family. Likewise, reference to an alkyl, alkenyl, alkoxide, or aryl group without specifying a particular isomer (*e.g.*, butyl) expressly discloses all isomers (*e.g.*, n-butyl, iso-butyl, sec-butyl, and tert-butyl).

[0035] As used herein, the term “hydroxyl” refers to an –OH group.

[0036] As used herein, “oxygenate” refers to a saturated, unsaturated, or polycyclic cyclized hydrocarbon radical containing from 1 to 40 carbon atoms and further containing one or more oxygen heteroatoms.

[0037] As used herein, “Grignard reagent” is R-M-X where R is an organic radical, M is an alkaline earth metal, usually magnesium, and X is halogen.

[0038] As used herein, “*ansa*-metallocene” is a bridged dicyclopentadienyl metallocycle of the formula T(Cp¹)(Cp²)ML_n where T is a divalent bridging group, Cp¹ and Cp² are independently substituted or unsubstituted cyclopentadienyl groups, including indenyl and fluorenyl, for example, covalently bound to the bridging group T, M is a metal, L is an anion, and n is a number equal to the valence of M, typically 3 or 4.

[0039] As used herein, the term “bridged dicyclopentadienyl” refers to a dicyclopentadienyl ligand in or capable of forming an *ansa*-metallocene, wherein the bridged dicyclopentadienyl ligand is according to the formula T(Cp¹)(Cp²), where T is a divalent bridging group, and Cp¹ and Cp² are substituted or unsubstituted cyclopentadienyl groups, including indenyl and fluorenyl, for example, and the ligand may be neutral or charged, *e.g.*, the dianionic form of the deprotonated ligand.

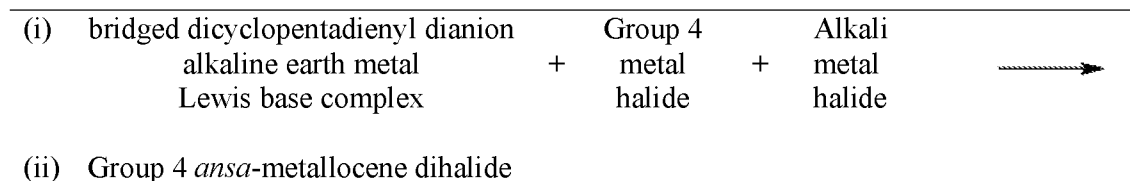
2018EM183 PCT

[0040] ^1H NMR data herein were collected at room temperature using a Bruker spectrometer with a ^1H frequency of either 400 MHz or 500 MHz.

[0041] In the specification and claims the “purity” of metallocenes is conventionally determined by quantitative NMR, i.e., by weighing out a specific amount of a sample and also weighing out a specific amount of another compound selected as an internal standard and comparing the signal ratios of the two compounds by ^1H NMR. The NMR data may be obtained in deuterated benzene (C_6D_6) or deuterated tetrahydrofuran ($\text{d}_8\text{-THF}$). The internal standard is selected as a compound of known purity that is non-reactive with the sample, soluble in a common deuterated solvent with the sample, and having at least one NMR signal completely separated from the sample signals. In the event of a conflict between the purity calculated from ^1H NMR in C_6D_6 and $\text{d}_8\text{-THF}$, the result from $\text{d}_8\text{-THF}$ shall control.

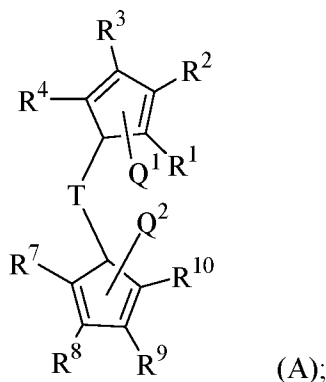
Synthesis of Group 4 *Ansa*-Metallocenes

[0042] In a class of embodiments, the present invention provides a method for synthesizing a Group 4 *ansa*-metallocene. The process comprises: (i) reacting a bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex with a Group 4 metal tetrahalide in the presence of an alkali metal halide; and (ii) forming the Group 4 *ansa*-metallocene dihalide; preferably according to Scheme 3:



Scheme 3

[0043] Preferably, the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex is represented by the formula (A):



where each R^1 to R^4 and R^7 to R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 to R^4 or two or

2018EM183 PCT

more of R⁷ to R¹⁰ join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, -CH₂-SiR'₃, or -CH₂-CR'₃ where each R' is independently hydrogen or a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

T is a bridging group; and

together Q¹ and Q² are a divalent alkaline earth metal complexed with a Lewis base, preferably according to the formula (D1), or each Q¹ and Q² is independently an alkaline earth metal cation as would be formed by reacting a neutral bridged dicyclopentadienyl ligand with a Grignard reagent and complexing with a Lewis base, preferably according to the formula (D2), wherein the formulae (D1) and (D2) are:



where M¹ is an alkaline earth metal, preferably magnesium;

X¹ is halogen, preferably chlorine, bromine, or iodine; and

together L¹ and L² are a difunctional Lewis base, or each L¹ and L² is independently a monofunctional Lewis base.

[0044] The Group 4 metal tetrahalide is preferably represented by the formula (B):



where M² is a Group 4 transition metal, preferably hafnium or zirconium; and each X² is independently halogen.

[0045] The alkali metal halide is preferably represented by the formula (C):



where M³ is an alkali metal such as lithium and X³ is independently halogen, preferably chlorine.

[0046] Preferably, in the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex in the formula (A):

each R¹ and R⁴ is independently hydrogen, alkoxide or a C₁ to C₄₀ substituted or unsubstituted hydrocarbyl group;

each R², R³, R⁸, and R⁹ is independently hydrogen, alkoxide or a C₁ to C₄₀ substituted or unsubstituted hydrocarbyl group or is -CH₂-SiR'₃ or -CH₂-CR'₃, and each R' is independently hydrogen or a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl, provided that at least one R' is not H and at least one of R² and R³ is -CH₂-SiR'₃ or -CH₂-CR'₃ (for example, if two of R' are

2018EM183 PCT

hydrogen and the other R' is methyl, $-\text{CH}_2\text{-CR}'_3$ is propylene);

each R⁷ and R¹⁰ is independently hydrogen, alkoxide or a C₁ to C₄₀ substituted or unsubstituted hydrocarbyl group;

R⁹ is preferably $-\text{CH}_2\text{-SiR}'_3$ or $-\text{CH}_2\text{-CR}'_3$, and each R' is independently hydrogen or a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl, provided that at least one R' is not H;

preferably R⁹ and R³ are, independently, $-\text{CH}_2\text{-SiR}'_3$ or $-\text{CH}_2\text{-CR}'_3$, and each R' is independently hydrogen or a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl, provided that at least one R' is not H, more preferably each R' is independently hydrogen or a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl;

preferably R⁹ and R³ or R² are, independently, $-\text{CH}_2\text{-CMe}_3$, or $-\text{CH}_2\text{-SiMe}_3$; and

preferably T is a bridging group comprising a group 14 atom and one or more of a C₁-C₁₀ linear hydrocarbyl group or substituted hydrocarbyl group, more preferably T is $-\text{Si}(\text{Me}_2)-$.

[0047] It has further been found that the purity of the reaction product from the reaction (i) of Scheme 3 is unexpectedly improved by conducting the reaction in the presence of an alkali metal halide such as LiCl. Surprisingly, the purity of the product in the crude reaction medium where LiCl is present is on the same order as the aliphatic extract where the reaction medium is aromatic and no LiCl is present. Preferably, an initial molar ratio of the alkali metal halide to the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex in the reaction (i) of Scheme 3 is equal to or greater than 1, preferably greater than 1, greater than 1.5, or equal to or greater than 2. The lower amounts of the alkali metal halide provide less benefit, whereas higher amounts are not needed.

[0048] Preferably, the Group 4 *ansa*-metallocene dihalide from the formation (ii) in Scheme 3 has a purity equal to or greater than 70 weight percent, preferably equal to greater than 75 weight percent, more preferably equal to or greater than 80 weight percent or equal to or greater than 85 weight percent, wherein the purity is determined on a solvent-free basis by quantitative ¹H NMR using an internal standard; or more preferably, the Group 4 *ansa*-metallocene dihalide from (ii) following solvent removal has a purity equal to or greater than 70 weight percent, preferably equal to greater than 75 weight percent, more preferably equal to or greater than 80 weight percent or equal to or greater than 85 weight percent, wherein the purity is determined on a total weight basis by quantitative ¹H NMR using an internal standard.

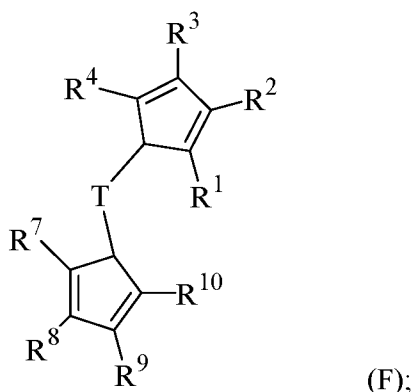
[0049] In any embodiment, the process may further comprise derivatizing the Group 4 *ansa*-metallocene dihalide from formation (ii) of Scheme 3, e.g., alkylating the Group 4 *ansa*-metallocene dihalide, preferably to form the corresponding Group 4 *ansa*-metallocene dialkyl.

2018EM183 PCT

The purity of the Group 4 *ansa*-metallocene dihalide in the reaction mixture from (i) may be such that, except for solvent removal if this is needed, no further purification is needed and the derivatization can be done using the reaction mixture directly. Preferably, the reaction in (i) and the alkylation are in the same reactor, more preferably without isolating the Group 4 *ansa*-metallocene between the reaction in (i) and the alkylation.

[0050] In any embodiment, the process may further comprise preparing the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex for the reaction (i) of Scheme 3. Preferably, the process comprises:

deprotonating a neutral bridged dicyclopentadienyl ligand with an alkaline earth metal compound to form the corresponding dianion, preferably wherein the neutral bridged dicyclopentadienyl ligand has the formula (F) or is an isomer of the formula (F):



where each R^1 to R^4 and R^7 to R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 to R^4 or two or more of R^7 to R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-CH_2-SiR'^3$, or $-CH_2-CR'^3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, provided that at least one R' is not H;

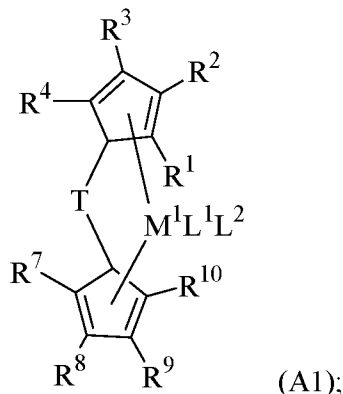
and

T is a bridging group, preferably comprising a group 14 atom and one or more of hydrogen, a C_1 - C_{10} hydrocarbyl group, or substituted hydrocarbyl group, more preferably T is $-Si(Me)_2-$; and

complexing the dianion with a Lewis base, preferably a difunctional Lewis base, to form the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex for the reaction (i) of Scheme 3.

2018EM183 PCT

[0051] Preferably, the alkaline earth metal compound in the deprotonation is an alkaline earth metal dialkyl, preferably $\text{Mg-}n\text{Bu}_2$ or $n\text{BuEtMg}$ or $\text{Mg-}i\text{Pr}_2$, and the complexed dianion comprises alkaline earth metal metallocene, preferably according to formula (A1):



5 where T, R^1 to R^4 , and R^7 to R^{10} are as defined above;

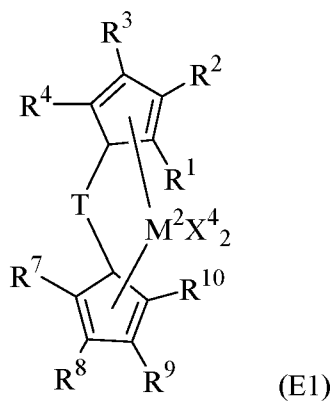
M^1 is an alkaline earth metal, preferably magnesium; and

together L^1 and L^2 are a difunctional Lewis base, preferably DME or 1,4-dioxolane, or each L^1 and L^2 is independently a monofunctional Lewis base, preferably THF.

[0052] The alkaline earth metal compound in the deprotonation is alternately a Grignard reagent, preferably $i\text{Pr-Mg-Cl}$ or $n\text{Bu-Mg-Cl}$, and the dianion comprises the product from contacting the neutral bridged dicyclopentadienyl ligand with the Grignard reagent, preferably the diGrignard product is formed and may be used as the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex for the reaction in (i) of Scheme 3.

[0053] If desired, the process may further comprise reacting a monocyclopentadiene anion with a bridging group compound to form the neutral bridged dicyclopentadienyl ligand. Preferably, the bridging group compound comprises TX_2 where T is a divalent bridging group and X is halogen.

[0054] In any embodiment, the *ansa*-metallocenes synthesized by the present process may be represented by the formula (E1):



2018EM183 PCT

where M^2 is Hf or Zr or Ti, preferably Hf or Zr;

each R^1 to R^4 and R^7 to R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 to R^4 or two or more of R^7 to R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-CH_2-SiR'_3$ or $-CH_2-CR'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

T is a bridging group, such as $CR^{21}R^{22}$ or $ZR^{21}R^{22}$ where Z is Si, Ge, or Sn, R^{21} and R^{22} are independently hydrogen, halogen, or a C_1 - C_{20} containing hydrocarbyl group (for example, linear hydrocarbyl group), substituted hydrocarbyl group, and optionally R^{21} and R^{22} join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, optionally R^{21} and R^{22} are the same or different; and

each X^4 is, independently, a univalent anionic ligand, or two X^4 are joined and bound to the metal atom to form a metallocycle ring, or two X^4 are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand (preferably halogen or C_1 to C_{12} alkyl or aryl, such as Cl, Me, Et, Ph).

[0055] In a preferred embodiment of the *ansa*-metallocenes of Formula (E1):

each R^1 , R^2 , R^4 , R^7 , R^8 , and R^{10} is independently hydrogen, or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, preferably each R^1 , R^2 , R^4 , R^7 , R^8 , and R^{10} is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl group; and

each R^3 and R^9 is independently a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, or is $-R^{20}-SiR'_3$ or $-R^{20}-CR'_3$ where R^{20} is a C_1 to C_4 hydrocarbyl, and each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl; more preferably R^3 is a C_1 to C_{20} substituted or unsubstituted hydrocarbyl group, preferably an alkyl group, or is $-R^{20}-SiR'_3$ or $-R^{20}-CR'_3$ where R^{20} is a C_1 to C_4 hydrocarbyl, and each R' is independently a C_1 to C_{20} substituted or unsubstituted hydrocarbyl.

