[0004] Even with the advent of CSA and dual catalyst combinations in multi-block copolymer preparation processes, further improvements to said processes can be made. For example, novel catalysts that enable a wider range of processing conditions would be valuable for commercial production.

Summary

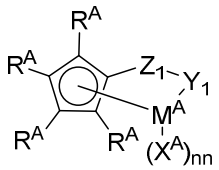
[0005] In certain examples, the present disclosure relates to a composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I):



(I), wherein:

M^A is a Group III or Lanthanide metal that is in a +3 formal oxidation state;

R^A, independently in each occurrence, is selected from the group consisting of $(C_1\text{-}C_{40})$hydrocarbyl; $(C_1\text{-}C_{40})$heterohydrocarbyl; $Si(R^{B1})_3$; $Ge(R^{B1})_3$; $P(R^{B1})_2$; $N(R^{B1})_2$; OR^{B1}; SR^{B1}; NO_2; CN; CF_3; $R^{B1}S(O)$-; $R^{B1}S(O)_2$-; $(R^{B1})_2C$=N-; $R^{B1}C(O)O$-; $R^{B1}OC(O)$-; $R^{B1}C(O)N(R)$-; $(R^{B1})_2NC(O)$-; halogen atom; hydrogen atom; and any combination thereof;

optionally two or more R^A groups can combine together into one or more ring structures, with such ring structures having from 3 to 50 atoms in each ring structure excluding any hydrogen atoms;

nn is an integer of 1 or 2;

Z1 is $[(R^{D1})_nG1]_m$, wherein m = 1, 2 ,3, or 4, and G1 is independently selected from carbon, silicon, germanium or boron; and when G1 is carbon, silicon, or germanium, n=2; when G1 is boron, n=1;

Y1 is bonded to M^A and Z1 and is selected from the group consisting of -O-, -S-, -NR^{E1}-, and –PR^{E1}-;

each R^{B1}, R^{D1}, or R^{E1} independently is (C_1-C_{30})hydrocarbyl or (C_1-C_{30})heterohydrocarbyl; X^A is (C_1-C_{40})hydrocarbon, (C_1-C_{40})heterohydrocarbon (C_1-C_{40})hydrocarbyl; (C_1-C_{40})heterohydrocarbyl; $Si(R^{C1})_3$; $Ge(R^{C1})_3$; $P(R^{C1})_2$; $N(R^{C1})_2$; OR^{C1}; SR^{C1}; CN; CF_3; $R^{C1}S(O)$-; $R^{C1}S(O)_2$-; $(R^{C1})_2C$=N-; $R^{C1}C(O)O$-; $R^{C1}OC(O)$-; $R^{C1}C(O)N(R)$-; $(R^{C1})_2NC(O)$-; halogen atom; or hydrogen atom;

each R^{C1} independently is (C_1-C_{30})hydrocarbyl or (C_1-C_{30})heterohydrocarbyl; each of the hydrocarbyl, heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, $R^{C1}S(O)$-, $R^{C1}S(O)_2$-, $(R^{C1})2C$=N-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$-, $R^{C1}C(O)N(R)$-, $(R^{C1})_2NC(O)$-, hydrocarbylene, and heterohydrocarbylene groups independently is unsubstituted or substituted with one or more R^S substituents;

each R^S independently is a halogen atom; polyfluoro substitution; perfluoro substitution; unsubstituted (C_1-C_{18})alkyl; F_3C-; FCH_2O-; F_2HCO-; F_3CO-; R_3Si-; R_3Ge-; RO-; RS-; RS(O)-; $RS(O)_2$-; R_2P-; R_2N-; R_2C=N-; NC-; RC(O)O-; ROC(O)-; RC(O)N(R)-; or $R_2NC(O)$-; or two of the R^S are taken together to form an unsubstituted (C_1-C_{18})alkylene, wherein each R independently is an unsubstituted (C_1-C_{18})alkyl; optionally, R^{C1} or R^S may have an additional interaction with M^A.

