CLAIMS

What is claimed is:

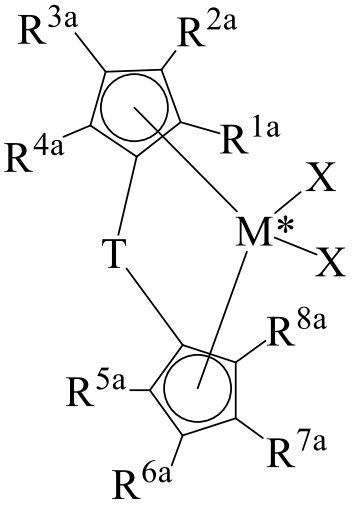
1. A supported catalyst system comprising:

a bridged group 4 metallocene catalyst;

an iron catalyst;

a support material; and

an activator; wherein the bridged group 4 metallocene compound is represented by the formula (A):



(A)

where

M* is a group 4 metal;

each of R^{1a}, R^{2a}, and R^{4a} is independently hydrogen, alkoxide or C_1 to C_{40} substituted or unsubstituted hydrocarbyl;

R^{3a} is independently hydrogen, a substituted C_1 to C_{12} hydrocarbyl group, an unsubstituted C_1 to C_{12} hydrocarbyl group, or is $-R^{20}-SiR'_3$ or is $-R^{20}-CR'_3$ 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, provided that at least one R' is not H, alternatively 2 R' are not H, alternatively 3 R' are not H;

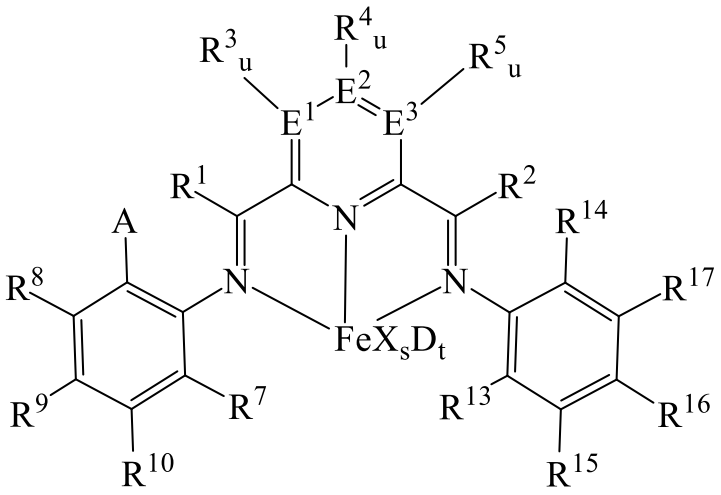
each of R^{5a}, R^{6a}, and R^{8a} is independently hydrogen, halide, alkoxide or C_1 to C_{40} substituted or unsubstituted hydrocarbyl;

R^{7a} is $-R^{20}-SiR'_3$ or is $-R^{20}-CR'_3$ where R^{20} is C_1 to C_4 hydrocarbyl, 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, alternatively 2 R' are not H, alternatively 3 R' are not H;

T is a bridging group; and

each X is independently a univalent anionic ligand, a diene ligand, an alkylidene ligand, or two Xs are joined to form a metallocyclic ring;

and the iron catalyst is represented by formula (B):



(B)

wherein:

A is chlorine, bromine, iodine, $-CF_3$ or $-OR^{11}$;

each of R^1 and R^2 is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O and S;

wherein each of R^1 and R^2 is optionally substituted by halogen, $-NR^{11}_2$, $-OR^{11}$ or $-SiR^{12}_3$;

wherein R^1 optionally bonds with R^3, and R^2 optionally bonds with R^5, in each case to independently form a five-, six- or seven-membered ring;

R^7 is a C_1-C_{20} alkyl;

each of R^3_u, R^4_u, R^5_u, R^8, R^9, R^{10}, R^{15}, R^{16}, and R^{17} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, $-NR^{11}_2$, $-OR^{11}$, halogen, $-SiR^{12}_3$ or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O, and S;

wherein R^3_u, R^4_u, R^5_u, R^7, R^8, R^9, R^{10}, R^{15}, R^{16}, and R^{17} are optionally substituted by halogen, $-NR^{11}_2$, $-OR^{11}$ or $-SiR^{12}_3$;

wherein R^3 optionally bonds with R^4, R^4 optionally bonds with R^5, R^7 optionally bonds with R^{10}, R^{10} optionally bonds with R^9, R^9 optionally bonds with R^8, R^{17} optionally bonds with R^{16}, and R^{16} optionally bonds with R^{15}, in each case to independently form a five-, six- or seven-membered carbocyclic or heterocyclic ring, the heterocyclic ring comprising at least one atom from the group consisting of N, P, O and S;