[0056] In a preferred embodiment of the invention, M^2 is Hf, alternately M^2 is Zr.

[0057] In a preferred embodiment of the invention, each R^1 , R^2 , R^4 , R^7 , R^8 , and R^{10} is independently hydrogen, or a substituted C_1 to C_{12} hydrocarbyl group or an unsubstituted C_1 to C_{12} hydrocarbyl group, preferably hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof.

2018EM183 PCT

[0058] In a preferred embodiment of the invention, each R^3 and R^9 is independently $-R^{20}-SiR'_3$ or $-R^{20}-CR'_3$ where R^{20} is a C_1 to C_4 hydrocarbyl (preferably methylene, ethylene, propylene, butylene, or an isomer thereof), and R' is a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, preferably a substituted C_1 to C_{12} hydrocarbyl group or an
 5 unsubstituted C_1 to C_{12} hydrocarbyl group, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof.

[0059] Alternately, R^9 and optionally R^3 are, independently, $-R^{20}-CMe_3$, or $-R^{20}-SiMe_3$ where R^{20} is a C_1 to C_4 hydrocarbyl (preferably methyl, ethyl, propyl, butyl), preferably $-CH_2-CMe_3$, or $-CH_2-SiMe_3$.

10 [0060] Alternately, each X^4 may be, independently, a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group.

[0061] Alternately, each X^4 is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, aryls, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof
 15 (two X^4 's may form a part of a fused ring or a ring system), preferably each X^4 is independently selected from halides, aryls and C_1 to C_5 alkyl groups, preferably each X^4 is a phenyl, methyl, ethyl, propyl, butyl, pentyl, bromo, or chloro group.

[0062] Preferably, T is a bridging group containing at least one Group 13, 14, 15, or 16 element, in particular boron or a Group 14, 15 or 16 element. Examples of suitable bridging
 20 groups include $P(=S)R'$, $P(=Se)R'$, $P(=O)R'$, R'_2C , R'_2Si , R'_2Ge , $R'_2CCR'_2$, $R'_2CCR'_2CR'_2$, $R'_2CCR'_2CR'_2CR'_2$, $R'C=CR'$, $R'C=CR'CR'_2$, $R'_2CCR'=CR'CR'_2$, $R'C=CR'CR'=CR'$, $R'C=CR'CR'_2CR'_2$, $R'_2CSiR'_2$, $R'_2SiSiR'_2$, $R'_2SiOSiR'_2$, $R'_2CSiR'_2CR'_2$, $R'_2SiCR'_2SiR'_2$, $R'C=CR'SiR'_2$, $R'_2CGeR'_2$, $R'_2GeGeR'_2$, and $R'_2CGeR'_2CR'_2$, where R' is hydrogen or a C_1 - C_{20} containing hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl
 25 or germylcarbyl substituent and optionally two or more adjacent R' may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent. Preferred examples for the bridging group T include CH_2 , CH_2CH_2 , $SiMe_2$, $SiPh_2$, $SiMePh$, $Si(CH_2)_3$, $Si(CH_2)_4$, and $Me_2SiOSiMe_2$.

[0063] In a preferred embodiment of the invention in any embodiment of any formula
 30 described herein, T is represented by the formula R^aJ or $(R^aJ)_2$, where J is C, Si, or Ge, and each R^a is, independently, hydrogen, halogen, C_1 to C_{20} hydrocarbyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl) or a C_1 to C_{20} substituted hydrocarbyl, and two R^a can form a cyclic structure including aromatic, partially

2018EM183 PCT

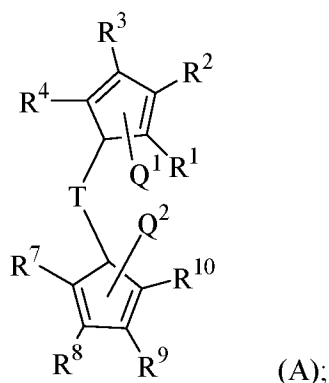
saturated, or saturated cyclic or fused ring system. Preferably, T is a bridging group comprising carbon or silica, such as dialkylsilyl, preferably T is selected from CH₂, CH₂CH₂, C(CH₃)₂, SiMe₂, SiPh₂, SiMePh, silylcyclobutyl (Si(CH₂)₃), (Ph)₂C, (p-(Et)₃SiPh)₂C, Me₂SiOSiMe₂, and cyclopentasilylene (Si(CH₂)₄).

- 5 [0064] In any embodiment of the invention, the molar ratio of rac to meso in the synthesized metallocene compound is from 1:100 to 100:1. Preferably, the rac:meso ratio is from 0.7 to 1.5, or from 0.75 to 1.4, or from 0.8 to 1.3, or from 0.9 to 1.1, or from 0.95 to 1.05, or about 1:1. In other embodiments, the rac:meso ratio is preferably 5:1 to 90:1, preferably 7:1 to 80:1, preferably 5:1 or greater, or 7:1 or greater, or 20:1 or greater, or 30:1 or greater, or 10 50:1 or greater. In an embodiment of the invention, the synthesized metallocene comprises an amount greater than or equal to 50 mol%, preferably greater than or equal to 60 mol% of the racemic isomer, or greater than or equal to 70 mol% of the racemic isomer, or greater than or equal to 80 mol% of the racemic isomer, or greater than or equal to 90 mol% of the racemic isomer, or greater than or equal to 92 mol% of the racemic isomer, or greater than or equal to 15 95 mol% of the racemic isomer, or greater than or equal to 97 mol% of the racemic isomer, based on the total amount of the racemic and meso isomer, if any, formed. In particular embodiments of the invention, the metallocene transition metal compound formed consists or consists essentially of equimolar amounts of the racemic and meso isomers, or consists or consists essentially of the racemic isomer. Amounts of rac and meso isomers are determined 20 by proton NMR.

[0065] This invention further relates to:

1. A process for synthesizing a Group 4 *ansa*-metallocene comprising:
 - (i) reacting a bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex with a Group 4 metal tetrahalide in the presence of an alkali metal 25 halide; and
 - (ii) forming the Group 4 *ansa*-metallocene dihalide.
2. The process of paragraph 1, wherein the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex is represented by the formula (A):

2018EM183 PCT



where each R^1 to R^4 and R^7 to R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 to R^4 or two or more of R^7 to R^{10} join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-\text{CH}_2\text{-SiR}'_3$ or $-\text{CH}_2\text{-CR}'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

T is a bridging group; and

together Q^1 and Q^2 are a divalent alkaline earth metal complexed with a Lewis base, preferably according to the formula (D1), or each Q^1 and Q^2 is independently an alkaline earth metal cation as would be formed by reacting a neutral bridged dicyclopentadienyl ligand with a Grignard reagent and complexing with a Lewis base, preferably according to the formula (D2), wherein the formulae (D1) and (D2) are:



where “>” indicates a divalent complex and “-” indicates a monovalent complex;

M^1 is an alkaline earth metal, such as magnesium;

where M^1 is an alkaline earth metal, preferably magnesium;

X^1 is halogen, preferably chlorine; and

together L^1 and L^2 are a difunctional Lewis base, or each L^1 and L^2 is independently a monofunctional Lewis base;

wherein the Group 4 metal tetrahalide is represented by the formula (B):



where M^2 is a Group 4 transition metal, preferably hafnium or zirconium; and

2018EM183 PCT

each X^2 is independently halogen; and

wherein the alkali metal halide is represented by the formula (C):



where M^3 is an alkali metal, preferably lithium, and X^3 is independently halogen, preferably chlorine.

3. The process of paragraph 2, wherein:

each R^1 and R^4 is independently hydrogen, alkoxide or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group;

each R^2 , R^3 , R^8 , and R^9 is independently hydrogen, alkoxide or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group or is $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$, and each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, provided that at least one R' is not H and at least one of R^2 and R^3 is $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$;

each R^7 and R^{10} is independently hydrogen, alkoxide or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group;

R^9 is preferably $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$, and each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, provided that at least one R' is not H;

preferably R^9 and R^3 are, independently, $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$, and each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, provided that at least one R' is not H, more preferably each R' is independently a C_1 to C_{20} substituted or unsubstituted hydrocarbyl;

preferably R^9 and R^3 or R^2 are, independently, $-\text{CH}_2-\text{CMe}_3$, or $-\text{CH}_2-\text{SiMe}_3$; and

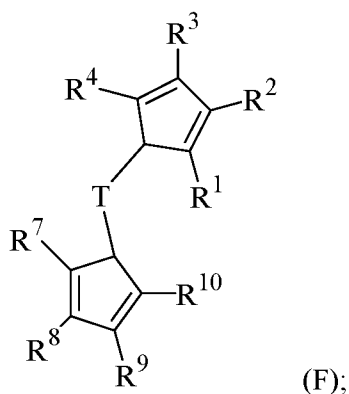
preferably T is a bridging group comprising a group 14 atom and one or more of hydrogen, a C_1 - C_{10} linear hydrocarbyl group, or substituted hydrocarbyl group, more preferably T is $-\text{Si}(\text{Me}_2)-$.

4. The process of paragraph 1, 2, or 3, wherein the reaction in (i) is in a fluid medium comprising a Lewis base, preferably an ether, preferably tetrahydrofuran.

5. The process of any of paragraphs 1 to 4 wherein an initial molar ratio of the alkali metal halide to the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex in the reaction in (i) is equal to or greater than 1, preferably greater than 1, greater than 1.5, or equal to or greater than 2.

2018EM183 PCT

6. The process of any of paragraphs 1 to 5 wherein the Group 4 *ansa*-metallocene dihalide from (ii) has a purity equal to or greater than 70 weight percent, preferably equal to greater than 75 weight percent, more preferably equal to or greater than 80 weight percent or equal to or greater than 85 weight percent, wherein the purity is determined on a solvent-free basis by quantitative ^1H NMR using an internal standard; or preferably wherein the Group 4 *ansa*-metallocene dihalide from (ii) following solvent removal has a purity equal to or greater than 70 weight percent, preferably equal to greater than 75 weight percent, more preferably equal to or greater than 80 weight percent or equal to or greater than 85 weight percent, wherein the purity is determined on a total weight basis by quantitative ^1H NMR in using an internal standard.
7. The process of any of paragraphs 1 to 6, further comprising alkylating the Group 4 *ansa*-metallocene dihalide from (ii).
8. The process of paragraph 7, wherein the reaction in (i) and the alkylation are in the same reactor, preferably without isolating the Group 4 *ansa*-metallocene between the reaction in (i) and the alkylation.
9. The process of any of paragraphs 1 to 8 further comprising:
deprotonating a neutral bridged dicyclopentadienyl ligand with an alkaline earth metal compound to form the corresponding dianion, preferably wherein the neutral bridged dicyclopentadienyl ligand has the formula (F) or is an isomer of the formula (F):



where each R^1 to R^4 and R^7 to R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 to R^4 or two or more of R^7 to R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any

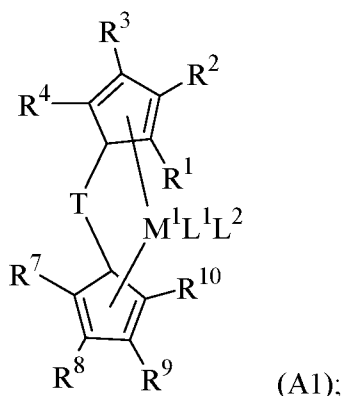
2018EM183 PCT

two or more of R¹ join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent; and

T is a bridging group, preferably comprising a group 14 atom and one or more of hydrogen, a C₁-C₁₀ hydrocarbyl group, or substituted hydrocarbyl group, more preferably T is -Si(Me₂)-; and

complexing the dianion with a Lewis base, preferably a difunctional Lewis base, to form the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex for the reaction (i).

10. The process of paragraph 9, wherein the alkaline earth metal compound in the deprotonation is an alkaline earth metal dialkyl, preferably Mg-nBu₂ or n-BuEtMg or Mg-iPr₂, and the complexed dianion comprises alkaline earth metal metallocene, preferably according to formula (A1):



where T, R¹ to R⁴, and R⁷ to R¹⁰ are as defined above;

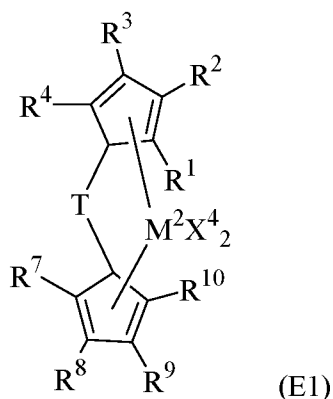
- 15 M¹ is an alkaline earth metal, preferably magnesium; and together L¹ and L² are a difunctional Lewis base, preferably DME or 1,4-dioxolane, or each L¹ and L² is independently a monofunctional Lewis base, preferably THF.

11. The process of paragraph 9, wherein the alkaline earth metal compound in the deprotonation is a Grignard reagent, preferably iPr-Mg-chloride or nBu-Mg-chloride, and the dianion comprises a diGrignard product.

12. The process of any of paragraphs 9 to 11, further comprising reacting a monocyclopentadiene anion with a bridging group compound to form the neutral bridged dicyclopentadienyl ligand, preferably where the bridging group compound comprises T¹X₂ where T¹ is a divalent bridging moiety and X is halogen.

13. The process of any of paragraphs 1 to 12, wherein the synthesized Group 4 *ansa*-metallocene is according to the formula (E1):

2018EM183 PCT



where M^2 is a Group 4 transition metal, preferably hafnium or zirconium;

each R^1 to R^4 and R^7 to R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 to R^4 or two or more of R^7 to R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-CH_2-SiR'_3$ or $-CH_2-CR'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

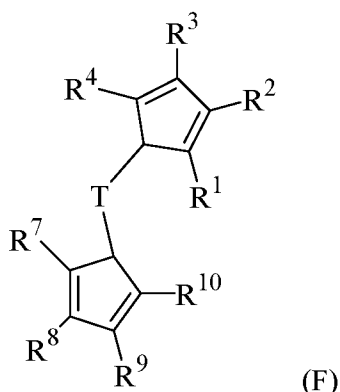
T is a bridging group, preferably $CR^{21}R^{22}$ or $ZR^{21}R^{22}$ where Z is Si, Ge, or Sn, R^{21} and R^{22} are independently hydrogen, halogen, or a C_1 - C_{20} containing hydrocarbyl group, preferably a linear hydrocarbyl group, substituted hydrocarbyl group, and optionally R^{21} and R^{22} join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, optionally R^{21} and R^{22} are the same or different; and

each X^4 is independently a univalent anionic ligand, or two X^4 are joined and bound to the metal atom to form a metallocycle ring, or two X^4 are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand, preferably each X^4 is halogen or C_1 to C_{12} alkyl or aryl, more preferably each X^4 is Cl, methyl, ethyl, or phenyl.

