FIVE-COORDINATE BIS-PHENYLPHENOXY CATALYSTS FOR THE PREPARATION OF ETHYLENE-BASED POLYMERS

REFERENCE TO RELATED APPLICATIONS

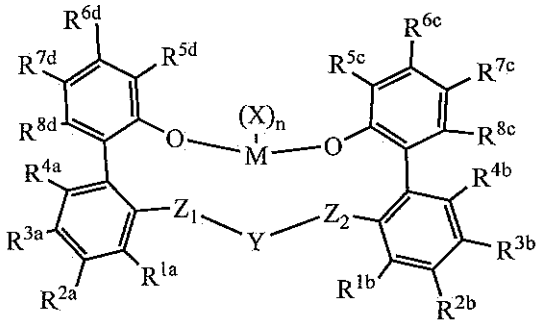
The present application claims the benefit of U.S. Provisional Application No. 62/087621, filed December 4, 2014, and incorporated herein by reference.

BACKGROUND

Low molecular weight, semi-crystalline ethylene-based polymers (for example, weight average molecule weights less than 5,000 g/mole) can be used in formulations to make hot melt adhesives (for example, as wax components), and in other types of adhesives. Such polymers may be produced with conventional catalyst systems, for example, constrained geometry type catalyst systems or other bis-phenylphenoxy catalysts; however, typically significantly low polymerization temperatures are needed (<135 °C) to produce theses polymers. It is desirable to find new polymerizations using new catalyst systems, which are capable of making these low molecular weight, semi-crystalline polymers at elevated temperatures, with good efficiencies to allow for increased reactor throughput. This need has been met by the following invention.

SUMMARY

The disclosure provides a molecular transition metal complex selected from Formula 1:



(Formula 1),

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

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

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

X and n are selected such that the metal-ligand complex is neutral;

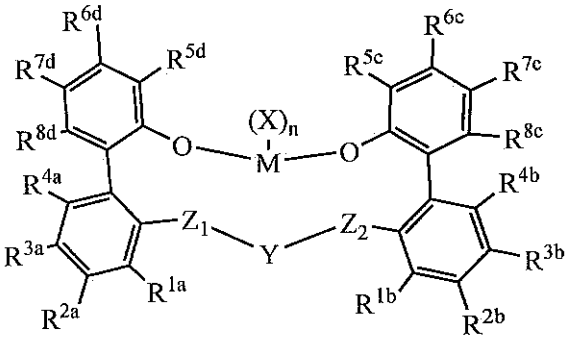
Z_1 and Z_2 are each independently selected from the following: -O-, -S-, -N[(C_1-C_{40})hydrocarbyl]-, or -P[(C_1-C_{40})hydrocarbyl]-;

Y is a single atom bridge selected from the following: $-CR_2-$, $-GeR_2-$, $-SiR_2-$, -P-, -NR-; wherein each R is independently a hydrogen, a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-OR^C$, $-SR^C$, -CN, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N{=}C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, or a halogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and

wherein R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} are each, independently, selected from the following: a substituted or unsubstituted (C_1-C_{40})-hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-OSi(R^C)_3$, $-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N{=}C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and

wherein, for Formula 1, two or more of R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} may optionally form one or more ring structures; and wherein either Z_1 or Z_2 is dative covalent (coordinate) to M.

In one aspect, there is provided a molecular transition metal complex selected from Formula 1:



(Formula 1),

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

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

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

X and n are selected such that the metal-ligand complex is neutral;

Z_1 and Z_2 are each independently selected from the following: -O-, -S-, -N[(C_1-C_{40})hydrocarbyl]-, or -P[(C_1-C_{40})hydrocarbyl]-;

Y is a single atom bridge selected from the following: $-CR_2-$, $-GeR_2-$, $-SiR_2-$; wherein each R is independently a hydrogen, a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-OR^C$, $-SR^C$, -CN, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N{=}C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, or a halogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl;

wherein R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} are each, independently, selected from the following: a substituted or unsubstituted (C_1-C_{40})-hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-OSi(R^C)_3$, $-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N{=}C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, a halogen, or a hydrogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and

wherein, for Formula 1, two or more of R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} may optionally form one or more ring structures; and wherein either Z_1 or Z_2 is dative covalent (coordinate) to M.

