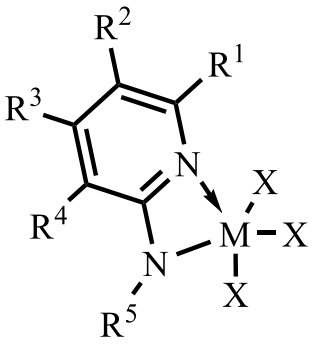
product dissolved in the diluent, together with unreacted ethylene and one or more optional co-monomers, is removed from the reactor. The reaction mixture, when removed from the reactor, may be processed to remove the polyethylene product from the diluent and the unreacted reactants, with the diluent and unreacted reactants typically being recycled back into the reactor. Alternatively, the reaction mixture may be sent to a second reactor, serially connected to the first reactor, where a second polyethylene fraction may be produced.

[0005] Despite the number of currently available homogeneous solution olefin polymerization catalyst systems, there is a need for high temperature polymerization catalysts that have improved molecular properties facilitating the production of high molecular weight (Mw) polymers having narrow polydispersities (PDIs), and/or high molecular weight (Mw) ethylene/comonomer copolymers having a range of comonomer incorporation (i.e. 0 – 20 mol% of 1-hexene or 1-octene, etc), and/or high molecular weight (Mw) polymers that can undergo chain transfer with chain transfer agents (CSAs) to produce olefin block copolymers (OBCs).

SUMMARY

[0006] ~~Embodiments of t~~This disclosure relates to ~~include~~ polymerization processes. These polymerization processes produce ethylene-based polymers. The polymerization process comprising contacting ethylene and optionally one or more (C_3–C_{12})α-olefin in the presence of a catalyst system, wherein the catalyst system comprises a metal–ligand complex having a structure according to formula (I):



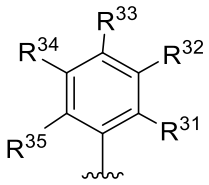
(I)

[0007] In formula (I), M is titanium, zirconium, or hafnium. Each X is a monodentate or bidentate ligand independently chosen from unsaturated (C_2–C_{20})hydrocarbon, unsaturated (C_2–C_{50})heterohydrocarbon, (C_1–C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl,

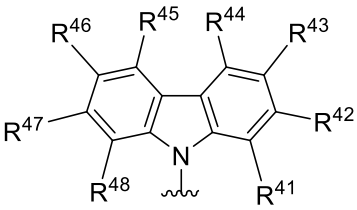
(C_6−C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4−C_{12})diene, halogen, −OR^X, −$N(R^X)_2$, or –$NCOR^X$, wherein each R^X is (C_1−C_{30})hydrocarbyl or –H.

[0008] In formula (I), R^1, R^2, R^3, and R^4 are independently chosen from −H, (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, −$Si(R^C)_3$, −$Ge(R^C)_3$, −$P(R^P)_2$, −$N(R^N)_2$, −OR^C, −SR^C, −NO_2, −CN, −CF_3, $R^CS(O)$−, $R^CS(O)_2$−, $(R^C)_2C$=N−, $R^CC(O)O$−, $R^COC(O)$−, $R^CC(O)N(R)$−, $(R^C)_2NC(O)$−, or halogen, wherein each R^C, each R^N, and each R^P are (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, or –H; and R^5 is –H, (C_1−C_{40})hydrocarbyl or (C_1−C_{40})heterohydrocarbyl, provided R^5 is not phenyl or a substituted phenyl.