14. A process for synthesizing a Group 4 *ansa*-metallocene comprising:

(a) deprotonating a neutral bridged dicyclopentadienyl ligand with an alkaline earth metal compound selected from alkaline earth metal dialkyls and Grignard reagents to form the corresponding dianion comprising the alkaline earth metal, wherein the neutral bridged dicyclopentadienyl ligand is according to formula (F) or is an isomer of the formula (F):

2018EM183 PCT

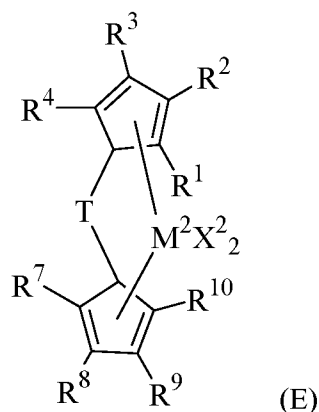


where each R^1 to R^4 and R^7 to R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 to R^4 or two or more of R^7 to R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, provided that at least one R' is not H; and

T is a bridging group, preferably comprising a group 14 atom and one or more of hydrogen, a C_1 - C_{10} hydrocarbyl group, or substituted hydrocarbyl group, more preferably T is $-\text{Si}(\text{Me}_2)-$;

- (b) complexing the dianion from (a) with a Lewis base, preferably a difunctional Lewis base, to form a bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex;
- (c) reacting the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex from (b) with a Group 4 metal tetrahalide, preferably hafnium tetrachloride or zirconium tetrachloride, in a fluid medium comprising an alkali metal halide, preferably LiCl, and a solvent, preferably THF;
- (d) forming Group 4 *ansa*-metallocene according to the formula (E):

2018EM183 PCT

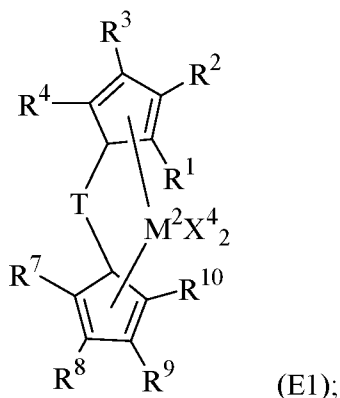


where T, R¹ to R⁴, and R⁷ to R¹⁰ are as defined above;

M² is the Group 4 metal;

each X² is independently halogen; and

- 5 (e) optionally alkylating the Group 4 *ansa*-metallocene from (d) with an alkylating agent to form the Group 4 *ansa*-metallocene according to the formula (E1):



where T, R¹ to R⁴, R⁷ to R¹⁰, and M² are as defined above; and

- 10 each X⁴ is independently a univalent anionic ligand, preferably alkyl, preferably methyl, or two X⁴ are joined and bound to the metal atom to form a metallocycle ring, or two X⁴ are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.

- 15 15. The process of paragraph 14, wherein the reaction in (c) and the alkylation in (e) are in the same reactor, preferably without isolating the Group 4 *ansa*-metallocene between (c) and (e).
16. The process of paragraph 14 or paragraph 15, further comprising solvent extraction of the Group 4 *ansa*-metallocene formed in (d).
17. The process of any of paragraphs 14 to 16, wherein an initial molar ratio of the alkali metal halide to the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base

2018EM183 PCT

complex in the reaction in (c) is equal to or greater than 1, preferably greater than 1 or equal to or greater than 2.

18. The process of any of paragraphs 14 to 17, wherein the alkaline earth metal compound in the deprotonation in (a) is an alkaline earth metal dialkyl, preferably Mg-nBu₂ n-BuEtMg or Mg-iPr₂, and the dianion comprises alkaline earth metal metallocene.
19. The process of any of paragraphs 14 to 18, wherein the alkaline earth metal compound in the deprotonation in (a) is a Grignard reagent, preferably iPr-Mg-chloride or nBu-Mg-chloride, and the dianion comprises a diGrignard product.
20. The process of any of paragraphs 14 to 19 comprising the alkylation of (e) and wherein in the formula (E1):

each R¹, R², R⁴, R⁷, R⁸, and R¹⁰ is independently hydrogen, or a C₁ to C₄₀ substituted or unsubstituted hydrocarbyl group, preferably each R¹, R², R⁴, R⁷, R⁸, and R¹⁰ is independently hydrogen or a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl group; and

each R³ and R⁹ is independently a C₁ to C₄₀ substituted or unsubstituted hydrocarbyl group, or is -R²⁰-SiR'₃ or -R²⁰-CR'₃ where R²⁰ is a C₁ to C₄ hydrocarbyl, and each R' is independently hydrogen or a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl; more preferably R³ is a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl group, preferably an alkyl group, or is -R²⁰-SiR'₃ or -R²⁰-CR'₃ where R²⁰ is a C₁ to C₄ hydrocarbyl, and each R' is independently a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl.
21. The process of paragraph 20, wherein:

M² is Hf, or M² is Zr;

each R¹, R², R⁴, R⁷, R⁸, and R¹⁰ is independently hydrogen, or a substituted C₁ to C₁₂ hydrocarbyl group or an unsubstituted C₁ to C₁₂ hydrocarbyl group, preferably hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof; and

each R³ and R⁹ is independently -R²⁰-SiR'₃ or -R²⁰-CR'₃ where R²⁰ is a C₁ to C₄ hydrocarbyl, preferably methylene, ethylene, propylene, butylene, or an isomer thereof, and R' is a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl, preferably a substituted C₁ to C₁₂ hydrocarbyl group or an unsubstituted C₁ to C₁₂ hydrocarbyl group, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, or an isomer thereof.

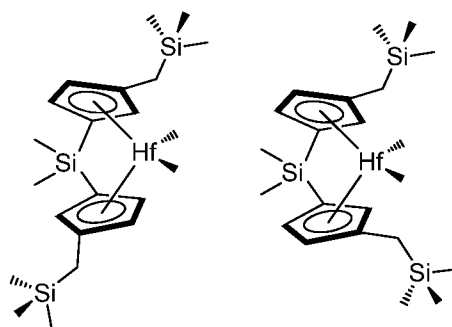
2018EM183 PCT

EXPERIMENTAL

[0066] It is to be understood that while the invention has been described in conjunction with the specific embodiments thereof, the foregoing description is intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications will be apparent to those skilled in the art to which the invention pertains.

[0067] Therefore, the following examples are put forth so as to provide those skilled in the art with a complete disclosure and description and are not intended to limit the scope of that which the inventors regard as their invention.

[0068] In the following examples, the bridged dicyclopentadiene ligand $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2$ is referred to as “Lig¹.” The bridged hafnocene (*rac*/*meso*-Lig¹HfMe₂) shown below and the corresponding zirconocene (Lig¹ZrMe₂) were prepared.



Rac-isomer

Meso-isomer

Lig¹ HfMe₂ Isomers

[0069] In the following examples, we refer to a “purity factor” or PF that is defined as the ratio of the integration of certain of the metallocene product resonances relative to the integration of a defined area of the ¹H NMR spectrum. This is done to simplify the determination of the relative effectiveness of various preparation procedures. The PF method herein ignores the presence of most solvents or other impurities that do not result as byproducts from the complexation reaction, but provides a relative indication of the effectiveness of the synthesis method against which other synthesis procedures may be compared.

[0070] The purity factor procedure uses as the internal standard the weighted areas of two resonances from the ligand corresponding to the peaks reflecting the least contamination from impurities, relative to the total areas of the peaks over the relevant resonance range, which for $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2$ are according to the following Equation (1):

$$\text{PF} = 100 \cdot 3 \cdot (A_1 + A_2) / A_T \quad (1)$$

2018EM183 PCT

where PF is the purity factor, A_1 and A_2 are the integrated areas of the ^1H NMR peaks at 4.95-5.05 ppm and 5.1-5.2 ppm, respectively, and A_T is the total integrated area of the ^1H NMR peaks at 4.5-6.9 ppm. FIG. 1 shows an example calculation for a typical $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{Cp})_2$ spectrum. In this example, the 4.95-5.05 ppm peak has an A_1 of 2.000, the 5.1-5.2 ppm peak has A_2 of 2.152, and the total A_T is 20.288. Plugging these values into Equation 1 gives the following for this example:

$$\text{PF} = 300 \times (2.152 + 2.000) / 20.288 = 61.$$

The NMR data may be obtained in deuterated benzene (C_6D_6) or deuterated tetrahydrofuran ($\text{d}_8\text{-THF}$).

[0071] All manipulations were performed in an inert N_2 purged glove box unless otherwise stated. All anhydrous solvents were purchased from Sigma Aldrich and were degassed and dried over molecular sieves prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were degassed and dried over molecular sieves prior to use. n-Butyl lithium (solution in hexane), dimethylsilyl dichloride (Me_2SiCl_2), and methylmagnesium bromide (3.0 M solution in diethyl ether) were purchased from Sigma-Aldrich. Hafnium tetrachloride (HfCl_4) 99+% and (trimethylsilyl)methyl trifluoromethanesulfonate were procured from Strem Chemicals and TCI America, respectively. All chemicals were used as purchased unless otherwise stated.

[0072] **Run 1: Synthesis of (Trimethylsilyl) methylcyclopentadiene, $(\text{Me}_3\text{Si})\text{CH}_2\text{CpH}$.** (Trimethylsilyl)methyl trifluoromethanesulfonate (10.57g, 44.7 mmol) was dissolved in 150 mL of diethyl ether and cooled to -25°C , to this a solid potassium cyclopentadienide (KCp) (4.66g, 44.7 mmol) was slowly added over a period of 5-10 minutes. It was prepared in accordance with the description in Amsharov, K.; Abdurakhmanova, N.; Stepanow, S.; Rauschenbach, S.; Jansen, M.; Kern, K. *Angew. Chem. Int. Ed.* 2010, 49, 9392-9396. The resulting mixture was stirred 5 hours at about 23°C . Volatiles from the reaction mixture were carefully removed under dynamic vacuum to avoid evaporating the volatile (trimethylsilyl)methylcyclopentadiene, $(\text{Me}_3\text{Si})\text{CH}_2\text{CpH}$. The reaction flask (250 mL round bottom flask) and frit with celite were weighted to calculate yield of the product after extraction. The crude materials were extracted into pentane (3 x 10 mL) and used without any further purification. Based on above mathematical method, the yield is calculated as 5.55 g (81.6%).

[0073] **Run 2: Synthesis of Lithium (trimethylsilyl) methylcyclopentadienide, $(\text{Me}_3\text{Si})\text{CH}_2\text{CpLi}$.** A hexane solution of n-butyl lithium (14.6 mL, 36.5 mmol) was added

2018EM183 PCT

drop-wise to a precooled solution (pentane and diethyl ether, 50/50 mL) of $(\text{Me}_3\text{Si})\text{CH}_2\text{CpH}$ (5.55 g, 36.5 mmol) over a period of 15-20 minutes at -25°C . The resulting mixture was gradually brought to about 23°C and then continuously stirred overnight. Volatiles were removed in vacuo and remaining crude materials were thoroughly washed with pentane. The final materials were dried under vacuum to obtain a colorless crystalline solid of $(\text{Me}_3\text{Si})\text{CH}_2\text{CpLi}$ in 5.75 g (99.7%) yield.

[0074] Run 3: Synthesis of Lig^1H_2 . Neat Me_2SiCl_2 (340 mg, 2.6 mmol) was dissolved in 10 mL of THF and cooled to -25°C . Solid lithium (trimethylsilyl) methylcyclopentadienide was added and the resulting mixture was stirred overnight at about 23°C . Volatiles from the reaction mixture were removed in vacuo and the mixture subsequently triturated with pentane to remove traces of THF. The crude materials were extracted into pentane and followed by solvent removal under vacuum to obtain a thick yellow viscous oil of $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{CpH})_2$ (750 mg; 80% yield).

[0075] Run 4: Synthesis of $\text{Lig}^1\text{Li}_2(\text{DME})$: A hexane solution of n-butyl lithium (1.7 mL, 4.2 mmol, 2.5 M solution) was added drop-wise to a precooled solution of $\text{Me}_2\text{Si}((\text{Me}_3\text{Si})\text{CH}_2\text{CpH})_2$ (750 mg, 2.1 mmol) in 10 mL of dimethoxyethane over a period of 5-10 minutes at -25°C . The resulting mixture was gradually warmed to about 23°C and then continuously stirred overnight. Volatiles from the reaction mixture were removed in vacuo, and triturated with pentane to remove DME. The crude materials were thoroughly washed with pentane to remove any soluble impurities, and dried under vacuum to give the colorless crystalline solid of $\text{Lig}^1\text{Li}_2(\text{DME})$ (830 mg; 93% yield).

2018EM183 PCT

Table A: Synthesis of Lig¹ from the Lig¹Li₂ and HfCl₄

Run	Reaction solvent	Reaction Condition	Reaction Time	Purity Factor
5	Et ₂ O	HfCl ₄ (s) added to solution of Lig ¹ Li ₂ (DME) in ether at -25 C	overnight	63
6	Et ₂ O	solid HfCl ₄ (s) added to slurry of Lig ¹ Li ₂ in ether	75 min	64
7	DME	solution of Lig ¹ Li ₂ added to solution of HfCl ₄ in DME	2.5	62
8	Et ₂ O	solid HfCl ₄ added to slurry of Lig ¹ Li ₂ in ether	overnight	59
9	Et ₂ O	solid HfCl ₄ added to slurry of Lig ¹ Li ₂ in ether at -25 C	16 h	68
10	Et ₂ O	solid HfCl ₄ added to slurry of Lig ¹ Li ₂ in ether at -25 C	16 h	68
11	Et ₂ O	solid HfCl ₄ added to solution of Lig ¹ Li ₂ in ether at -25 C	overnight	65
12	Et ₂ O	solid HfCl ₄ added to solution of Lig ¹ Li ₂ in ether at -25 C	overnight	55
13	Et ₂ O	solid HfCl ₄ added to solution of Lig ¹ Li ₂ in ether at -25 C	overnight	54
14	Et ₂ O	solid HfCl ₄ added to solution of Lig ¹ Li ₂ in ether at -25 C	overnight	65

[0076] Run 5: Synthesis of Lig¹HfCl₂ from Lig¹Li₂. Solid HfCl₄ (570 mg, 1.8 mmol) was added to a precooled diethyl ether (20 mL) solution of Me₂Si((Me₃Si)CH₂Cp)₂Li₂(DME) (830 mg, 1.8 mmol) at -25°C. The resulting mixture was stirred overnight at about 23°C. The ¹H NMR of the reaction product mixture is shown in FIG. 1. Volatiles from the reaction mixture were removed in vacuo, and then extracted into dichloromethane. Solvent removal under vacuum gave a yellow crystalline solid of Lig¹HfCl₂ (1.02 g; 94% yield). The ¹H NMR spectrum of final material indicated a ~1:1 ratio of *rac/meso* isomers.