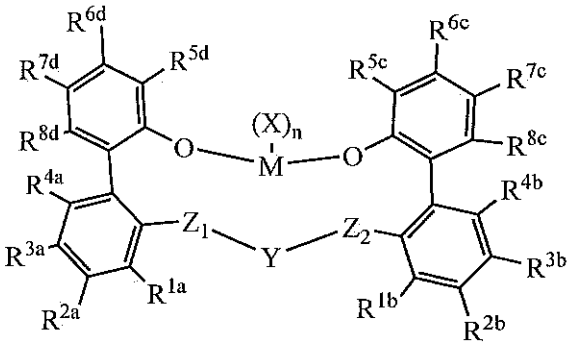
In another aspect, there is provided a process to form an ethylene-based polymer, said process comprising polymerizing a mixture comprising ethylene, and optionally at least one comonomer, in the presence of at least one molecular transition metal complex as defined herein.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts the x-ray, molecular structure of CAT E (see experimental section). Hydrogens are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. (R1 = 2.6%).

CLAIMS

1. A molecular transition metal complex selected from Formula 1:



(Formula 1),

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

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

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

X and n are selected such that the metal-ligand complex is neutral;

Z_1 and Z_2 are each independently selected from the following: -O-, -S-, -N[(C_1-C_{40})hydrocarbyl]-, or -P[(C_1-C_{40})hydrocarbyl]-;

Y is a single atom bridge selected from the following: $-CR_2-$, $-GeR_2-$, $-SiR_2-$; wherein each R is independently a hydrogen, a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-OR^C$, $-SR^C$, -CN, $-CF_3$, $-OCF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N{=}C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, or a halogen; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl;

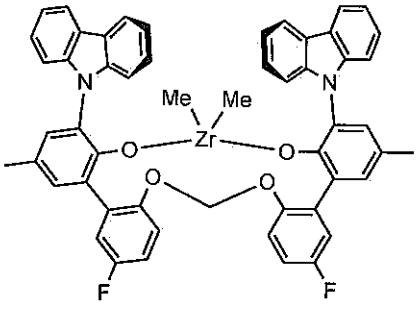
wherein R^{1a}, R^{2a}, R^{3a}, R^{4a}, R^{1b}, R^{2b}, R^{3b}, R^{4b}, R^{5c}, R^{6c}, R^{7c}, R^{8c}, R^{5d}, R^{6d}, R^{7d} and R^{8d} are each, independently, selected from the following: a substituted or unsubstituted (C_1-C_{40})-hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-OSi(R^C)_3$, $-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN, $-CF_3$, $-OCF_3$, $-S(O)R^C$,

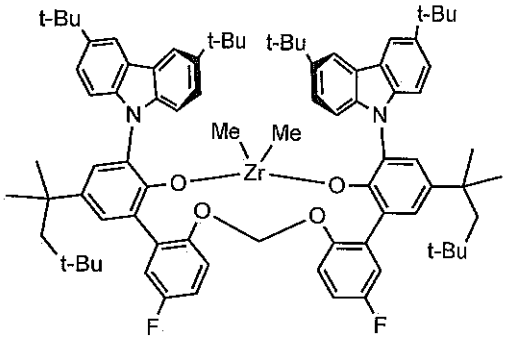
5. The molecular transition metal complex of claim 1, wherein Y is selected from the following: -CHR-, -CRR'-, $-CR_2-$, $-CH_2-$, $-SiR_2-$, -SiRR'-, $-GeR_2-$, -CHOR-, and

wherein each R is independently an alkyl or an aryl, and

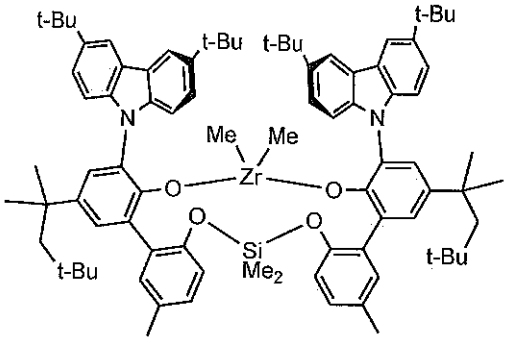
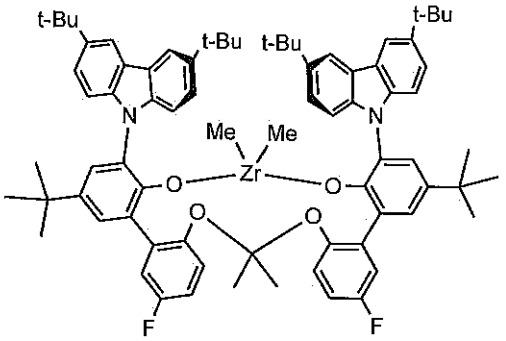
wherein each R' is independently an alkyl or an aryl.