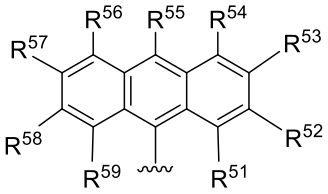
[0009] In various ~~embodiments~~examples, R^1 is selected from the group consisting of radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



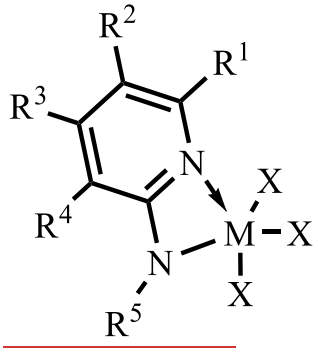
(III)



(IV)

[0010] In formulas (II), (III), (IV), R^{31}–R^{35}, R^{41}–R^{48}, and R^{51}–R^{59} is independently chosen from (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, −$Si(R^T)_3$, −$Ge(R^T)_3$, −$P(R^T)_2$, −$N(R^T)_2$, −N=CHR^T, −OR^T, −SR^T, −NO_2, −CN, −CF_3, $R^TS(O)$−, $R^TS(O)_2$−, $(R^T)_2C$=N−, $R^TC(O)O$−, $R^TOC(O)$−, $R^TC(O)N(R^T)$−, $(R^T)_2NC(O)$−, halogen, or –H, wherein each R^T is (C_1−C_{30})hydrocarbyl or –H.

[0010a] In one aspect, there is provided a process for polymerizing olefin, the process comprising contacting ethylene and optionally one or more (C_3–C_{12})α-olefin in the presence of a catalyst system, wherein the catalyst system comprises a metal–ligand complex having a structure according to formula (I):

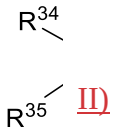


where:

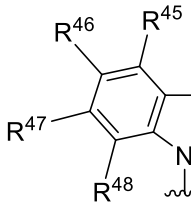
M is titanium, zirconium, or hafnium;

each X is benzyl, (C_1–C_{12})alkyl, halogen atom, $-CH_2SiR^R_3$, or $-(CH_2)_n(SiR^C)_3$, wherein n is an integer from 1 to 10, wherein each R^R is (C_1–C_{12})alkyl, and wherein each R^C is independently (C_1–C_{30})hydrocarbyl, (C_1–C_{30})heterohydrocarbyl, or –H;

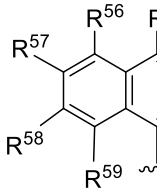
R^1 is selected from the group consisting of radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



II)



III)



IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, $-Si(R^T)_3$, $-Ge(R^T)_3$, $-P(R^T)_2$, $-N(R^T)_2$, $-N=CHR^T$, $-OR^T$, $-SR^T$, $-NO_2$, $-CN$, $-CF_3$, $R^TS(O)-$, $R^TS(O)_2-$, $(R^T)_2C=N-$, $R^TC(O)O-$, $R^TOC(O)-$, $R^TC(O)N(R^T)-$, $(R^T)_2NC(O)-$, halogen, or –H, wherein R^T is (C_1–C_{30})hydrocarbyl or –H;

R^2, R^3, and R^4 are independently chosen from –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $(R^C)_2NC(O)-$, or halogen, wherein each R^C and each R^N is (C_1–C_{30})hydrocarbyl, (C_1–C_{30})heterohydrocarbyl, or –H; and

R^5 is –H, (C_1–C_{40})hydrocarbyl or (C_1–C_{40})heterohydrocarbyl, provided R^5 is not phenyl or a substituted phenyl.

BRIEF SUMMARY OF THE DRAWINGS

[0011] FIG. 1 depicts Ligand 1 to Ligand 8.