[0077] Runs 6-14: Synthesis of Lig¹HfCl₂ from Lig¹Li₂ at various reaction conditions.

The procedure of Run 5 was repeated using a variety of solvents and other conditions as shown in Table A. All procedures of Runs 6-14 were similarly found to produce impurities in the reaction with similar purity factors found in Run 5. In most cases, these impurities were soluble in the aliphatic hydrocarbon used to do the extraction and thus contaminated the final product, Lig¹HfCl₂. These had purity factors in the range of 54-68, average about 62.

[0078] Run 15: Synthesis of Lig¹-Mg(DME). LiCpCH₂SiMe₃ (24.5 g; 155 mmol) was dissolved in THF (60 mL), Me₂SiCl₂ (10.1 g; 78.3 mmol) added in portions over ~1 minute, the reaction stirred 30 minutes at room temperature, and the THF was removed under vacuum at 35 °C to give a viscous slurry. The slurry was extracted with heptane (40 mL), the liquid

2018EM183 PCT

isolated by filtration, and the solid residue washed with additional heptane (20 mL). The combined extracts were placed in a 250 mL rb flask and Bu₂Mg (1.0M in heptanes; 75 mL; 75 mmol) was added in 10 mL portions with stirring over several minutes. The reaction was heated to 60°C for 30 minutes; then heated to 93°C for 3 hours. The solution was partially cooled and 40 mL of DME was added. The reaction was cooled to just below room temperature by addition of ~20 mL pentane and evaporating it off, which caused rapid precipitation of a colorless solid. The solid was isolated by filtration and the cake washed 2 x 30 mL with pentane. The solid was then collected, stirred for 5 minutes in 100 mL pentane, isolated by filtration, and dried under vacuum at 45°C. Yield = 23.0 g; 63%; very clean by ¹H NMR with a trace of pentane left.

[0079] Run 16: Synthesis of Lig¹-Mg(DME). LiCpCH₂SiMe₃ (23.28 g; 147.1 mmol) was dissolved in THF (~60 mL) and with stirring, Me₂SiCl₂ (9.54 g; 73.9 mmol) added in one portion. A precipitate formed immediately and the reaction was hot but did not reflux. After stirring 20 minutes the THF was removed under vacuum and the resulting oily mixture was extracted with heptane (~40 mL), filtered and the colorless solid on the frit was washed with 20 mL heptane. The solutions were filtered directly into a solution of Mg-nBu₂ in a flask with a stirbar, (1.0 M/heptane; 70.0 mL; 70.0 mmol). The reaction mixture was heated to 90°C overnight (14 h). There was some oily material stuck to the bottom of the flask and floating in the solution. After cooling somewhat, 40 mL DME was added, a precipitate formed, and the slurry stirred for 45 minutes. No oily material was present. The solid was filtered and washed 2 x 50 mL with pentane, and dried under vacuum. Yield = 22.0 g.

[0080] Run 17: Synthesis of Lig¹-Mg(DME). LiCpCH₂SiMe₃ (31.58 g; 199.6 mmol) was dissolved in THF (~70 mL) and Me₂SiCl₂ (12.87 g; 99.7 mmol) added with stirring over about a minute. A precipitate formed immediately and the reaction was hot but did not reflux. After stirring 20 minutes the THF was removed under vacuum at 42°C, the resulting oily mixture extracted with heptane (~50 mL), filtered, and washed with 25 mL heptane, leaving a colorless solid on the frit. To the combined stirring solutions was added Mg-nBu₂ (1.0 M/heptane; 95.0 mL; 95 mmol). The reaction mixture was heated to 90°C for three hours then DME (~30 mL) was added and an emulsion formed. With further cooling a very light pink solid precipitated. The solid was washed with 2 X 40 mL pentane and dried under vacuum at 50°C. The solid was gummy, yield=38 g. The ¹H NMR in d₈-THF showed unreacted Mg-nBu₂ and other impurity. The solid was slurried in pentane (100 mL) and DME (50 mL) added with vigorous stirring. The almost colorless solid was isolated by filtration; washed with pentane (~50 mL)

2018EM183 PCT

and dried under vacuum at 50°C. Yield = 28.2 g; ^1H NMR in d_8 -THF. A portion (27.4 g) was slurried in DME (50 mL), heated to 80°C with vigorous stirring. After slight cooling pentane (75 mL) was added and some pentane boiled off. The slurry was cooled to -20°C for 90 minutes, the colorless precipitate isolated by filtration, washed with pentane (~40 mL), and dried under vacuum. Yield = 24.2 g; very clean by ^1H NMR.

[0081] Run 18: Reaction of Lig¹-Mg(DME) with HfCl₄ in toluene. Solid Lig¹-Mg(DME) (0.542g; 1.15 mmol) was dumped into a rapidly stirring slurry of HfCl₄ (0.372 g; 1.16 mmol) in toluene (~20 mL). After stirring 2 hours at room temperature the solvent was pumped off and the residue extracted with warm pentane (~20 mL) leaving a colorless solid. An aliquot of the pentane solution was dried down and redissolved in C₆D₆ (17-AC2531-B). This turned out to be fairly clean product of the rac/meso Lig¹HfCl₂. The bulk solution was dried down and gave a crystalline solid. Yield = 0.35 g; the isolated colorless solid was washed with pentane 20 mL then dried under vacuum. Yield of this was 0.31 g; this was attempted to dissolve in C₆D₆ with brief warming to 65°C but not much went in: the ^1H NMR showed very little but low concentration of product and impurity and solvent. The initial ^1H NMR showed that only about 60% of the Lig¹HfCl₂ was made and that about 40% was impurity.

[0082] Run 19: Reaction of Lig¹-Mg(DME) with HfCl₄ in toluene. Lig¹-Mg(DME) (0.890g; 1.88 mmol) was slurried in toluene (~25 mL) and 0.34 mL of 1,4-dioxane (3.98 mmol) was added. With stirring, solid HfCl₄ (0.60 g; 1.88 mmol) was added. There appeared to be a fairly rapid reaction. After stirring 80 minutes an aliquot was removed, dried down and the NMR taken in C₆D₆. The NMR was very similar to the previous prep in Run 18 except slightly cleaner; purity factor = 67. The reaction was dried down, extracted with pentane (~25 mL), and filtered to give a yellow solution. This was dried down to give a yellow solid. ^1H NMR in C₆D₆ showed a purity factor of 83.

[0083] Run 20: Reaction of Lig¹-Mg(DME) with HfCl₄ in toluene. Solid Lig¹-Mg(DME) (from Run 15) (12.0 g; 25.4 mmol) was dumped into a rapidly stirring slurry of HfCl₄ (8.12 g; 25.4 mmol) in toluene (~65 mL). The reaction turned yellow and was stirred for 1 hour at room temperature. The reaction was allowed to settle briefly and an aliquot removed, dried down and ^1H NMR taken, PF = 61. The remaining slurry was dried down under vacuum at 50°C. The residue was extracted with 3 x 50 mL pentane. The combined extracts were dried down to give a yellow solid. Yield = 9.0 g; 58% ^1H NMR in C₆D₆, Purity Factor = 85.

2018EM183 PCT

[0084] Run 21: Reaction of Lig¹-Mg(DME) with HfCl₄ in Toluene at High Temperature. Lig¹-Mg(DME) (0.86 g; 1.82 mmol) was added to toluene (~40 mL) and heated to 93°C to form a colorless solution. Solid HfCl₄ (0.59 g; 1.84 mmol) was added in with stirring. The solution was stirred for 15 minutes then allowed to cool. The ¹H NMR of the reaction mixture was taken in d8-THF.

[0085] Run 22: Reaction of Lig¹-Mg(THF)₂ with HfCl₄ in Toluene. To Lig¹-Mg(THF)₂ (0.65 g; 1.23 mmol) slurried in toluene (~10 mL) was added solid HfCl₄ (0.39 g; 1.22 mmol) with stirring at room temp. After about 15 minutes there was only a small amount of solids present and a yellow color. After about 75 minutes an aliquot was removed and dried down, the ¹H NMR in C₆D₆ showed rac/meso Lig¹HfCl₂ in about 60% yield and a typical looking impurity with broad peaks in about 40% yield. The toluene was removed under vacuum. The residue extracted with pentane (~8 mL) filtered. An aliquot was removed, dried down and the ¹H NMR taken in C₆D₆.

[0086] Run 23: Reaction of Lig¹-Mg(DME) with HfCl₄ in Toluene. Solid Lig¹-Mg(DME) from Run 16 (17.95 g; 37.9 mmol) was dumped into a rapidly stirring slurry of HfCl₄ (12.2 g; 38.1 mmol) in toluene (~80 mL). The reaction turned yellow and was stirred for 2 hours at room temperature. The yellow solution was filtered away from a light yellow colored solid and the solid was washed 2 x 25 mL with toluene. An aliquot of the toluene solution was dried down and the NMR taken in d8-THF. This showed a rac/meso if 1:1 and a purity factor of 69. The combined toluene filtrates were dried under vacuum at 35°C and then extracted with iso-hexane (~180 mL) at 35°C. The remaining solid was washed 2 x 25 mL with isohexane. The isohexane washings and filtrates were combined. An aliquot of the isohexane solution was dried down and the NMR taken in d8-THF. This showed a rac/meso ratio of 1:1 and a purity factor of 86. The entire solution was dried down at 35°C under vacuum to give a yellow solid. Yield = 15.4 g. The isohexane insoluble solid was dried under vacuum to give 5.1 g. The ¹H NMR of this solid in d8-THF showed fairly clean impurity, as seen in FIG. 2. The originally isolated solid from the initial reaction mixture was washed 2 x 25 mL with pentane, then dried under vacuum. Yield = 7.70 g. Not very soluble in d8-THF (not all solid dissolved).

[0087] The results from synthesizing Lig¹-HfCl₂ from HfCl₄ and Lig¹-Mg(DME) are summarized in Table B:

2018EM183 PCT

Table B: Synthesis of Lig¹-HfCl₄ from the Lig¹-Mg(DME) and HfCl₄

Run	Reaction Solvent	Reaction Condition	Reaction Time, min	Purity Factor, Reaction Mix	Purity Factor, C ₅ Extract
18	toluene	solid HfCl ₄ added to slurry of Lig ¹ -Mg(DME)	15	61	89
19	toluene\trace dioxane	solid HfCl ₄ added to slurry of Lig ¹ -Mg(DME)	80	67	83
20	toluene	solid Lig ¹ -Mg(DME) added to slurry of HfCl ₄	60	61	85
21	toluene	solid HfCl ₄ added to solution of Lig ¹ -Mg(DME) at 85 C	15	65	ND
22	toluene	solid HfCl ₄ added to slurry of Lig ¹ -Mg(THF) ₂	75	59	61
23	toluene	solid Lig ¹ -Mg(DME) added to slurry of HfCl ₄	120	69	86

[0088] Run 24: Synthesis of Lig¹ DiGrignard. Lig¹ (10.01 g; 27.75 mmol) was dissolved in THF (~18 mL) and iPrMgCl solution (2.01 M in THF; 26.0 mL; 52.3 mmol) was added. The reaction mixture was heated to 60°C and stirred 3 hours. An aliquot was dried down, and the ¹H NMR in d8-THF showed the iPrMgCl had reacted, but the reaction was not particularly clean. About 200 mL pentane was added to the remaining reaction mixture, most of the oily material went into the solution and was decanted off, cooled to -20°C and an oil formed. The solvent was decanted off the oil and the oil dried down to an off-white foam, which was crushed to an off-white powder, yield = 9.2 g. The solid was dissolved in about 20 mL ether, about 120 mL pentane was added, the mixture cooled to -20°C, and an oil formed, which was isolated by decanting and dried under vacuum. The ¹H NMR in d8-THF looked essentially the same as the off-white powder. About 3.4 g were slurried in about 50 mL pentane and the addition of about 20 mL DME caused an oily solid to form. The solution was concentrated to about 30 mL with heating to precipitate a solid powder, and 30 mL more pentane was added, the solid isolated by filtration, washed with 25 mL pentane and dried under vacuum, yield about 3.2 g. The ¹H NMR in d8-THF showed 4 DME's total attached and significant clean-up from the previous isolates. The NMR also looked strikingly like the NMR of the impurity isolated in Run 23, suggesting the isolated impurity is the diGrignard. See FIG. 2.

[0089] Run 25: Reaction of Lig¹ DiGrignard with HfCl₄/LiCl. Anhydrous LiCl (0.216 g; 5.09 mmol) was dissolved in THF (~12 mL) and solid Lig¹ diGrignard (1.14 g; 1.36 mmol) from Run 24 was added. There was immediate formation of a light pink color. After several

2018EM183 PCT

minutes an aliquot was removed, dried down and the ^1H NMR taken in d_8 -THF. The remainder of the solution was added to a slurry of HfCl_4 (0.414g; 1.30 mmol) in ether (~3 ml). The HfCl_4 dissolved and a light yellow color formed. After stirring 10 minutes an aliquot was removed, dried down and the ^1H NMR taken in d_8 -THF. Purity Factor = 87. The ^1H NMR is shown in FIG. 3.

5 [0090] **Run 26: Reaction of $\text{Li}^1\text{-Mg(DME)}$ with $\text{HfCl}_4/\text{LiCl}$.** Anhydrous LiCl (0.180 g; 4.23 mmol) was mostly dissolved in THF, solid $\text{Li}^1\text{-Mg(DME)}$ (1.00g; 2.11 mmol) was added and dissolved, rapidly forming a very light pink solution. After about 20 minutes an aliquot was dried down and the ^1H NMR in d_8 -THF looked remarkably like the product from Run 25.