[0006] In certain examples, the present disclosure relates to a composition for use in the polymerization of at least one addition polymerizable monomer to form a multi-block (segmented) copolymer, said copolymer containing therein two or more blocks or segments differing in one or more chemical or physical properties, the composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0007] In certain examples, the present disclosure relates to a composition for use in the polymerization of ethylene and at least one copolymerizable comonomer other than ethylene to form a multi-block (segmented) copolymer, said copolymer containing therein two or more blocks or segments differing in one or more chemical or physical properties, the composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0008] In certain examples, the present disclosure relates to an olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

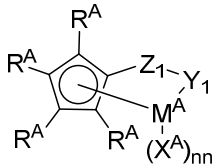
[0008a] In one aspect, the present disclosure refers to an olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I):



(I),

wherein M^A is a Group III or Lanthanide metal that is in a +3 formal oxidation state;

R^A, independent in each occurrence, is selected from the group consisting of $(C_1\text{-}C_{40})$hydrocarbyl,; $(C_1\text{-}C_{40})$heterohydrocarbyl; $Si(R^{B1})_3$; $Ge(R^{B1})_3$; $P(R^{B1})_2$; $N(R^{B1})^2$; OR^{B1}; SR^{B1}; NO_2; CN; CF_3; $R^{B1}S(O)$-; $R^{B1}S(O)_2$-; $(R^{B1})_2C$=N-; $R^{B1}C(O)O$-; $R^{B1}OC(O)$-; $R^{B1}C(O)N(R)$-; $(R^{B1})_2NC(O)$-; halogen atom; hydrogen atom; and any combination thereof;

optionally two or more R^A groups can combine together into one or more ring structures, with such ring structures having from 3 to 50 atoms in each ring structure excluding any hydrogen atoms;

nn is an integer of 1 or 2;

Z1 is $[(R^{D1})_nG1]_m$, wherein m = 1, 2 ,3, or 4, and G1 is independently selected from carbon, silicon, germanium or boron; and when G1 is carbon, silicon, or germanium, n=2; when G1 is boron, n=1;

Y1 is bonded to M^A and Z1 and is selected from the group consisting of -O-, -S-, $-NR^{E1}$-, and $–PR^{E1}$-;

each R^{B1}, R^{D1}, or R^{E1} independently is $(C_1\text{-}C_{30})$hydrocarbyl or $(C_1\text{-}C_{30})$heterohydrocarbyl;

each X^A is independently monoanionic or neutral wherein n > 0, and each X^A is independently $(C_1\text{-}C_{40})$hydrocarbon, $(C_1\text{-}C_{40})$heterohydrocarbon, $(C_1\text{-}C_{40})$hydrocarbyl; $(C_1\text{-}C_{40})$heterohydrocarbyl; $Si(R^{C1})_3$; $Ge(R^{C1})_3$; $P(R^{C1})_2$; $N(R^{C1})_2$; OR^{C1}; SR^{C1}; CN; CF_3; $R^{C1}S(O)$-; $R^{C1}S(O)_2$-; $(R^{C1})_2C$=N-; $R^{C1}C(O)O$-; $R^{C1}OC(O)$-; $R^{C1}C(O)N(R)$-; $(R^{C1})_2NC(O)$-; halogen atom; or hydrogen atom;

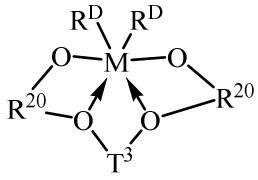
each R^{C1} independently is $(C_1\text{-}C_{30})$hydrocarbyl or $(C_1\text{-}C_{30})$heterohydrocarbyl;

each of the hydrocarbyl, heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, $R^{C1}S(O)$-, $R^{C1}S(O)2$-, $(R^{C1})2C$=N-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$-, $R^{C1}C(O)N(R)$-, $(R^{C1})_2NC(O)$-, hydrocarbylene, and heterohydrocarbylene groups independently is unsubstituted or substituted with one or more R^S substituents;