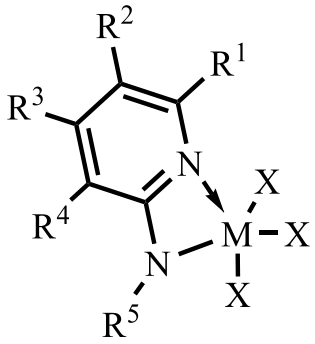
DETAILED DESCRIPTION

[0012] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

[0013] Common abbreviations are listed below:

CLAIMS

1. A process for polymerizing olefin, the process comprising contacting ethylene and optionally one or more (C_3–C_{12})α-olefin in the presence of a catalyst system, wherein the catalyst system comprises a metal–ligand complex having a structure according to formula (I):



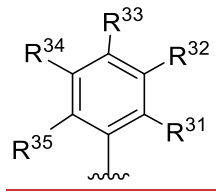
(I)

where:

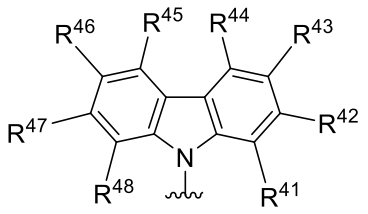
M is titanium, zirconium, or hafnium;

each X is benzyl, (C_1–C_{12})alkyl, halogen atom, $-CH_2SiR^R_3$, or $-(CH_2)_n(SiR^C)_3$, wherein n is an integer from 1 to 10, wherein each R^R is (C_1–C_{12})alkyl, and wherein each R^C is independently (C_1–C_{30})hydrocarbyl, (C_1–C_{30})heterohydrocarbyl, or –H;

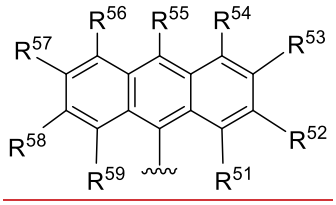
R^1 is selected from the group consisting of radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of $R^{31–35}$, $R^{41–48}$, and $R^{51–59}$ is independently chosen from (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, $-Si(R^T)_3$, $-Ge(R^T)_3$, $-P(R^T)_2$, $-N(R^T)_2$, $-N=CHR^T$, $-OR^T$, $-SR^T$, $-NO_2$, –CN, $-CF_3$, $R^TS(O)-$, $R^TS(O)_2-$, $(R^T)_2C=N-$, $R^TC(O)O-$, $R^TOC(O)-$, $R^TC(O)N(R^T)-$, $(R^T)_2NC(O)-$, halogen, or –H, wherein R^T is (C_1–C_{30})hydrocarbyl or –H;

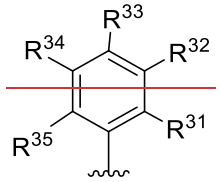
~~independently chosen from (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, –CN, $-CF_3$,~~

~~R^CS(O)−, R^CS(O)$_2$−, (R^C)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R)−, (R^C)$_2$NC(O)−, or halogen, wherein each R^C, each R^N, and each R^P are independently (C_1−C_{30})hydrocarbyl, (C_1−C_{30})heterohydrocarbyl, or −H;~~

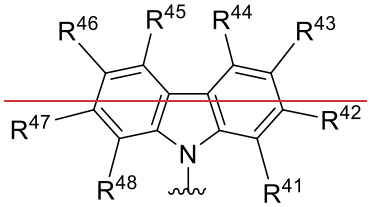
R^2, R^3, and R^4 are independently chosen from −H, (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, −Si(R^C)$_3$, −Ge(R^C)$_3$, −P(R^P)$_2$, −N(R^N)$_2$, −OR^C, −SR^C, −NO_2, −CN, −CF_3, R^CS(O)−, R^CS(O)$_2$−, (R^C)$_2$C=N−, R^CC(O)O−, R^COC(O)−, ~~R^CC(O)N(R)−,~~ (R^C)$_2$NC(O)−, or halogen, wherein each R^C and each R^N is (C_1−C_{30})hydrocarbyl, (C_1−C_{30})heterohydrocarbyl, or –H; and

R^5 is –H, (C_1−C_{40})hydrocarbyl or (C_1−C_{40})heterohydrocarbyl, provided R^5 is not phenyl or a substituted phenyl.