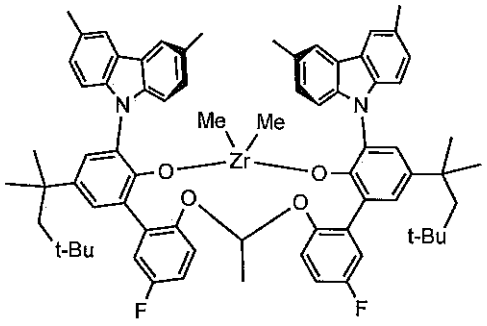
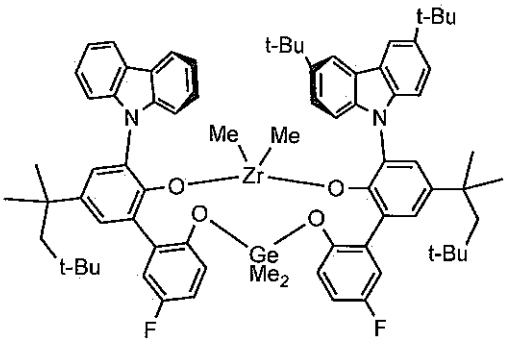
6. The molecular transition metal complex of claim 1, wherein Formula 1 is selected from the following structures a) through ee):

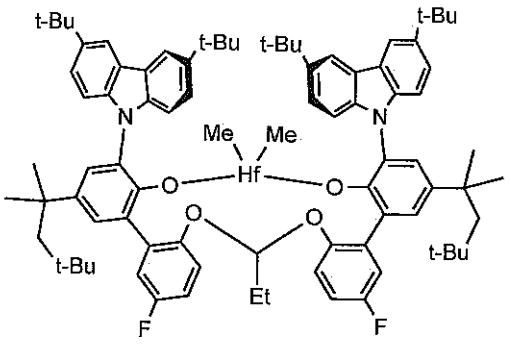
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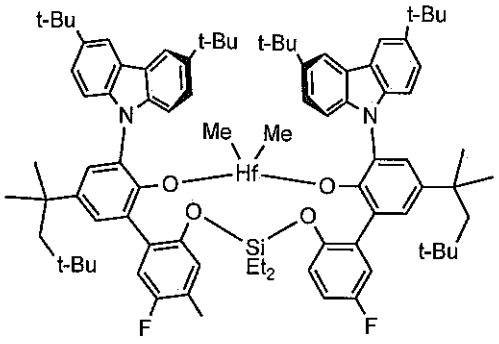
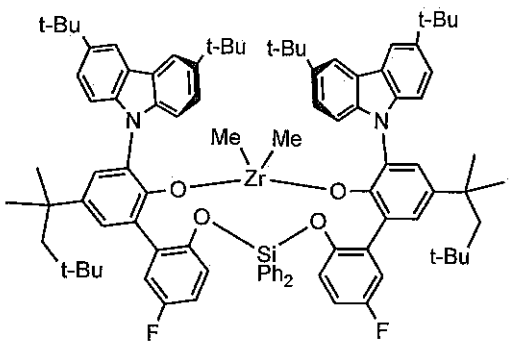
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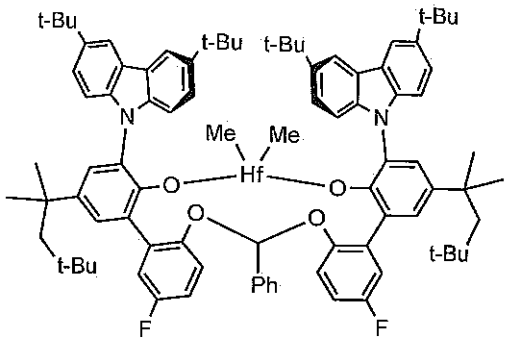
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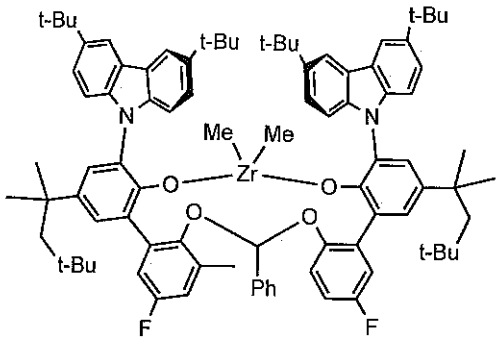
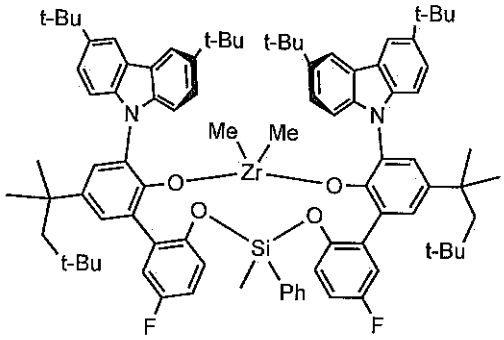