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

optionally, R^{c1} or R^S may have an additional interaction with M^A;

wherein the first olefin polymerization procatalyst (A) comprises a metal-ligand complex of Formula (III):



(III), wherein:

M is zirconium or hafnium;

R^{20} independently at each occurrence is a divalent aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen;

T^3 is a divalent hydrocarbon or silane group having from 3 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof; and

R^D independently at each occurrence is a monovalent ligand group of from 1 to 20 atoms, not counting hydrogen, or two R^D groups together are a divalent ligand group of from 1 to 20 atoms, not counting hydrogen.

[0009] In further examples, the present disclosure relates to a process for preparing a multi-block (segmented) copolymer, said process comprising contacting one or more addition polymerizable monomers under addition polymerizable conditions with a composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0010] In further examples, the present disclosure relates to a process for preparing a multi-block (segmented) copolymer comprising ethylene and at least one

copolymerizable comonomer other than ethylene, said process comprising contacting ethylene and one or more addition polymerizable monomers other than ethylene under addition polymerizable conditions with a composition comprising an admixture or reaction product resulting from combining:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0011] In further examples, the present disclosure relates to a process for preparing a multi-block (segmented) copolymer, said process comprising contacting one or more addition polymerizable monomers under addition polymerizable conditions with an olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0012] In further examples, the present disclosure relates to a process for preparing a multi-block (segmented) copolymer comprising ethylene and at least one copolymerizable comonomer other than ethylene, said process comprising contacting ethylene and one or more addition polymerizable monomers other than ethylene under addition polymerizable conditions with an olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I).

[0013] In certain examples, the foregoing processes take the form of continuous solution processes for forming block copolymers, such as multi-block copolymers (preferably linear multi-block copolymers of two or more monomers, especially ethylene and a C_{3-20} olefin or cycloolefin, and most especially ethylene and a C_{3-20} α-olefin), using multiple catalysts that are incapable of interconversion. That is, the catalysts are chemically distinct. Under continuous solution polymerization conditions, the process is ideally suited for polymerization of mixtures of monomers at high monomer conversions. Under these polymerization conditions, shuttling from the chain shuttling agent to the catalyst becomes advantaged compared to chain growth, and multi-block copolymers, especially linear multi-block copolymers according to the present disclosure, are formed in high efficiency.

[0014] In another example of the present disclosure, there is provided a segmented copolymer (multi-block copolymer), especially a copolymer comprising ethylene in polymerized form, said copolymer containing therein two or more (preferably three or more) segments differing in comonomer content or density or other chemical or physical properties. The copolymer preferably possesses a molecular weight distribution, Mw/Mn, of equal to or less than 10.0 (e.g., equal to or less than 9.0, equal to or less than 8.0, equal to or less than 7.0, equal to or less than 6.0, equal to or less than 5.0, equal to or less than 4.0, equal to or less than 3.0, equal to or less than 2.8, etc.). Most preferably, the polymers of the present disclosure are ethylene multi-block copolymers.

[0015] In yet another example of the present disclosure, there are provided functionalized derivatives of the foregoing segmented or multi-block copolymers.

Brief Description of the Drawings

[0016] FIG. 1 exemplifies the chain shuttling process that occurs in the polymerization processes of the present disclosure.

[0017] FIG. 2 provides GPC traces for certain examples of the present disclosure.