R^{13} is C_1-C_{20}-alkyl bonded with the aryl ring via a primary or secondary carbon atom;

R^{14} is chlorine, bromine, iodine, -CF_3, -OR^{11}, or C_1-C_{20}-alkyl bonded with the aryl ring;
each R^{11} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or -SiR^{12}_3, wherein R^{11} is optionally substituted by halogen, or two R^{11} radicals optionally bond to form a five- or six-membered ring;
each R^{12} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or two R^{12} radicals optionally bond to form a five- or six-membered ring;
each of E^1, E^2, and E^3 is independently carbon, nitrogen or phosphorus;
each u is independently 0 if E^1, E^2, and/or E^3 is nitrogen or phosphorus and is 1 if E^1, E^2, and/or E^3 is carbon;
each X is independently fluorine, chlorine, bromine, iodine, hydrogen, C_1-C_{20}-alkyl, C_2-C_{10}-alkenyl, C_6-C_{20}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, -NR^{18}_2, -OR^{18}, -SR^{18}, -SO_3R^{18}, -$OC(O)R^{18}$, -CN, -SCN, β-diketonate, -CO, -BF_4^-, -PF_6^- or bulky non-coordinating anions, and the radicals X can be bonded with one another;
each R^{18} is independently hydrogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{20}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or -SiR^{19}_3, wherein R^{18} can be substituted by halogen or nitrogen- or oxygen-containing groups and two R^{18} radicals optionally bond to form a five- or six-membered ring;
each R^{19} is independently hydrogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{20}-aryl or arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, wherein R^{19} can be substituted by halogen or nitrogen- or oxygen-containing groups or two R^{19} radicals optionally bond to form a five- or six-membered ring;
s is 1, 2, or 3;
D is a neutral donor; and
t is 0 to 2.

2. The supported catalyst system according to claim 1, wherein M* of formula (A) is Hf or Zr, each R^{1a}, R^{2a}, R^{3a}, and R^{4a} is a C_1 to C_{20} alkyl group and R^{7a} is –$CH_2SiR'_3$ or –$CH_2CR'_3$ where R' is C_1 to C_{20} alkyl or aryl.

3. The supported catalyst system according to claim 1, wherein for the catalyst represented by formula (B):

each of A and R^{14} is chlorine;

each of R^1 and R^2 is methyl;

each of R^3-R^5 is hydrogen;

each of R^7 and R^9 is methyl;

each of R^8 and R^{10}, and R^{15}, R^{16}, R^{17} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, -NR^{11}_2, -OR^{11}, halogen, -SiR^{12}_3 or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O, and S;

wherein R^7, R^8, R^9, R^{10}, R^{15}, R^{16}, and R^{17} are optionally substituted by halogen, -NR^{11}_2, -OR^{11} or -SiR^{12}_3; and

wherein R^7 optionally bonds with R^{10}, R^{10} optionally bonds with R^9, R^9 optionally bonds with R^8, R^{17} optionally bonds with R^{16}, and R^{16} optionally bonds with R^{15}, in each case to independently form a five-, six- or seven-membered carbocyclic or heterocyclic ring, the heterocyclic ring comprising at least one atom selected from the group consisting of N, P, O, and S;

R^{13} is independently a C_1-C_3-alkyl bonded with the aryl ring via a primary or secondary carbon atom;

each R^{11} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or -SiR^{12}_3, wherein R^{11} is optionally substituted by halogen, or two R^{11} radicals optionally bond to form a five- or six-membered ring;

each R^{12} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl or arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or two R^{12} radicals optionally bond to form a five- or six-membered ring;

each of E^1, E^2, and E^3 is carbon; and

each u is 1.

