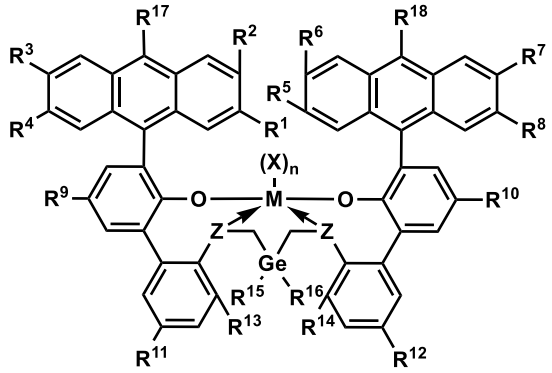
Claims

1. A supported catalyst system comprising a metal-ligand complex disposed on one or more support materials, wherein the metal-ligand complex has a structure according to formula (I):



(I)

wherein:

M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from (C_1-C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, (C_6−C_{50})aryl, (C_4−C_{50})heteroaryl, halogen, –N(R^N)$_2$, N(R^N)COR^C, –OR, –OPh, –OAr and -H;

the metal-ligand complex is overall charge-neutral;

each Z is independently chosen from –O−, −S−, (C_6−C_{50})aryl, (C_2−C_{50})heteroaryl, N(C_1−C_{50})hydrocarbyl, N(C_1-C_{50})aryl, P(C_1-C_{50})aryl, and P(C_1−C_{50})hydrocarbyl;

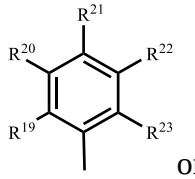
R^9 and R^{10} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{11} and R^{12} are independently chosen from halogen, (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^1−R^8 are each independently (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{13} and R^{14} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{15} and R^{16} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;



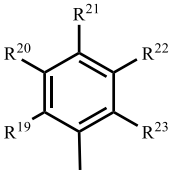
R^{17} and R^{18} are both: (C_1-C_{20})hydrocarbyl, (C_1-C_{20})heterohydrocarbyl, or -H, where R^{19-23} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H; and

each R, R^C and R^N are independently chosen from −H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})heterohydrocarbyl.

2. The supported catalyst system of claim 1, wherein Z is -O-; or wherein n is 2 and each X is methyl.

3. The supported catalyst system of claim 1, wherein R^9 and R^{10} are each 1,1,-dimethyl-3,3,-dimethylbutyl or *tert*-octyl.

4. The supported catalyst system of claim 3, wherein R^{11} and R^{12} are each 1,1,-dimethyl-3,3,-dimethylbutyl or *tert*-octyl; or wherein R^{11} and R^{12} are each -F.

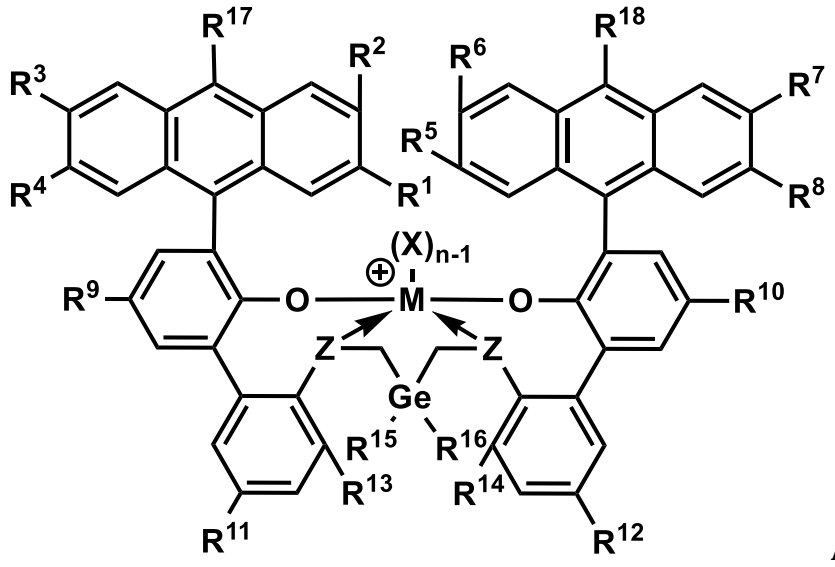
5. The supported catalyst system of any one of claims 1-4, wherein R^1, R^4, R^5 and R^8 are each *tert*-butyl and R^2, R^3, R^6 and R^7 are each -H; or wherein R^1, R^4, R^5 and R^8 are each -H and R^2, R^3, R^6 and R^7 are each *tert*-butyl; or wherein R^{17} and R^{18} are both 