10 The solution was added to a slurry of HfCl_4 (0.660 g; 2.06 mmol) in ~4 mL Et_2O . The reaction turned light yellow, some of the HfCl_4 became gummy and only slowly dissolved over about an hour. After stirring for 2 days, the solution was almost colorless. An aliquot was dried down and the ^1H NMR taken in d_8 -THF. Purity Factor = 84.

[0091] **Run 27: Reaction of $\text{Li}^1\text{-Mg(DME)}$ with $\text{HfCl}_4/\text{LiCl}$.** Anhydrous LiCl (0.100 g; 2.36 mmol) was dissolved in THF (~5 mL) and $\text{Li}^1\text{-Mg(DME)}$ (1.10 g; 2.32 mmol) was added as a solid and rapidly dissolved to form a very light pink solution. The reaction was stirred 15 minutes and the solution was added to HfCl_4 (0.772; 2.25 mmol) in Et_2O (~5mL) with rapid stirring, and the color became bright yellow, similar to reactions in which the $\text{Li}^1\text{-Li}_2$ dianion had significant impurities, and much stronger yellow than Runs 25 and 26 in which

20 2 equivalents of LiCl was added. The reaction was stirred for 3 hours at room temperature, over which the intensity of the yellow color appeared to decrease some. An aliquot was removed, dried down, and the ^1H NMR taken in d_8 -THF. Purity Factor = 78.

[0092] **Run 28: Reaction of $\text{Li}^1\text{-Mg(DME)}$ with $\text{HfCl}_4/\text{LiCl}$.** Anhydrous LiCl (0.0975 g; 2.30 mmol) was added to DME (~5 mL) and stirred for 20 minutes at RT. Most of the LiCl appeared to be undissolved. $\text{Li}^1\text{-Mg(DME)}$ (1.08 g; 2.28 mmol) was added to form a slurry, which was stirred for 30 minutes at room temperature. Solid HfCl_4 (0.732 g; 2.29 mmol) was added, and the resulting light yellow slurry was stirred for 1 hour. An aliquot was removed, dried down, extracted into pentane, filtered to give a yellow solution, and dried down. ^1H NMR in C_6D_6 (18-AC2560-A) showed the presence of unreacted $\text{Li}^1\text{-Mg(DME)}$.

30 [0093] **Run 29: Reaction of $\text{Li}^1\text{-Mg(DME)}$ with $\text{HfCl}_4/\text{LiCl}$.** Anhydrous LiCl (0.260 g; 6.13 mmol) was dissolved in THF (~5 mL) at RT. Solid HfCl_4 (0.935 g; 2.92 mmol) was added and quickly dissolved with warming. After stirring about 10 minutes, solid $\text{Li}^1\text{-}$

2018EM183 PCT

Mg(DME) (1.38 g; 2.92 mmol) was added which quickly dissolved to form a yellow solution. The reaction was stirred for 1 hour at room temperature. NMR in d8-THF gave PF = 88.

5 **[0094] Run 30: Reaction of Lig¹-Mg(DME) with HfCl₄/LiCl.** Anhydrous LiCl (0.192 g; 4.53 mmol) and solid Lig¹-Mg(DME) from Run 18 (1.01 g; 2.13 mmol) were added together and dissolved in THF (~5mL) with stirring. After several minutes solid HfCl₄ (0.682 g; 2.13 mmol) was added, a yellow solution formed and stirring continued for 90 minutes, during which the yellow color decreased. ¹H NMR of a dried down aliquot taken in d8-THF showed Purity Factor = 89. The ¹H NMR is shown in FIG. 4.

10 **[0095] Run 31: Reaction of Lig¹-Mg(DME) with HfCl₄/LiCl.** Anhydrous LiCl (0.171 g; 4.03 mmol) and solid Lig¹-Mg(DME) from Run 18 (0.90 g; 1.92 mmol) were added together and dissolved in THF (~5mL). The solution was cooled to -20°C and then placed in a cold bath at -20°C. Solid HfCl₄ (0.614 g; 1.92 mmol) was added, a yellow solution formed, and the reaction was allowed to warm to room temperature and stirred for 65 minutes. ¹H NMR of a dried down aliquot taken in d8-THF (18-AC2565-A) showed Purity Factor = 83.

15 **[0096] Run 32: Reaction of Lig¹-Mg(DME) with HfCl₄/LiCl.** Anhydrous LiCl (2.91 g; 68.6 mmol) and solid Lig¹-Mg(DME) from Run 19 (15.46 g; 32.67 mmol) were added together and dissolved in THF (75mL). Solid HfCl₄ (10.46 g; 32.66 mmol) was added, a yellow solution formed, and the reaction warmed considerably. After 90 minutes during which the intensity of the yellow decreased to a very lightly pale yellow, an aliquot was removed, dried down, and
20 the ¹H NMR taken in d8-THF (18-AC2566-A). Purity Factor = 89. The THF was removed under vacuum at 40°C. The almost colorless solid was extracted with pentane (180 mL) by stirring vigorously for 20 minutes. The very light yellow solution was isolated by filtration and the remaining solid was extracted with pentane (80 mL) by stirring vigorously for 20 minutes. The combined filtrates were dried under vacuum at 40°C to give an almost colorless
25 solid containing some gummy material. Yield = 16.05 g; 80.8% yield. The solid was extracted with iso-hexane (40 mL) stirring vigorously at 65°C, filtered hot, and a colorless crystalline solid immediately precipitated. The solid was again extracted with iso-hexane (40 mL) stirring vigorously at 65°C and the filtrates combined and dried down. Yield = 2.70 g; ¹H NMR in C₆D₆ (18-AC2566-C) showed Purity Factor = 87; rac/meso = 1 : 1.02.

30 **[0097] Run 33: Reaction of Lig¹-Mg(DME) with HfCl₄ in THF without LiCl.** Lig¹-Mg(DME) (18-AC2550) from Run 16 (0.790 g; 1.67 mmol) was dissolved in THF (~5 mL), solid HfCl₄ (0.53 g; 1.67 mmol) was added with rapid stirring, and the reaction turned light yellow and a precipitate formed rapidly. The reaction was stirred 20 minutes. An aliquot was

2018EM183 PCT

removed, dried down and showed very low yield by ^1H NMR.

[0098] Run 34: Reaction of Lig¹-Mg(DME) with HfCl₄ in Ether without LiCl. Lig¹-Mg(DME) (1.37 g; 2.90 mmol) was slurried in ~30 mL ether. Solid HfCl₄ (0.93 g; 2.90 mmol) was added in one portion, and after several minutes the reaction mixture turned yellow. After 40 minutes of stirring at room temperature, the reaction was allowed to settle and an aliquot removed. ^1H NMR (17-AC2528-A) in C₆D₆ showed formation of product with a purity factor of 60 as seen in FIG. 5 but the reaction did not appear to be complete. After 2 hours another aliquot was removed and the ^1H NMR in C₆D₆ showed no change. After stirring overnight, two aliquots were removed and the ^1H NMR in C₆D₆ still showed no change.

Table C: Synthesis of Lig¹-HfCl₂ from Lig¹-Mg(DME) and HfCl₄/LiCl

Run	LiCl/Lig ¹ -Mg (DME), mol/mol	Solvent	Reaction Condition	Reaction Time	PF, Reaction Mix
25	3.7	THF	Lig ¹ DiGrignard added to HfCl ₄ /Et ₂ O slurry	10 min	87
26	2	THF	Lig ¹ -Mg added to HfCl ₄ slurry in Et ₂ O	3 d	84
27	1	THF	Lig ¹ -Mg added to HfCl ₄ slurry in Et ₂ O	3 h	78
28	1	DME	solid HfCl ₄ added to DME slurry of LiCl/Lig ¹ -Mg	1 h	low
29	2	none	LiCl(sol) in THF, then HfCl ₄ added then Lig ¹ -Mg	1 h	88
30	2	THF	LiCl(s) and Lig ¹ -Mg(s) together in THF; then HfCl ₄ (sol/s) added	1.5 h	89
31	2	THF	Same as Run 29, but at -20°C	65 min	83
32	2	THF	Same as Run 29; larger scale	1.5 h	89
33	0	THF	HfCl ₄ (s) added to THF (sol) of Lig ¹ -Mg	20 min	low
34	0	Et ₂ O	HfCl ₄ (s) added to Et ₂ O slurry of Lig ¹ -Mg	40 min	60
35	0	C ₅ /DME	Lig ¹ -Mg (sol) in DME added to C ₅ /DME slurry of HfCl ₄	60 min	30

[0099] Run 35: Reaction of Lig¹-Mg(DME) with HfCl₄ in Pentane/DME without LiCl. HfCl₄ (0.68 g; 2.1 mmol) was slurried in pentane (~15 mL) and DME (~10 mL) was added. To the resulting stirring slurry was added Lig¹Mg(DME) (1.00 g; 2.1 mmol) dissolved in DME (~30 mL). The slurry was stirred for ~1 hour and an aliquot containing both liquid and solid (~5 mL) was removed, dried down and the ^1H NMR taken in C₆D₆. The reaction was stirred over the weekend at room temperature. The solvent was removed under vacuum and the

2018EM183 PCT

residue extracted 3 x 10 mL with pentane. An aliquot was dried down and the ^1H NMR taken in C_6D_6 .

[0100] The results from synthesizing $\text{Lig}^1\text{-HfCl}_2$ from $\text{Lig}^1\text{-Mg(DME)}$ and $\text{HfCl}_4/\text{LiCl}$ are summarized in Table C.

5 [0101] **Run 36: Reaction of $\text{Lig}^1\text{-Mg(DME)}$ with $\text{HfCl}_4/\text{LiCl}$ Followed by *In-Situ* Methylation.** Anhydrous LiCl (1.70 g; 40.1 mmol) and solid $\text{Lig}^1\text{-Mg(DME)}$ (8.920 g; 18.85 mmol; combination of three batches, mostly from Run 18 were combined in a flask and dissolved in THF (~40 mL) with stirring. Solid HfCl_4 (6.04 g; 18.85 mmol) was added, the reaction turned yellow and warmed. The reaction was stirred 90 minutes and became less
10 yellow. To the stirring reaction was added MeMgBr (13.2 mL; 2.95 M in ether; 37.7 mmol) in 4 portions of 3.20 mL over a minute. The color turned from light yellow to light gray. After stirring for 20 minutes an aliquot was removed, dried down and the ^1H NMR taken in $\text{d}_8\text{-THF}$ showed the reaction was complete. Purity Factor = 81. After a total of 35 minutes stirring the solvent was removed under vacuum. Iso-hexane (~90 mL) was added and the flask warmed to
15 50°C . The solids formed were gummy and clung to the side of the flask. The slightly cloudy solution was decanted off and additional iso-hexane (~45 mL) was added to the remaining solids with stirring at 50°C . This solution was decanted and combined with the first and dried down at 50°C . The isolated solid weighed 9.70 g; 0.320 g of this was dissolved in ~3 mL C_6D_6 for NMR with some cloudiness. Purity Factor = 84. The remaining isolated solid was
20 dissolved in pentane (45mL), and an estimated 200 mg of salt remained undissolved. The solution was filtered to give a clear, light yellow solution that was dried down. Yield = 9.25 g. Taking into account the 0.32 g removed for NMR, the calculated overall yield is 9.63 g; 89%; Purity Factor = 88. The ^1H NMR is shown in FIG. 6.

[0102] **Run 37: Reaction of $\text{Lig}^1\text{-Mg(DME)}/2 \text{ LiCl}$ with ZrCl_4 Followed by *In-Situ* Methylation.** Solid $\text{Lig}^1\text{-Mg(DME)}$ (1.33 g; 2.81 mmol) and anhydrous LiCl (0.250 g; 5.90 mmol) were combined together and THF (~5 mL) was added, stirred for about 10 minutes to form a clear solution and solid ZrCl_4 (0.655 g; 2.81 mmol) was added in one portion, forming an orange solution. The reaction was stirred at room temp for 2 hours at which time the color was light yellow. About 0.5 mL was removed, dried down and the ^1H NMR taken in $\text{d}_8\text{-THF}$.
25 Purity Factor = 82. To the remaining solution was added MeMgBr (1.68 mL; 5.04 mmol; 3.0 M in ether). The reaction turned light brown. After stirring 30 minutes the reaction was dried down under vacuum, extracted with 10 mL iso-hexane at 60°C , and the solution isolated by decanting. The remaining gooey solid was extracted with an additional 5 mL of iso-hexane
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2018EM183 PCT

and the solution isolated by decanting. The combined solutions were dried down and redissolved in 5 mL of warm iso-hexane, filtered, and the filter was washed with 2 mL of warm isohexane. The combined solutions were dried under vacuum at 60°C to give a light brown colored solid. Yield = 0.94 g. ^1H NMR taken in C_6D_6 showed Purity Factor = 85.

5 [0103] **Run 38: Reaction of $\text{Lig}^1\text{-Mg(DME)}/2 \text{ LiCl}$ with HfCl_4 Followed by *In-Situ* Methylation.** $\text{Lig}^1\text{-Mg(DME)}$ (64.26 g, 136 mmol) and anhydrous LiCl (12.2 g; 287 mmol) were combined as solids and THF (240 mL) was added. After stirring for 15 minutes the $\text{Lig}^1\text{-Mg(DME)}$ and nearly all the LiCl had dissolved. Solid HfCl_4 (43.5 g; 136 mmol) was added rapidly to the solution with vigorous stirring. The solution turned yellow and warmed. There
10 were chunks of solid HfCl_4 that took up to 20 minutes to dissolve. After 2.75 hours an aliquot was removed, dried down and the NMR taken in $d_8\text{-THF}$ showed PF = 85. To the solution was added MeMgBr (88.7 mL; 257 mmol; 2.95 M in ether) in 9 portions over several minutes, the solution warmed and turned grey. This was stirred 25 minutes then the volatiles were removed under vacuum at 50°C jacket temperature. This gave a thick off-white gooey material,
15 to which 160 mL of iso-hexane was added. This flask was stirred by swirling vigorously by hand to get the gooey material moving. It was heated to 50°C with intermittent swirling, then a yellow, cloudy solution was decanted off. An additional 80 mL of iso-hexane was added and the process was repeated, followed by a rinse of the gooey material with 10 mL iso-hexane. The combined solutions were dried down to a solid. This solid was dissolved in pentane (~300
20 mL) and filtered to give a clear yellow solution. There was a very small amount of solid recovered from the frit. An aliquot of the pentane solution was dried down and the ^1H NMR taken in $d_8\text{-THF}$ showed Purity Factor = 87. The pentane was dried down to give an off-white solid. Isolated Yield = 67.0 g; 118 mmol; 87% from $\text{Lig}^1\text{-Mg(DME)}$. The solid was ground into a powder, and the ^1H NMR in C_6D_6 showed Purity Factor = 87. The purity was 87 wt%
25 based on ^1H NMR using an internal standard.