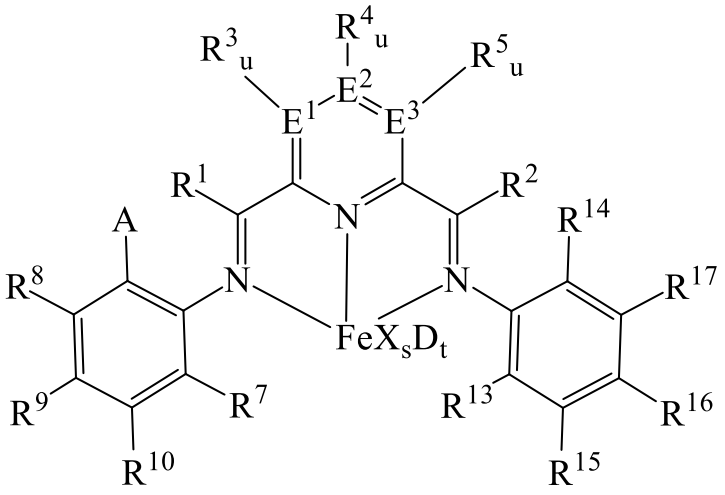
4. A supported catalyst system comprising:

a bridged group 4 metallocene catalyst;

an iron catalyst;

a support material; and

an activator; wherein the iron catalyst is represented by formula (B):



(B)

wherein:

A is chlorine, bromine, iodine, $-CF_3$ or $-OR^{11}$;

each of R^1 and R^2 is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O and S;

wherein each of R^1 and R^2 is optionally substituted by halogen, $-NR^{11}_2$, $-OR^{11}$ or $-SiR^{12}_3$;

wherein R^1 optionally bonds with R^3, and R^2 optionally bonds with R^5, in each case to independently form a five-, six- or seven-membered ring;

R^7 is a C_1-C_{20} alkyl;

each of R^3_u, R^4_u, R^5_u, R^8, R^9, R^{10}, R^{15}, R^{16}, and R^{17} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, $-NR^{11}_2$, $-OR^{11}$, halogen, $-SiR^{12}_3$ or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O, and S;

wherein R^3_u, R^4_u, R^5_u, R^7, R^8, R^9, R^{10}, R^{15}, R^{16}, and R^{17} are optionally substituted by halogen, $-NR^{11}_2$, $-OR^{11}$ or $-SiR^{12}_3$;

wherein R^3 optionally bonds with R^4, R^4 optionally bonds with R^5, R^7 optionally bonds with R^{10}, R^{10} optionally bonds with R^9, R^9 optionally bonds with R^8, R^{17} optionally bonds with R^{16}, and R^{16} optionally bonds with R^{15}, in each case to independently form a five-, six- or seven-membered carbocyclic or heterocyclic ring, the heterocyclic ring comprising at least one atom from the group consisting of N, P, O and S;

R^{13} is C_1-C_{20}-alkyl bonded with the aryl ring via a primary or secondary carbon atom;

R^{14} is chlorine, bromine, iodine, $-CF_3$, $-OR^{11}$, or C_1-C_{20}-alkyl bonded with the aryl ring;

each R^{11} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or -SiR^{12}_3, wherein R^{11} is optionally substituted by halogen, or two R^{11} radicals optionally bond to form a five- or six-membered ring;

each R^{12} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or two R^{12} radicals optionally bond to form a five- or six-membered ring;

each of E^1, E^2, and E^3 is independently carbon, nitrogen or phosphorus;

each u is independently 0 if E^1, E^2, and/or E^3 is nitrogen or phosphorus and is 1 if E^1, E^2, and/or E^3 is carbon;

each X is independently fluorine, chlorine, bromine, iodine, hydrogen, C_1-C_{20}-alkyl, C_2-C_{10}-alkenyl, C_6-C_{20}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, -NR^{18}_2, -OR^{18}, -SR^{18}, -SO_3R^{18}, -$OC(O)R^{18}$, -CN, -SCN, β-diketonate, -CO, -BF_4^-, -PF_6^- or bulky non-coordinating anions, and the radicals X can be bonded with one another;

each R^{18} is independently hydrogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{20}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or -SiR^{19}_3, wherein R^{18} can be substituted by halogen or nitrogen- or oxygen-containing groups and two R^{18} radicals optionally bond to form a five- or six-membered ring;

each R^{19} is independently hydrogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{20}-aryl or arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, wherein R^{19} can be substituted by halogen or nitrogen- or oxygen-containing groups or two R^{19} radicals optionally bond to form a five- or six-membered ring;

s is 1, 2, or 3;

D is a neutral donor; and

t is 0 to 2; and

wherein the bridged metallocene compound is one or more of:

Rac/meso-$Me_2Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac-$Me_2Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac/meso-$Ph_2Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac/meso-$PhMeSi(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac/meso-$(CH_2)_4Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac/meso-$(CH_2)_3Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; $Me(H)Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; $Ph(H)Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac/meso-$(biphenyl)_2Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac/meso-$(F\text{-}C_6H_4)_2Si(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac/meso-$Me_2Ge(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac-$Me_2Ge(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; rac/meso-$Ph_2Ge(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)_2HfMe_2$; $Me_2Si(Me_4Cp)(3\text{-}Me_3Si\text{-}CH_2\text{-}Cp)HfMe_2$; $Ph_2Si(Me_4Cp)(3\text{-}$