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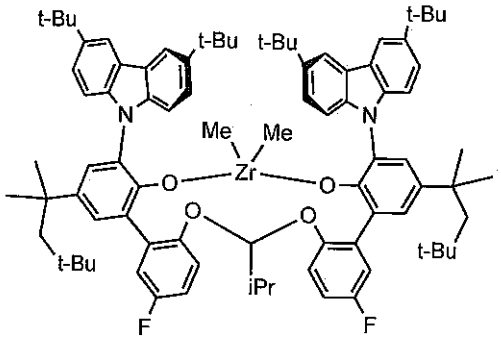
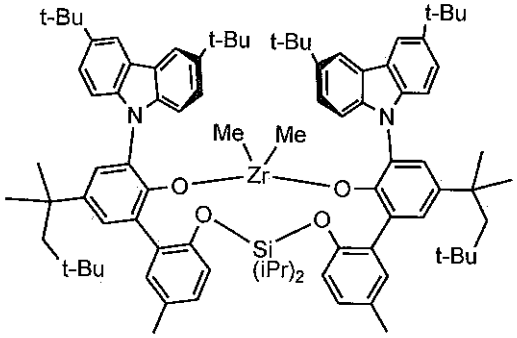
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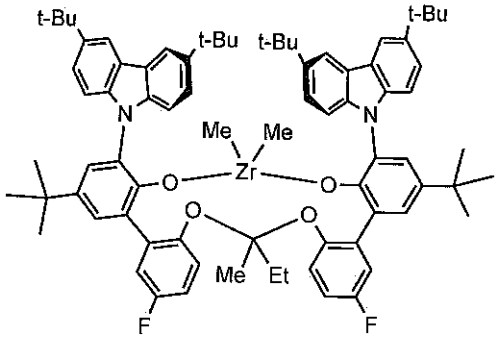
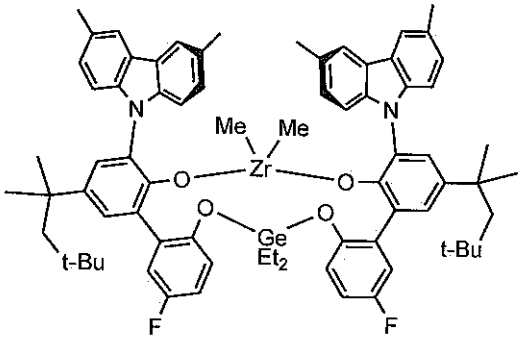
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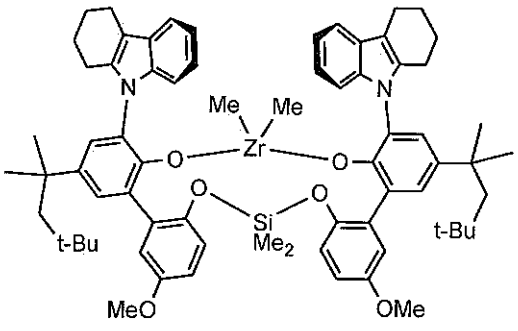
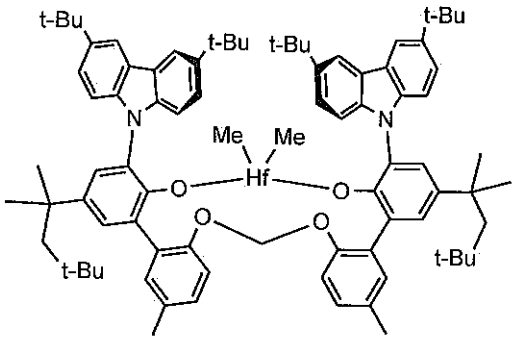
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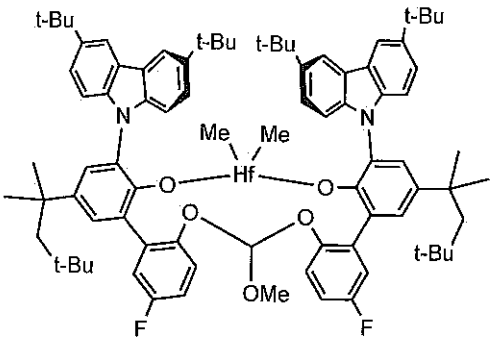
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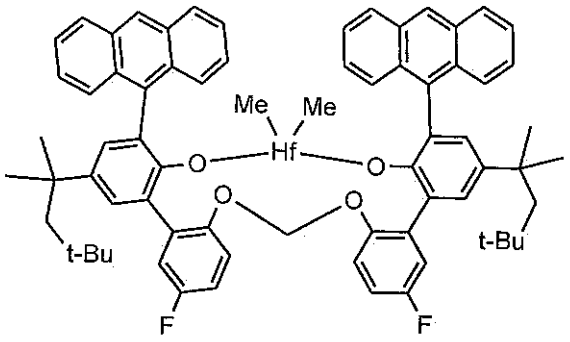