[0104] **Run 39: Synthesis of $\text{Lig}^1\text{ZrCl}_2$ from Lig^1Li_2 .** The Lig^1Li_2 dianion (0.50 g; 1.3 mmol) was slurried in Et_2O (~25 mL) and solid ZrCl_4 (0.31 g; 1.3 mmol) was added. The reaction was stirred overnight at room temperature. The solvent was evaporated off and the residue was extracted with pentane (~15 mL) and filtered to give a yellow/orange solution. An
30 aliquot was dried down and the ^1H NMR taken in C_6D_6 showed purity factor = 62.

[0105] **Run 40 Reaction of $\text{Lig}^1\text{-Mg(DME)}/2 \text{ LiCl}$ with HfCl_4 Followed by Methylation in a Second Step.** $\text{Lig}^1\text{-Mg(DME)}$ (59.62g, 126 mmol) and anhydrous LiCl (11.2 g; 264 mmol, 2.1 equ) were combined as solids and THF (250 mL) was added. After stirring for 15 minutes

2018EM183 PCT

the $\text{Li}^1\text{-Mg(DME)}$ and nearly all the LiCl had dissolved. Solid HfCl_4 (40.36 g; 136 mmol) was slowly added as the mixture temperature cooled down to room temperature. After 2 hours and 45 minutes all volatiles were removed and the crude materials were extracted into dichloromethane, the solution isolated by filtration. All volatiles from the solution were removed in vacuo and the product was dissolved in diethylether (300 mL) and cooled to -25°C . To this, a solution of MeMgBr (88 mL, 252 mmol) was added dropwise over a period of 20 to 25 minutes. The resulting mixture was stirred overnight at room temperature and aliquot was tested to ensure completion of reaction. All volatiles from the reaction mixture were removed under vacuum and extracted into hexane several times. The solvent was removed from the combined filtrates and the purity was determined to be 85 wt% by use of ^1H NMR with an added internal standard.

[0106] The phrases, unless otherwise specified, "consists essentially of" and "consisting essentially of" do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the invention, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

[0107] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited.

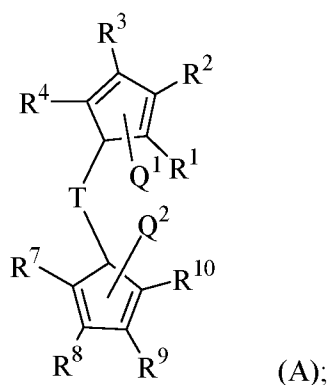
[0108] All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted and to the extent such disclosure is consistent with the description of the present invention. Further, all documents and references cited herein, including testing procedures, publications, patents, journal articles, etc. are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted and to the extent such disclosure is consistent with the description of the present invention.

[0109] While the invention has been described with respect to a number of embodiments and examples, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope and spirit of the invention as disclosed herein.

2018EM183 PCT

CLAIMS*What is claimed is:*

1. A process for synthesizing a Group 4 *ansa*-metallocene comprising:
 - (i) reacting a bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex with a Group 4 metal tetrahalide in the presence of an alkali metal halide; and
 - (ii) forming the Group 4 *ansa*-metallocene dihalide.
2. The process of claim 1, wherein the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex is represented by the formula (A):



where each R^1 , R^2 , R^3 and R^4 and R^7 , R^8 , R^9 and R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 , R^2 , R^3 and R^4 or two or more of R^7 , R^8 , R^9 and R^{10} join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-\text{CH}_2\text{-SiR}'_3$ or $-\text{CH}_2\text{-CR}'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

T is a bridging group; and

together Q^1 and Q^2 are a divalent alkaline earth metal complexed with a Lewis base, according to the formula (D1), or each Q^1 and Q^2 is independently an alkaline earth metal cation as would be formed by reacting a neutral bridged dicyclopentadienyl ligand with a Grignard reagent and complexing with a Lewis base, according to the formula (D2), wherein the formulae (D1) and (D2) are:



2018EM183 PCT



where “>” indicates a divalent complex and “-” indicates a monovalent complex;

M^1 is an alkaline earth metal, such as magnesium;

where M^1 is an alkaline earth metal, preferably magnesium;

5 X^1 is halogen; and

together L^1 and L^2 are a difunctional Lewis base, or each L^1 and L^2 is independently a monofunctional Lewis base;

wherein the Group 4 metal tetrahalide is represented by the formula (B):



10 where M^2 is a Group 4 transition metal; and

each X^2 is independently halogen; and

wherein the alkali metal halide is represented by the formula (C):



where M^3 is an alkali metal and X^3 is independently halogen.

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3. The process of claim 2, wherein:

each R^1 and R^4 is independently hydrogen, alkoxide or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group;

each R^2 , R^3 , R^8 , and R^9 is independently hydrogen, alkoxide or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group or is $-CH_2-SiR'^3$ or $-CH_2-CR'^3$, and each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, provided that at least one R' is not H and at least one of R^2 and R^3 is $-CH_2-SiR'^3$ or $-CH_2-CR'^3$;

20

each R^7 and R^{10} is independently hydrogen, alkoxide or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group; and

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T is a bridging group comprising a group 14 atom and one or more of hydrogen, a C_1 - C_{10} linear hydrocarbyl group, or substituted hydrocarbyl group.

4. The process of claim 1, wherein the reaction in (i) is in a fluid medium comprising a Lewis base.

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5. The process of claim 1, wherein an initial molar ratio of the alkali metal halide to the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex in the reaction in (i) is equal to or greater than 1.

2018EM183 PCT

6. The process of claim 1, wherein the Group 4 *ansa*-metallocene dihalide from (ii) has a purity equal to or greater than 70 weight percent wherein the purity is determined on a solvent-free basis by quantitative ^1H NMR in using an internal standard.

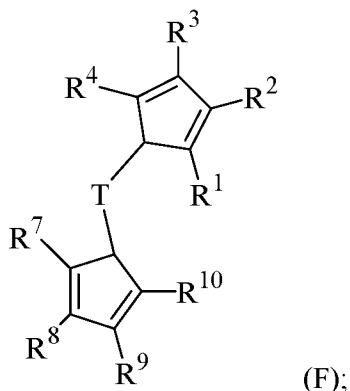
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7. The process of claim 1, further comprising alkylating the Group 4 *ansa*-metallocene dihalide from (ii).

8. The process of claim 7, wherein the reaction in (i) and the alkylation are in the same reactor, optionally without isolating the Group 4 *ansa*-metallocene between the reaction in (i) and the alkylation.

9. The process of claim 1 further comprising:
deprotonating a neutral bridged dicyclopentadienyl ligand with an alkaline earth metal compound to form the corresponding dianion, wherein the neutral bridged dicyclopentadienyl ligand has the formula (F) or is an isomer of the formula (F):

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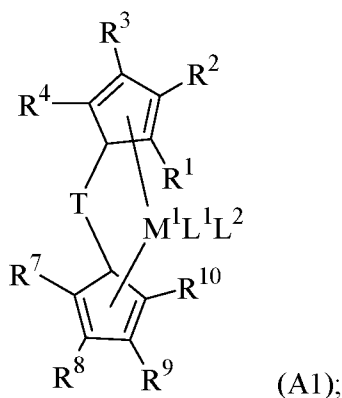
where each R^1 , R^2 , R^3 and R^4 and R^7 , R^8 , R^9 and R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 , R^2 , R^3 and R^4 or two or more of R^7 , R^8 , R^9 and R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent; and
T is a bridging group; and

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2018EM183 PCT

complexing the dianion with a Lewis base to form the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex for the reaction (i).

10. The process of claim 9, wherein the alkaline earth metal compound in the deprotonation is an alkaline earth metal dialkyl and the complexed dianion comprises alkaline earth metal metallocene, preferably according to formula (A1):



where T, R¹, R², R³ and R⁴ and R⁷, R⁸, R⁹ and R¹⁰ are as defined in claim 9;

M¹ is an alkaline earth metal; and

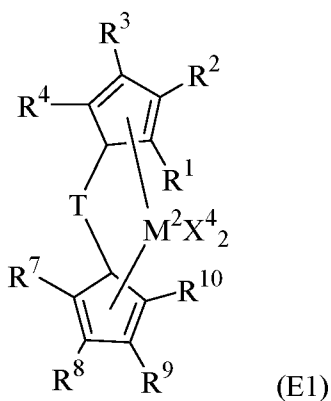
- 10 together L¹ and L² are a difunctional Lewis base, or each L¹ and L² is independently a monofunctional Lewis base.

11. The process of claim 9, wherein the alkaline earth metal compound in the deprotonation is a Grignard reagent, and the dianion comprises a diGrignard product.

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12. The process of claim 9, further comprising reacting a monocyclopentadiene anion with a bridging group compound to form the neutral bridged dicyclopentadienyl ligand.

13. The process of claim 1, wherein the synthesized Group 4 *ansa*-metallocene is according to the formula (E1):



2018EM183 PCT

where M^2 is a Group 4 transition metal;

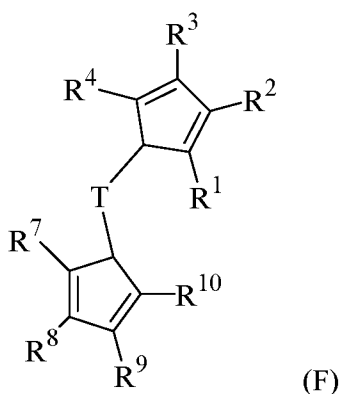
each R^1 , R^2 , R^3 and R^4 and R^7 , R^8 , R^9 and R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 , R^2 , R^3 and R^4 or two or more of R^7 , R^8 , R^9 and R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-CH_2-SiR'_3$ or $-CH_2-CR'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

T is a bridging group; and

each X^4 is independently a univalent anionic ligand, or two X^4 are joined and bound to the metal atom to form a metallocycle ring, or two X^4 are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.

14. A process for synthesizing a Group 4 *ansa*-metallocene comprising:

(a) deprotonating a neutral bridged dicyclopentadienyl ligand with an alkaline earth metal compound selected from alkaline earth metal dialkyls and Grignard reagents to form the corresponding dianion comprising the alkaline earth metal, wherein the neutral bridged dicyclopentadienyl ligand is according to formula (F) or is an isomer of the formula (F):



where each R^1 , R^2 , R^3 and R^4 and R^7 , R^8 , R^9 and R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 , R^2 , R^3 and R^4 or two or more of R^7 , R^8 , R^9 and R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-CH_2-SiR'_3$ or $-CH_2-CR'_3$ where each R' is independently

2018EM183 PCT

hydrogen or a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, provided that at least one R' is not H; and

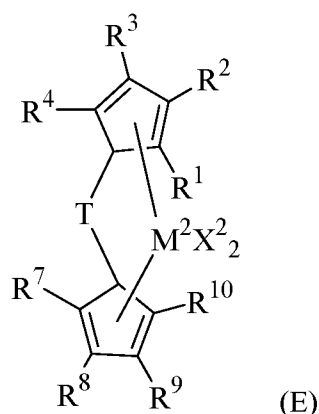
5 T is a bridging group;

(b) complexing the dianion from (a) with a Lewis base to form a bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex;

(c) reacting the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex from (b) with a Group 4 metal tetrahalide in a fluid medium comprising an alkali metal halide and a solvent;

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(d) forming Group 4 *ansa*-metallocene according to the formula (E):



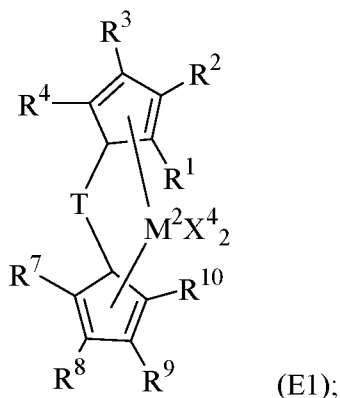
where T, R¹, R², R³ and R⁴ and R⁷, R⁸, R⁹ and R¹⁰ are as defined above;

M² is the Group 4 metal;

15

each X² is independently halogen; and

(e) optionally alkylating the Group 4 *ansa*-metallocene from (d) with an alkylating agent to form the Group 4 *ansa*-metallocene according to the formula (E1):



where T, R¹, R², R³ and R⁷, R⁸, R⁹ and R¹⁰, and M² are as defined above; and

2018EM183 PCT

each X^4 is independently a univalent anionic ligand, or two X^4 are joined and bound to the metal atom to form a metallocycle ring, or two X^4 are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.

5 15. The process of claim 14, wherein the reaction in (c) and the alkylation in (e) are in the same reactor, optionally without isolating the Group 4 *ansa*-metallocene between (c) and (e).

16. The process of claim 14, further comprising solvent extraction of the Group 4 *ansa*-metallocene formed in (d).

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17. The process of claim 14, wherein an initial molar ratio of the alkali metal halide to the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex in the reaction in (c) is equal to or greater than 1.

15 18. The process of claim 14, wherein the alkaline earth metal compound in the deprotonation in (a) is an alkaline earth metal dialkyl and the dianion comprises alkaline earth metal metallocene.

19. The process of claim 14, wherein the alkaline earth metal compound in the
20 deprotonation in (a) is a Grignard reagent and the dianion comprises a diGrignard product.

20. The process of claim 14 comprising the alkylation of (e) and wherein in the formula (E1):

25 each R^1, R^2, R^4, R^7, R^8 , and R^{10} is independently hydrogen, or a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group; and

each R^3 and R^9 is independently a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, or is $-R^{20}-SiR'_3$ or $-R^{20}-CR'_3$ where R^{20} is a C_1 to C_4 hydrocarbyl, and each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl.