and R^{20} and R^{22} are each *tert*-butyl and R^{19}, R^{21} and R^{23} are each -H; or wherein R^{17} and R^{18} are both -H; or wherein at least two R groups of R^{19-23} are (C_1−C_{20})hydrocarbyl; or wherein R^{11} and R^{12} are halogen R^1, R^4, R^5 and R^8 are each independently (C_1−C_{20})hydrocarbyl and R^2, R^3, R^6 and R^7 are -H or R^1, R^4, R^5 and R^8 are each -H and R^2, R^3, R^6 and R^7 are each independently (C_1−C_{20})hydrocarbyl; or

wherein the one or more support materials comprise fumed silica; or wherein the supported catalyst system is a spray-dried supported catalyst system; or further including one or more activators; or further including an activator comprising methylalumoxane (MAO).

6. A method for producing a supported activated metal-ligand catalyst, the method comprising:

contacting one or more support materials and one or more activators with a metal-ligand complex in an inert hydrocarbon solvent to produce the supported activated metal-ligand catalyst, wherein the metal-ligand complex has a structure according to formula (Ib):



(Ib)

wherein:

A^- is an anion;

M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from (C_1-C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, (C_6−C_{50})aryl, (C_4−C_{50})heteroaryl, halogen, –$N(R^N)_2$, –$N(R^N)COR^C$, –OR, –OPh, –OAr and -H;

each Z is independently chosen from –O−, −S−, (C_6−C_{50})aryl, (C_2−C_{50})heteroaryl, N(C_1−C_{50})hydrocarbyl, N(C_1-C_{50})aryl, P(C_1-C_{50})aryl, and P(C_1−C_{50})hydrocarbyl;

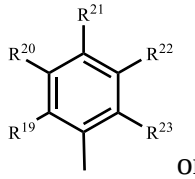
R^9 and R^{10} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{11} and R^{12} are independently chosen from halogen, (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^1–R^8 are each independently (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{13} and R^{14} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{15} and R^{16} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;



R^{17} and R^{18} are both: (C_1-C_{20})hydrocarbyl, (C_1-C_{20})heterohydrocarbyl, or -H, where R^{19-23} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H; and

each R, R^C and R^N are independently chosen from −H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})heterohydrocarbyl.

7. The method of claim 6, wherein the activator comprises methylalumoxane (MAO); or further including drying the supported activated metal-ligand catalyst, wherein drying includes spray drying the supported activated metal-ligand catalyst to produce particles of a spray-dried supported activated metal-ligand catalyst; or

wherein the method further comprises:

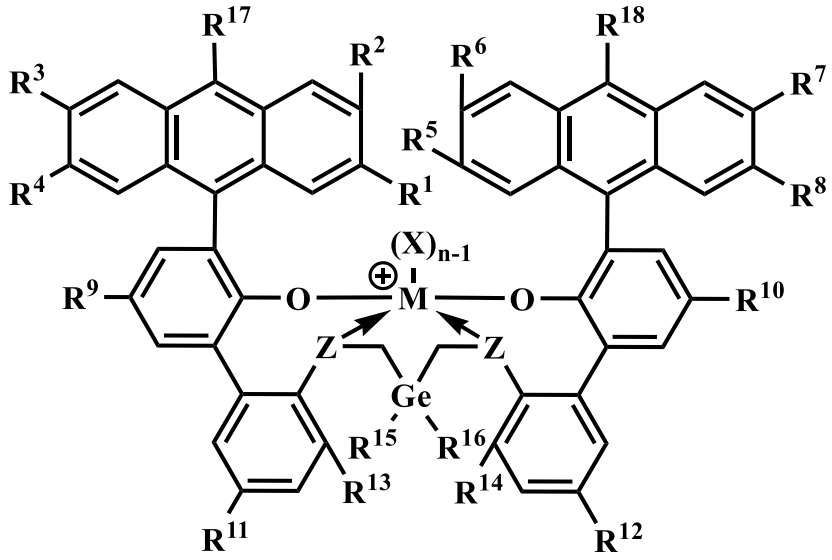
disposing the one or more activators on the one or more support materials to produce a supported activator; and

contacting the supported activator with a solution of the metal-ligand complex in the inert hydrocarbon solvent; or wherein disposing the one or more activators on the one or more support materials comprises spray drying to produce a spray-dried supported activator; or

wherein at least two R groups of R^{19-23} are (C_1−C_{20})hydrocarbyl; or wherein R^{11} and R^{12} are halogen R^1, R^4, R^5 and R^8 are each independently (C_1−C_{20})hydrocarbyl and R^2, R^3, R^6 and R^7 are -H or R^1, R^4, R^5 and R^8 are each -H and R^2, R^3, R^6 and R^7 are each independently (C_1−C_{20})hydrocarbyl.

8. A process for producing a polyethylene or polyethylene copolymer resin in a gas phase polymerization reactor comprising:

contacting ethylene and, optionally, one or more (C_3−C_{12})α-olefin comonomers with a supported activated metal-ligand catalyst in a gas-phase polymerization reactor, wherein the supported activated metal-ligand catalyst comprises a metal-ligand complex disposed on one or more support materials and one or more activators; wherein the metal-ligand complex has a structure according to formula (Ib):



(Ib)

wherein:

A^- is an anion;

M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from (C_1-C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, (C_6−C_{50})aryl, (C_4−C_{50})heteroaryl, halogen, –N(R^N)$_2$, –N(R^N)COR^C, –OR, –OPh, –OAr and -H;

each Z is independently chosen from –O−, −S−, (C_6−C_{50})aryl, (C_2−C_{50})heteroaryl, N(C_1−C_{50})hydrocarbyl, N(C_1-C_{50})aryl, P(C_1-C_{50})aryl, and P(C_1−C_{50})hydrocarbyl;

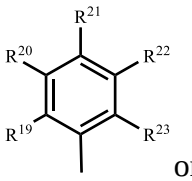
R^9 and R^{10} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{11} and R^{12} are independently chosen from halogen, (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^1–R^8 are each independently (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{13} and R^{14} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{15} and R^{16} are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H;

R^{17} and R^{18} are both: (C_1-C_{20})hydrocarbyl, (C_1-C_{20})heterohydrocarbyl, 

or -H, where $R^{19\text{-}23}$ are independently chosen from (C_1−C_{20})hydrocarbyl, (C_1−C_{20})heterohydrocarbyl and -H; and

each R, R^C and R^N are independently chosen from −H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})heterohydrocarbyl.

9. The process of claim 8, wherein the one or more activators comprise methylalumoxane (MAO); or wherein the supported catalyst system is fed to the gas-phase polymerization reactor in neat form, as a solution, or as a slurry; or

wherein the supported catalyst system is a spray dried supported catalyst system.

10. The process of any one of claims 8-9, wherein at least two R groups of R^{19-23} are (C_1−C_{20})hydrocarbyl; or

wherein R^{11} and R^{12} are halogen R^1, R^4, R^5 and R^8 are each independently (C_1−C_{20})hydrocarbyl and R^2, R^3, R^6 and R^7 are -H or R^1, R^4, R^5 and R^8 are each -H and R^2, R^3, R^6 and R^7 are each independently (C_1−C_{20})hydrocarbyl.