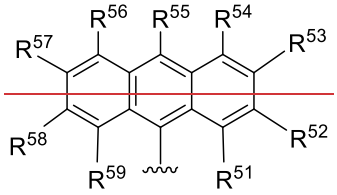
~~2. The process of claim 1, wherein R^1 is selected from the group consisting of radicals having formula (II), radicals having formula (III), and radicals having formula (IV):~~



~~(II)~~



~~(III)~~



~~(IV)~~

~~where each of R^{31-35}, R^{41-48}, and R^{51-59} is independently chosen from (C_1−C_{40})hydrocarbyl, (C_1−C_{40})heterohydrocarbyl, −Si(R^T)$_3$, −Ge(R^T)$_3$, −P(R^T)$_2$, −N(R^T)$_2$, −N=CHR^T, −OR^T, −SR^T, −NO_2, −CN, −CF_3, R^TS(O)−, R^TS(O)$_2$−, (R^T)$_2$C=N−, R^TC(O)O−, R^TOC(O)−, R^TC(O)N(R^T)−, (R^T)$_2$NC(O)−, halogen, or −H, wherein R^T is (C_1−C_{30})hydrocarbyl or −H.~~

~~3~~2. The process of claim ~~2~~1, wherein R^1 is a radical having formula (II), and wherein R^{31}, R^{33}, and R^{35} are independently (C_1−C_{12})alkyl or (C_1−C_{20})aryl.

~~4~~3. The process of claim ~~2~~1, wherein R^1 is a radical having formula (II), and wherein R^{32} and R^{34} are independently (C_1−C_{12})alkyl or (C_1−C_{20})aryl.

~~5~~4. The process of claim ~~2~~1, wherein R^1 is a radical having formula (IV), and wherein R^{52} and R^{58} are independently (C_1−C_{12})alkyl or (C_1−C_{20})aryl.

~~6~~5. The process of claim ~~2~~1, wherein R^1 is a radical having formula (IV), and wherein R^{53} and R^{58} are independently (C_1-C_{12})alkyl or (C_1-C_{20})aryl.

~~7~~6. The process of claim ~~2~~1, wherein R^1 is a radical having formula (IV), and wherein R^{53} and R^{57} are independently (C_1-C_{12})alkyl or (C_1-C_{20})aryl.

~~8~~7. The process of claim ~~2~~1, wherein R^1 is a radical having formula (IV), and wherein R^{53}, R^{55}, and R^{57} are independently (C_1-C_{12})alkyl or (C_1-C_{20})aryl.

~~9~~8. The process of any one of the preceding claims, wherein R^5 is benzyl, (C_1-C_{20})alkyl, or $-CH_2SiR^R{}_3$, wherein R^R is (C_1-C_{12})alkyl.

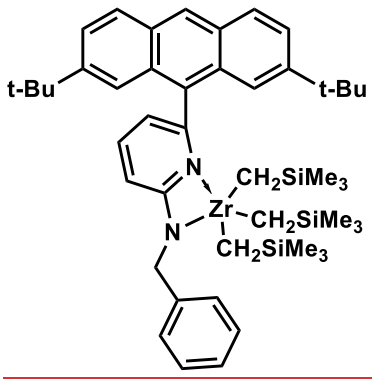
~~10~~9. The polymerization process of any one of the preceding claims, wherein the contacting occurs in a reactor at a reactor temperature of greater than or equal to 120 °C.

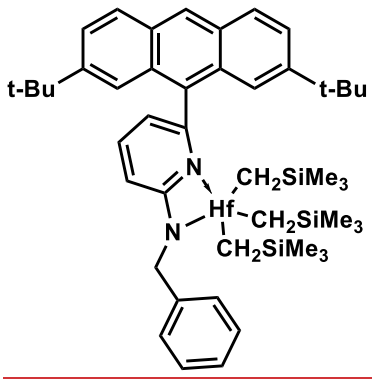
~~11~~10. The polymerization process of any one of the preceding claims, wherein the contacting occurs in a solution polymerization reactor at a reactor pressure from 10 psi to 2000 psi.