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21. The process of claim 20, wherein:

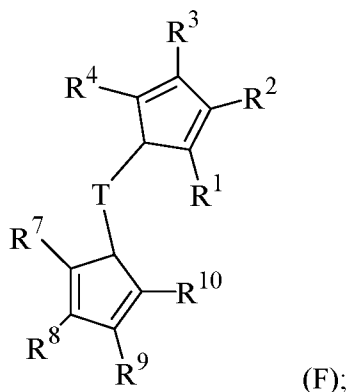
M^2 is Hf, or M^2 is Zr;

each R^1, R^2, R^4, R^7, R^8 , and R^{10} is independently hydrogen, or a substituted C_1 to C_{12} hydrocarbyl group or an unsubstituted C_1 to C_{12} hydrocarbyl group; and

35 each R^3 and R^9 is independently $-R^{20}-SiR'_3$ or $-R^{20}-CR'_3$ where R^{20} is a C_1 to C_4 hydrocarbyl and R' is a C_1 to C_{20} substituted or unsubstituted hydrocarbyl.

2018EM183 PCT

22. The process of claim 3, wherein each R' is independently a C₁ to C₂₀ substituted or unsubstituted hydrocarbyl.
23. The process of claim 2, wherein the reaction in (i) is in a fluid medium comprising a Lewis base.
24. The process of claim 3, wherein the reaction in (i) is in a fluid medium comprising a Lewis base.
25. The process of claim 2, wherein an initial molar ratio of the alkali metal halide to the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex in the reaction in (i) is equal to or greater than 1.
26. The process of claim 2, wherein the Group 4 *ansa*-metallocene dihalide from (ii) has a purity equal to or greater than 75 weight percent, wherein the purity is determined on a solvent-free basis by ¹H NMR using an internal standard.
27. The process of claim 2, further comprising alkylating the Group 4 *ansa*-metallocene dihalide from (ii).
28. The process of claim 9, further comprising:
deprotonating a neutral bridged dicyclopentadienyl ligand with an alkaline earth metal compound to form the corresponding dianion, wherein the neutral bridged dicyclopentadienyl ligand has the formula (F) or is an isomer of the formula (F):



where each R¹, R², R³ and R⁴ and R⁷, R⁸, R⁹ and R¹⁰ is independently hydrogen, alkoxide, a C₁ to C₄₀ substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R¹, R², R³ and R⁴ or two or more of R⁷, R⁸, R⁹ and

2018EM183 PCT

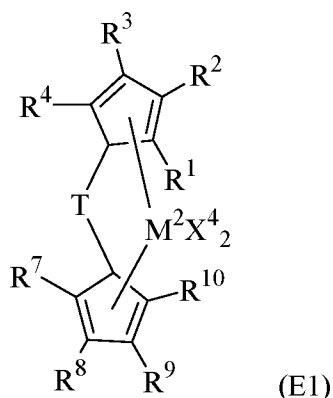
R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent; and

T is a bridging group; and

complexing the dianion with a Lewis base to form the bridged dicyclopentadienyl dianion-alkaline earth metal-Lewis base complex for the reaction (i).

10

29. The process of claim 2 wherein the synthesized Group 4 *ansa*-metallocene is according to the formula (E1):



where M^2 is hafnium or zirconium;

15

each R^1 , R^2 , R^3 and R^4 and R^7 , R^8 , R^9 and R^{10} is independently hydrogen, alkoxide, a C_1 to C_{40} substituted or unsubstituted hydrocarbyl group, optionally where any two or more of R^1 , R^2 , R^3 and R^4 or two or more of R^7 , R^8 , R^9 and R^{10} , join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, $-\text{CH}_2-\text{SiR}'_3$ or $-\text{CH}_2-\text{CR}'_3$ where each R' is independently hydrogen or a C_1 to C_{20} substituted or unsubstituted hydrocarbyl, optionally where any two or more of R' join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

20

T is $\text{CR}^{21}\text{R}^{22}$ or $\text{ZR}^{21}\text{R}^{22}$ where Z is Si, Ge, or Sn, R^{21} and R^{22} are independently hydrogen, halogen, or a C_1 - C_{20} containing hydrocarbyl group substituted hydrocarbyl group, and optionally R^{21} and R^{22} join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, optionally R^{21} and R^{22} are the same or different; and

25

2018EM183 PCT

each X^4 is independently a univalent anionic ligand, or two X^4 are joined and bound to the metal atom to form a metallocycle ring, or two X^4 are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.

5 30. The process of claim 15, further comprising solvent extraction of the Group 4 *ansa*-metallocene formed in (iv).

31. The process of claim 20, wherein R^3 is a C_1 to C_{20} substituted or unsubstituted hydrocarbyl group or is $-R^{20}-SiR'_3$ or $-R^{20}-CR'_3$ where R^{20} is a C_1 to C_4 hydrocarbyl, and each
10 R' is independently a C_1 to C_{20} substituted or unsubstituted hydrocarbyl.

Run 5 in d8-THF

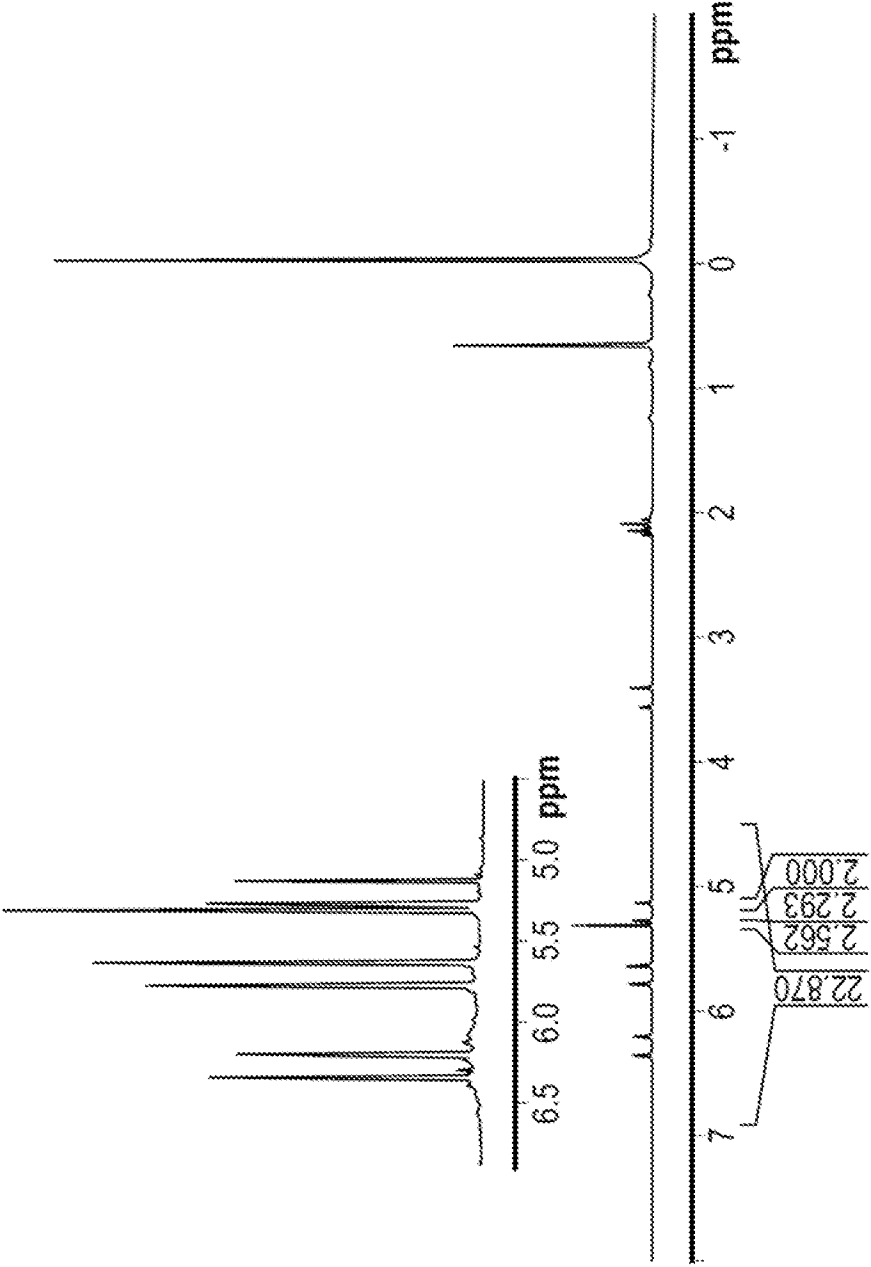


FIG. 1
(Prior Art)