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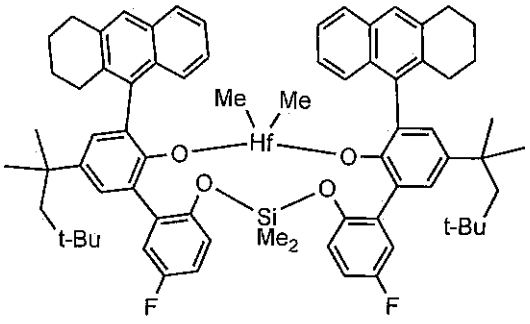
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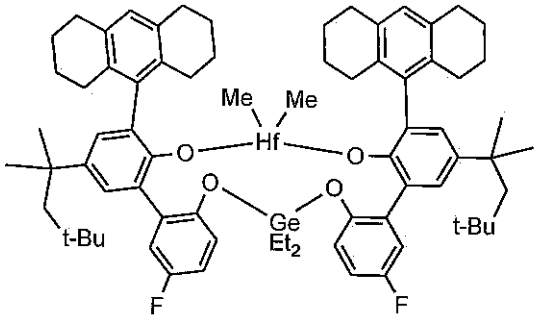
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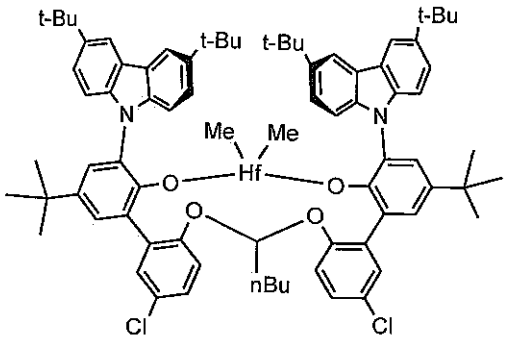
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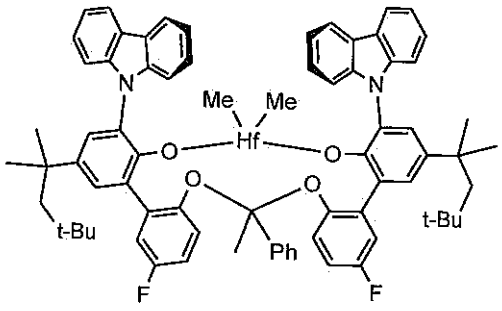
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7. A process to form an ethylene-based polymer, said process comprising polymerizing a mixture comprising ethylene, and optionally at least one comonomer, in the presence of at least one molecular transition metal complex claim 1.