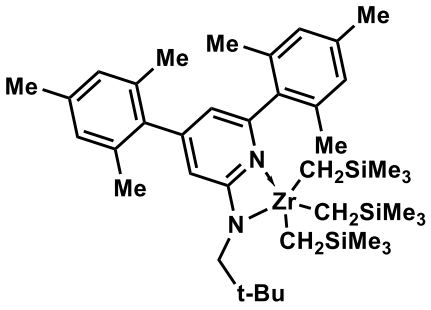
~~12~~11. The polymerization process of any of one of claims 1 to ~~11~~10, wherein the contacting occurs within a reactor including therein the catalyst system and a chain transfer agent or chain shuttling agent.

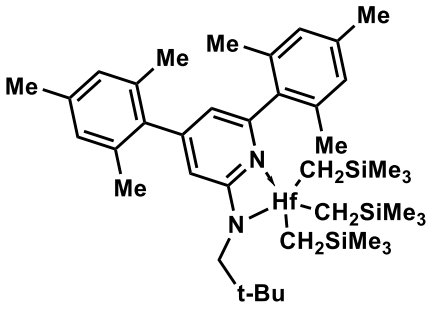
~~13~~12. The polymerization process of claim ~~12~~11, wherein the chain transfer or chain shuttling agent is diethyl zinc.

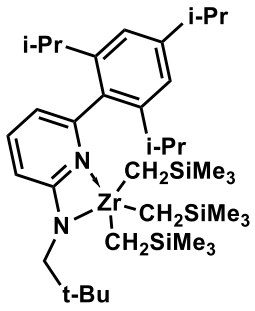
13. The polymerization process of any one of the preceding claims, wherein the structure according to formula (I) is selected from the group consisting of:

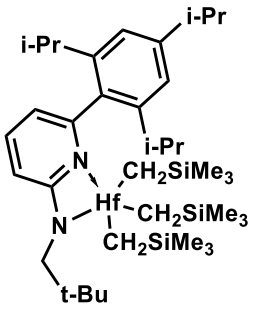


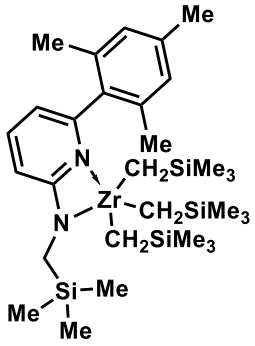


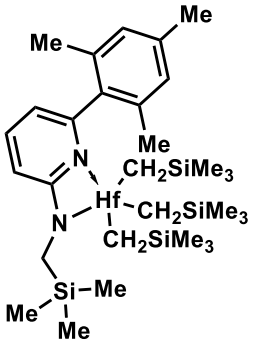

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Zr
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N
CH2SiMe3
t-Bu

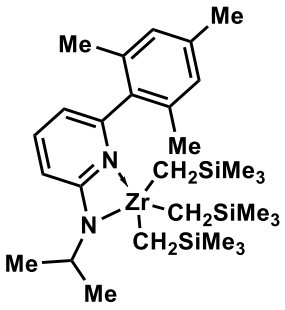

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Me
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N
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t-Bu

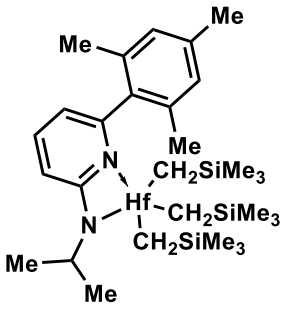

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i-Pr
i-Pr
N
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Zr
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N
CH2SiMe3
t-Bu