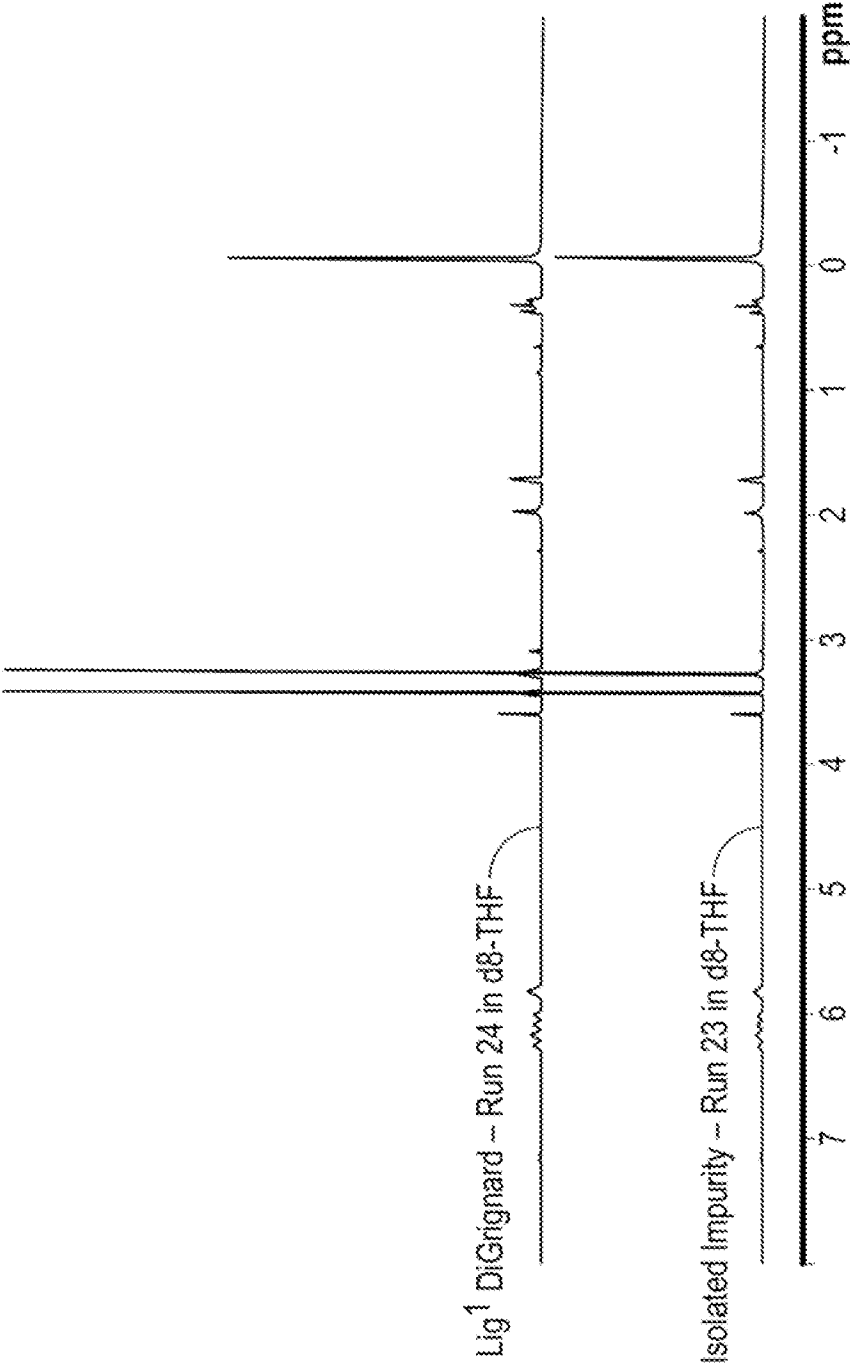


FIG. 2

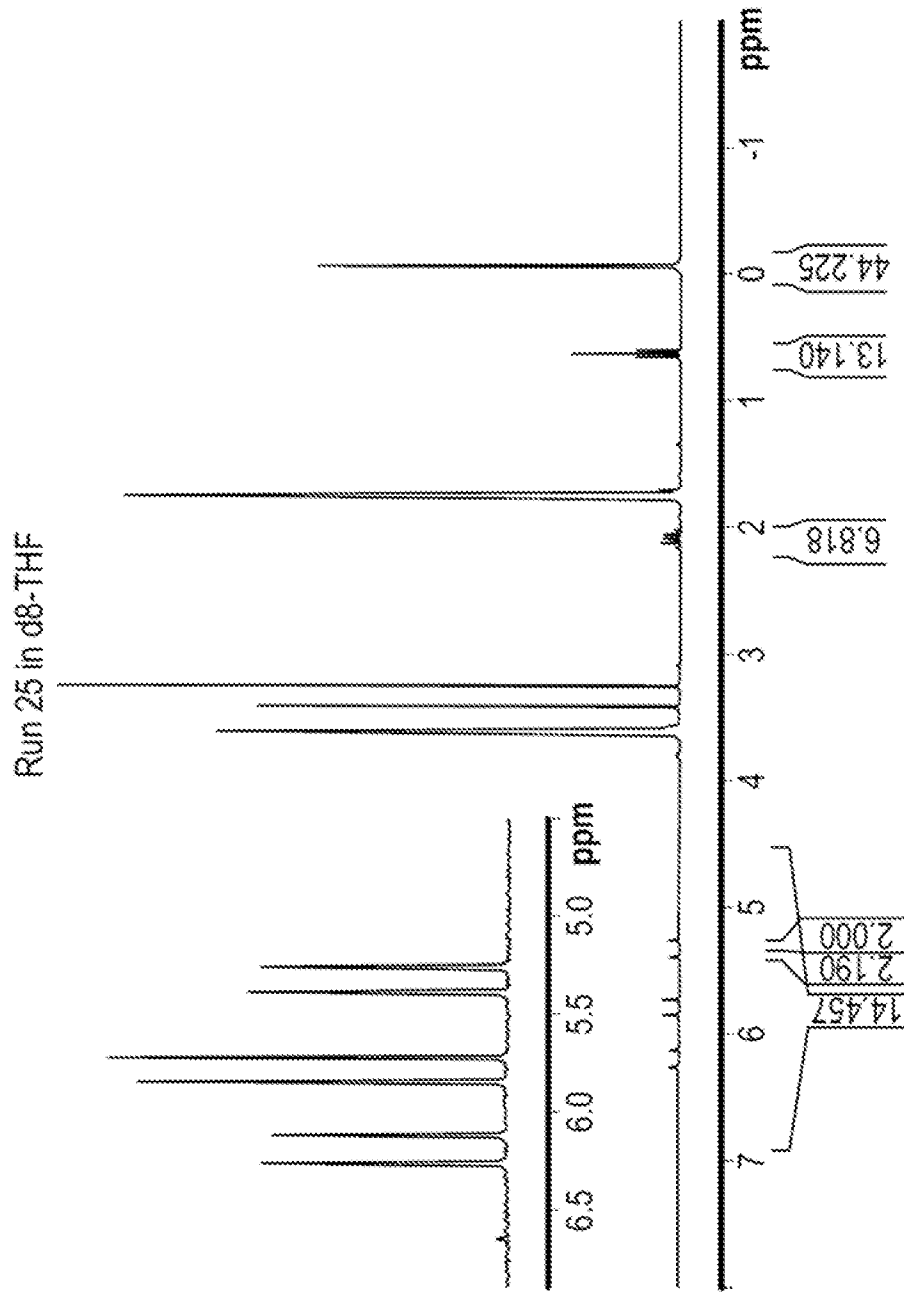


FIG. 3

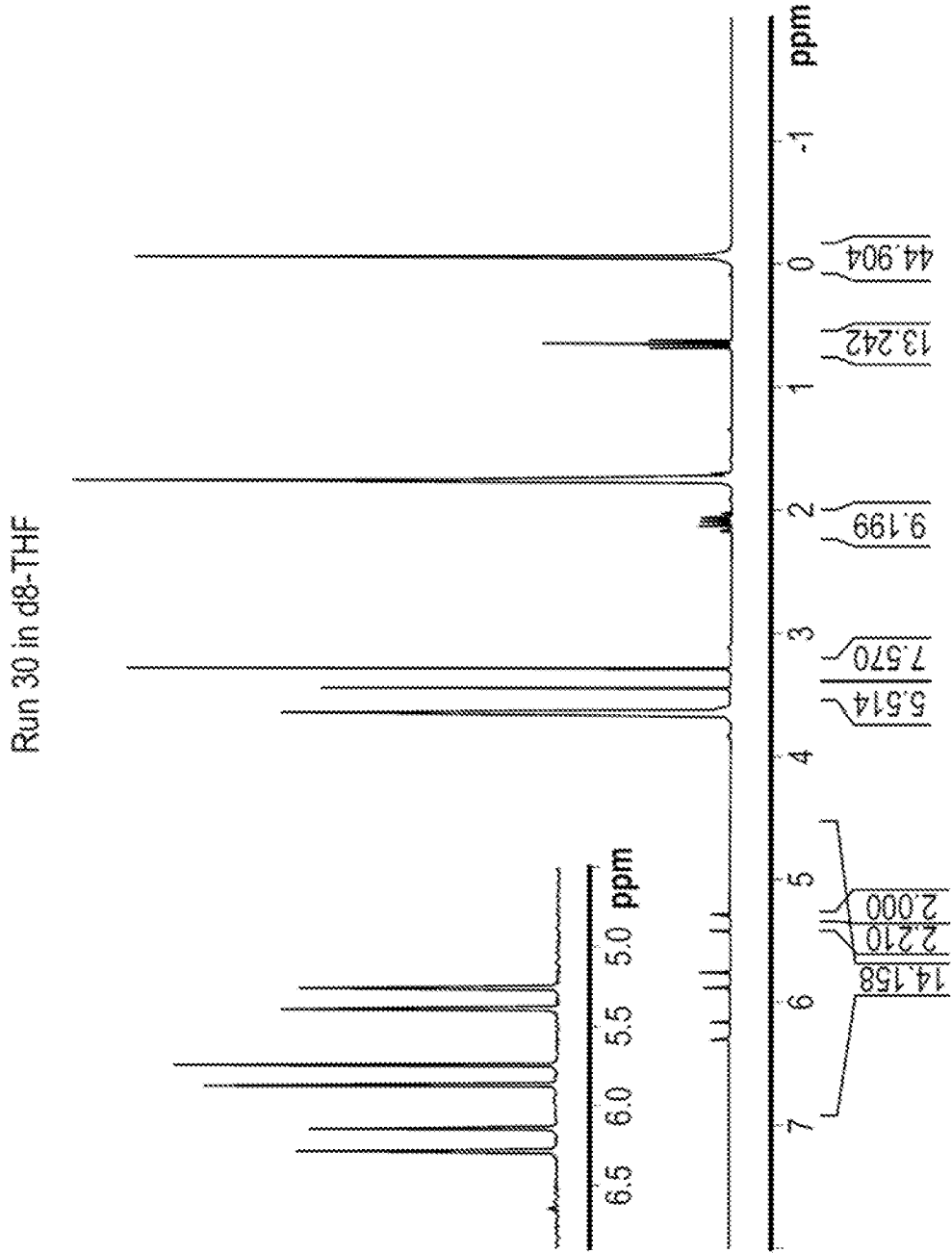


FIG. 4

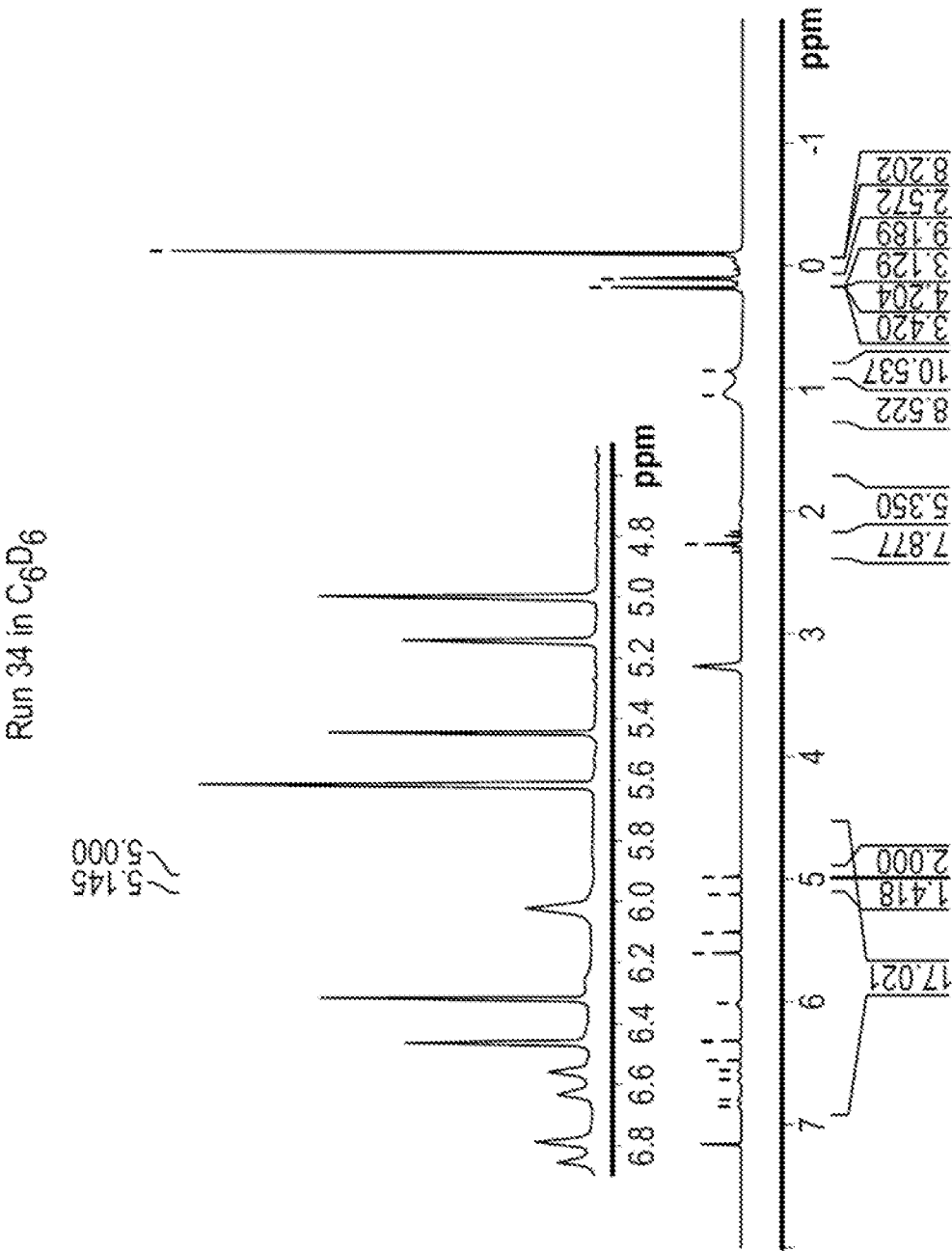


FIG. 5

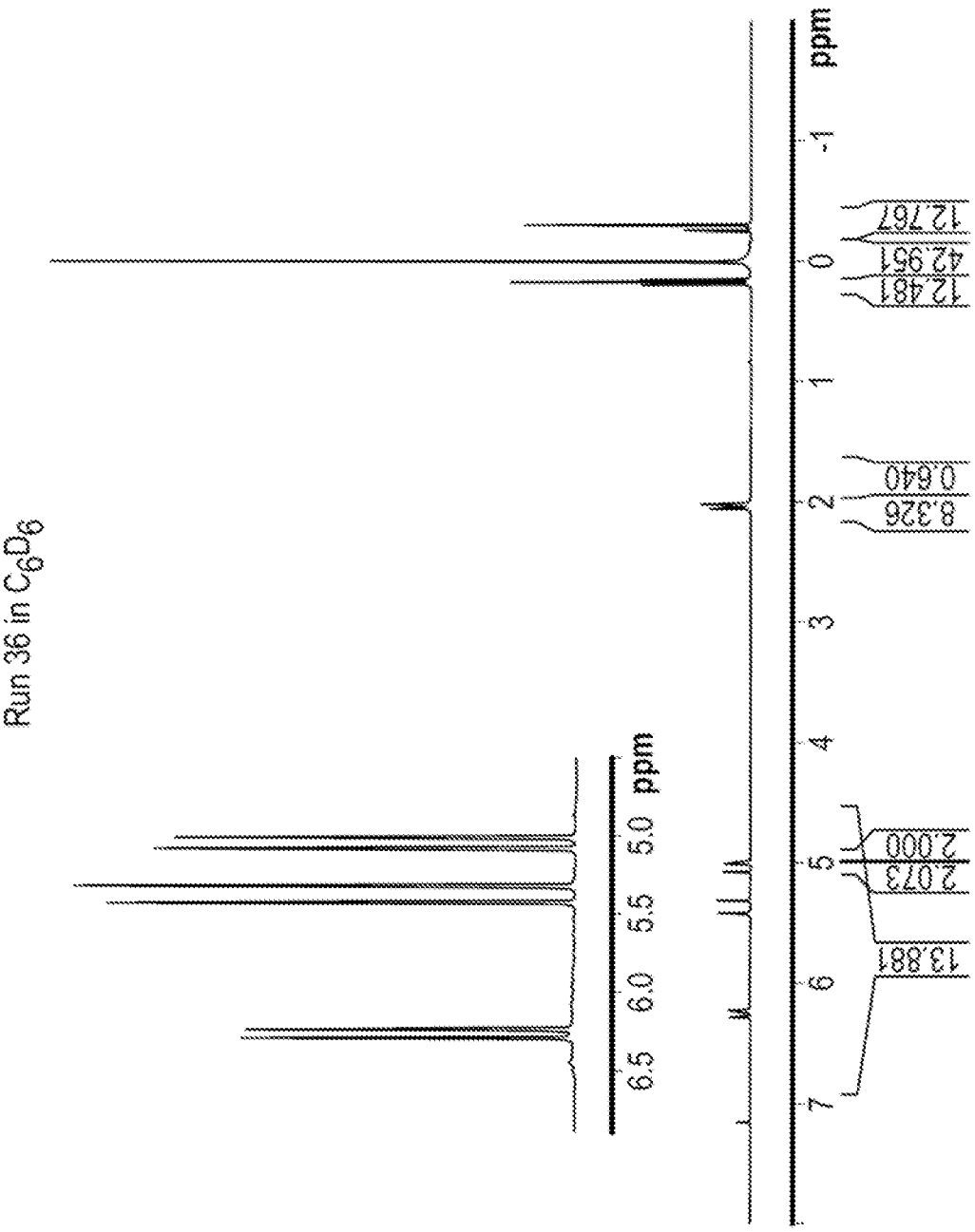


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/038169**A. CLASSIFICATION OF SUBJECT MATTER****C07F 17/00(2006.01)i**

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07F 17/00; B01J 31/00; B01J 31/38; B01J 37/00; C07F 3/02; C07F 7/00; C07F 7/08; C08F 4/64

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) , STN (Registry, Caplus), Google & Keywords:ansa-metallocene, neutral bridged ligand, dicyclopentadienyl, alkaline earth metal, Grignard reagent, Lewis base, Group 4 metal tetrahalide, HfCl₄, alkali metal halide, LiCl, purity**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5359105 A (STRICKLER, J. R. et al.) 25 October 1994 See claims 1-3, 5; and column 2, lines 40-53.	1-31
A	US 6177376 B1 (FRITZE, C. et al.) 23 January 2001 See the whole document.	1-31
A	US 5679816 A (TIMMERS, F. J. et al.) 21 October 1997 See the whole document.	1-31
A	US 7193099 B2 (DAMRAU, H.-R.-H. et al.) 20 March 2007 See the whole document.	1-31
A	KR 10-2018-0006319 A (LG CHEM, LTD.) 17 January 2018 See the whole document.	1-31
A	EP 0834514 A2 (KANTO KAGAKU KABUSHIKI KAISHA) 08 April 1998 See the whole document.	1-31



Further documents are listed in the continuation of Box C.



See patent family annex.

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

"&" document member of the same patent family

Date of the actual completion of the international search

18 October 2019 (18.10.2019)

Date of mailing of the international search report

18 October 2019 (18.10.2019)

Name and mailing address of the ISA/KR

International Application Division

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2019/038169

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