Detailed Description

Definitions

What is claimed is:

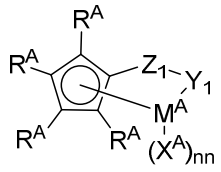
1. An olefin polymerization catalyst system comprising:

(A) a first olefin polymerization procatalyst,

(B) a second olefin polymerization procatalyst, and

(C) a chain shuttling agent,

wherein the second olefin polymerization procatalyst comprises a metal-ligand complex of Formula (I):



(I),

wherein M^A is a Group III or Lanthanide metal that is in a +3 formal oxidation state;

R^A, independent in each occurrence, is selected from the group consisting of (C_1-C_{40})hydrocarbyl,; (C_1-C_{40})heterohydrocarbyl; $Si(R^{B1})_3$; $Ge(R^{B1})_3$; $P(R^{B1})_2$; $N(R^{B1})^2$; OR^{B1}; SR^{B1}; NO_2; CN; CF_3; $R^{B1}S(O)$-; $R^{B1}S(O)_2$-; $(R^{B1})_2C$=N-; $R^{B1}C(O)O$-; $R^{B1}OC(O)$-; $R^{B1}C(O)N(R)$-; $(R^{B1})_2NC(O)$-; halogen atom; hydrogen atom; and any combination thereof;

optionally two or more R^A groups can combine together into one or more ring structures, with such ring structures having from 3 to 50 atoms in each ring structure excluding any hydrogen atoms;

nn is an integer of 1 or 2;

Z1 is $[(R^{D1})_nG1]_m$, wherein m = 1, 2 ,3, or 4, and G1 is independently selected from carbon, silicon, germanium or boron; and when G1 is carbon, silicon, or germanium, n=2; when G1 is boron, n=1;

Y1 is bonded to M^A and Z1 and is selected from the group consisting of -O-, -S-, $-NR^{E1}$-, and $-PR^{E1}$-;

each R^{B1}, R^{D1}, or R^{E1} independently is (C_1-C_{30})hydrocarbyl or (C_1-C_{30})heterohydrocarbyl;

each X^A is independently monoanionic or neutral wherein n > 0, and each X^A is independently (C_1-C_{40})hydrocarbon, (C_1-C_{40})heterohydrocarbon, (C_1-C_{40})hydrocarbyl; (C_1-C_{40})heterohydrocarbyl; $Si(R^{C1})_3$; $Ge(R^{C1})_3$; $P(R^{C1})_2$; $N(R^{C1})_2$; OR^{C1}; SR^{C1}; CN; CF_3; $R^{C1}S(O)$-; $R^{C1}S(O)_2$-; $(R^{C1})_2C$=N-; $R^{C1}C(O)O$-; $R^{C1}OC(O)$-; $R^{C1}C(O)N(R)$-; $(R^{C1})_2NC(O)$-; halogen atom; or hydrogen atom;

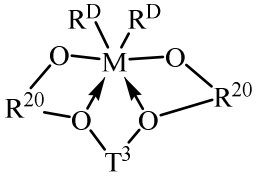
each R^{C1} independently is (C_1-C_{30})hydrocarbyl or (C_1-C_{30})heterohydrocarbyl;

each of the hydrocarbyl, heterohydrocarbyl, $Si(R^{C1})_3$, $Ge(R^{C1})_3$, $P(R^{C1})_2$, $N(R^{C1})_2$, OR^{C1}, SR^{C1}, $R^{C1}S(O)$-, $R^{C1}S(O)2$-, $(R^{C1})2C$=N-, $R^{C1}C(O)O$-, $R^{C1}OC(O)$-, $R^{C1}C(O)N(R)$-, $(R^{C1})_2NC(O)$-, hydrocarbylene, and heterohydrocarbylene groups independently is unsubstituted or substituted with one or more R^S substituents;

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

optionally, R^{c1} or R^S may have an additional interaction with M^A;

wherein the first olefin polymerization procatalyst (A) comprises a metal-ligand complex of Formula (III):



(III), wherein:

M is zirconium or hafnium;

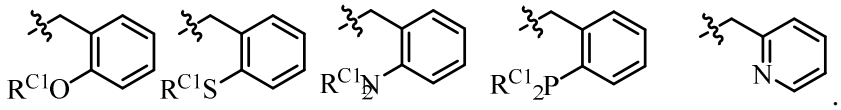
R^{20} independently at each occurrence is a divalent aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen;

T^3 is a divalent hydrocarbon or silane group having from 3 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof; and

R^D independently at each occurrence is a monovalent ligand group of from 1 to 20 atoms, not counting hydrogen, or two R^D groups together are a divalent ligand group of from 1 to 20 atoms, not counting hydrogen.