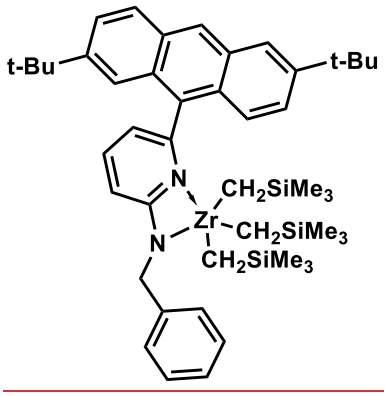

i-Pr
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i-Pr
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Hf
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CH2SiMe3
t-Bu

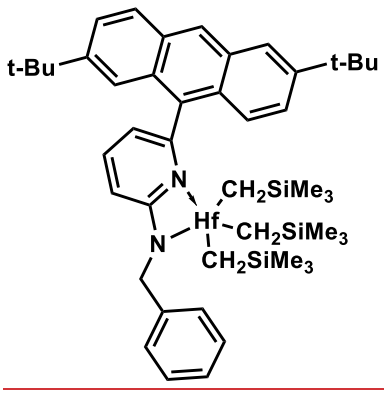

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Zr
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Si
Me
Me
Me

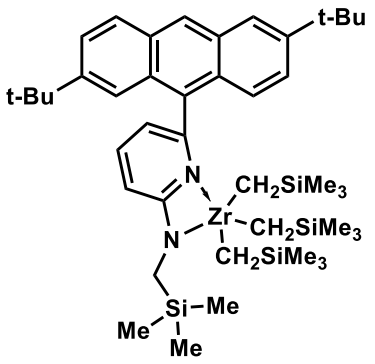

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Hf
CH2SiMe3
N
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Si
Me
Me
Me

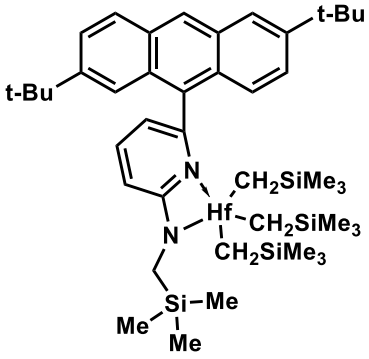

Me
Me
Me
N
CH2SiMe3
Zr
CH2SiMe3
N
CH2SiMe3
Me
Me

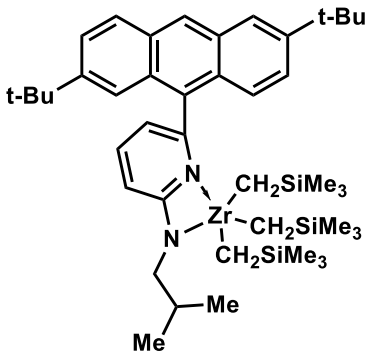

Me
Me
Me
N
CH2SiMe3
Hf
CH2SiMe3
N
CH2SiMe3
Me
Me

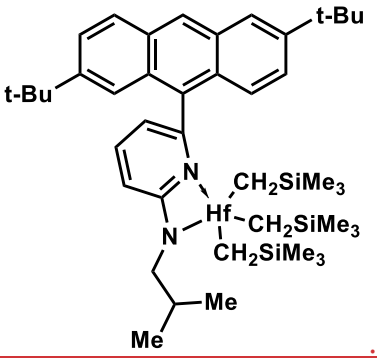

t-Bu
t-Bu
N
CH2SiMe3
Zr
CH2SiMe3
N
CH2SiMe3


t-Bu
t-Bu
N
CH2SiMe3
Hf
CH2SiMe3
N
CH2SiMe3


t-Bu
t-Bu
N
Zr
CH2SiMe3
CH2SiMe3
CH2SiMe3
N
Si
Me
Me
Me


t-Bu
t-Bu
N
Hf
CH2SiMe3
CH2SiMe3
CH2SiMe3
N
Si
Me
Me
Me


t-Bu
t-Bu
N
Zr
CH2SiMe3
CH2SiMe3
CH2SiMe3
N
Me
Me


t-Bu
t-Bu
N
Hf
CH2SiMe3
CH2SiMe3
CH2SiMe3
N
Me
Me