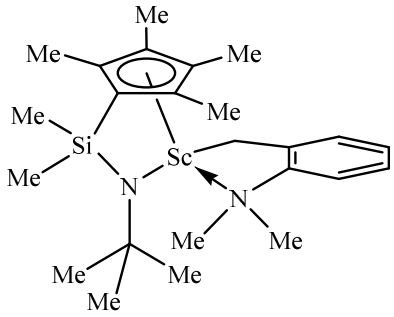
2. The catalyst system of claim 1, further comprising (D) an activator.

3. The catalyst system of any of the preceding claims, wherein X^A is selected from the group consisting of:

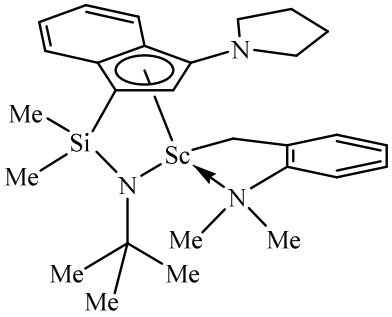


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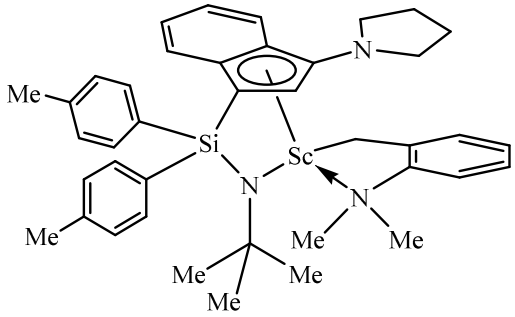
4. The catalyst system of any of the preceding claims, wherein the structure of formula (I) comprises one or more of the following:



;



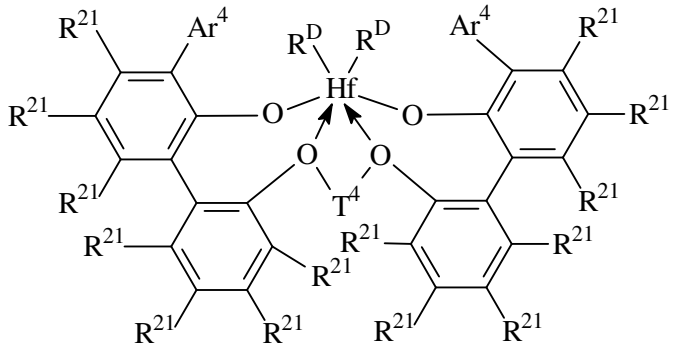
; and



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5. The catalyst system of any of the preceding claims, wherein the first olefin polymerization procatalyst (A) and the second olefin polymerization procatalyst (B) have respective reactivity ratios r_{1A} and r_{1B}, such that the ratio (r_{1A}/r_{1B}) under polymerization conditions is 0.5 or less.

6. The catalyst system of any of the preceding claims, wherein said metal-ligand complex of Formula (III) has the following structure:



, wherein:

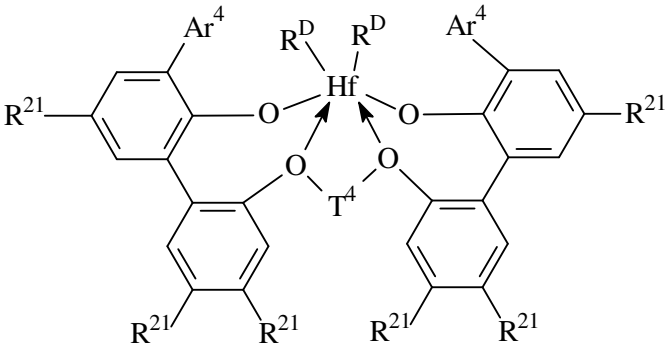
Ar^4 independently at each occurrence is C_{6-20} aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, naphthyl, anthracen-5-yl, 1,2,3,4,6,7,8,9-octahydroanthracen-5-yl;

T^4 independently at each occurrence is a propylene-1,3-diyl group, a bis(alkylene)cyclohexan-1,2-diyl group, or an inertly substituted derivative thereof substituted with from 1 to 5 alkyl, aryl or aralkyl substituents having up to 20 carbons each;

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen; and

R^D, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a divalent hydrocarbylene, hydrocarbadiyl or trihydrocarbylsilyl group of up to 40 atoms not counting hydrogen.

7. The catalyst system of any of the preceding claims, wherein said metal-ligand complex of Formula (III) has the following structure:



, wherein,

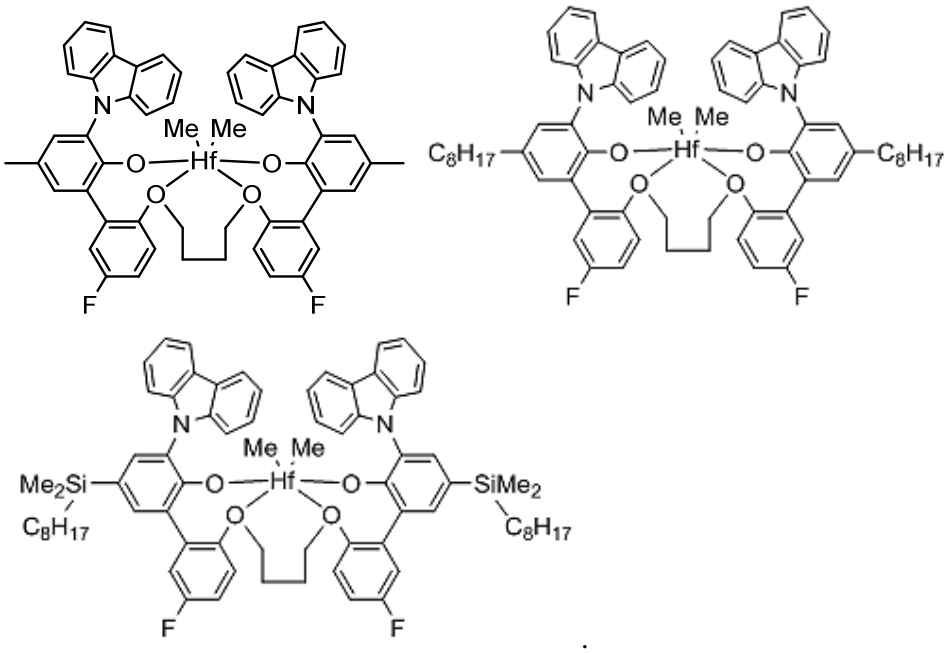
Ar^4 independently at each occurrence, is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl,

R^{21} independently at each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, alkoxy or amino of up to 50 atoms not counting hydrogen;

T^4 is propan-1,3-diyl or bis(methylene)cyclohexan-1,2-diyl; and

R^D, independently at each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 R^D groups together are a hydrocarbylene, hydrocarbadiyl or hydrocarbylsilanediyl group of up to 40 atoms not counting hydrogen.

8. The catalyst system of any ofthe preceding claims, wherein said metal-ligand complex of Formula (III) is selected from the group consisting of:



.

9. The catalyst system of any of the preceding claims, wherein the chain shuttling agent is an aluminum, zinc, or gallium compound containing at least one hydrocarbyl substituent having from 1 to 12 carbons.