Me_3Si-CH_2-Cp)$HfMe_2$; $Me_2Ge(Me_4Cp)$(3-Me_3Si-CH_2-Cp)$HfMe_2$; $Ph_2Ge(Me_4Cp)$(3-Me_3Si-CH_2-Cp)$HfMe_2$; $PhMeSi(Me_4Cp)$(3-Me_3Si-CH_2-Cp)$HfMe_2$; $(CH_2)_3Si(Me_4Cp)$(3-Me_3Si-CH_2-Cp)$HfMe_2$; $(CH_2)_4Si(Me_4Cp)$(3-Me_3Si-CH_2-Cp)$HfMe_2$; $Et_2Si(Me_4Cp)$(3-Me_3Si-CH_2-Cp)$HfMe_2$; rac/meso-Me_2Si(3-nPrCp)$_2HfMe_2$; rac/meso-Ph_2Si(3-nPrCp)$_2HfMe_2$; rac/meso-PhMeSi(3-nPrCp)$_2HfMe_2$; rac/meso-$(CH_2)_4Si$(3-nPrCp)$_2HfMe_2$; rac/meso-$(CH_2)_3Si$(3-nPrCp)$_2HfMe_2$; Me(H)Si(3-nPrCp)$_2HfMe_2$; Ph(H)Si(3-nPrCp)$_2HfMe_2$; rac/meso-(biphenyl)$_2Si$(3-nPrCp)$_2HfMe_2$; rac/meso-(F-$C_6H_4)_2Si$(3-nPrCp)$_2HfMe_2$; rac/meso-Me_2Ge(3-nPrCp)$_2HfMe_2$; rac/meso-Ph_2Ge(3-nPrCp)$_2HfMe_2$; rac/meso-Me_2Si(3-nBuCp)$_2HfMe_2$; rac/meso-Ph_2Si(3-nBuCp)$_2HfMe_2$; rac/meso-PhMeSi(3-nBuCp)$_2HfMe_2$; rac/meso-$(CH_2)_4Si$(3-nBuCp)$_2HfMe_2$; rac/meso-$(CH_2)_3Si$(3-nBuCp)$_2HfMe_2$; Me(H)Si(3-nBuCp)$_2HfMe_2$; Ph(H)Si(3-nBuCp)$_2HfMe_2$; rac/meso-(biphenyl)$_2Si$(3-nBuCp)$_2HfMe_2$; rac/meso-(F-$C_6H_4)_2Si$(3-nBuCp)$_2HfMe_2$; rac/meso-Me_2Ge(3-nBuCp)$_2HfMe_2$; rac/meso-Ph_2Ge(3-nBuCp)$_2HfMe_2$; $Me_2Si(Me_4Cp)$(3-nPrCp)$HfMe_2$; $Ph_2Si(Me_4Cp)$(3-nPrCp)$HfMe_2$; $Me_2Ge(Me_4Cp)$(3-nPrCp)$HfMe_2$; $Ph_2Ge(Me_4Cp)$(3-nPrCp)$HfMe_2$; $PhMeSi(Me_4Cp)$(3-nPrCp)$HfMe_2$; $(CH_2)_3Si(Me_4Cp)$(3-nPrCp)$HfMe_2$; $(CH_2)_4Si(Me_4Cp)$(3-nPrCp)$HfMe_2$; $Et_2Si(Me_4Cp)$(3-nPrCp)$HfMe_2$; $Me_2Si(Me_4Cp)$(3-nBuCp)$HfMe_2$; $Ph_2Si(Me_4Cp)$(3-nBuCp)$HfMe_2$; $Me_2Ge(Me_4Cp)$(3-nBuCp)$HfMe_2$; $Ph_2Ge(Me_4Cp)$(3-nBuCp)$HfMe_2$; $PhMeSi(Me_4Cp)$(3-nBuCp)$HfMe_2$; $(CH_2)_3Si(Me_4Cp)$(3-nBuCp)$HfMe_2$; $(CH_2)_4Si(Me_4Cp)$(3-nBuCp)$HfMe_2$; $Et_2Si(Me_4Cp)$(3-nBuCp)$HfMe_2$; Me_2Si(3-CH_2-$SiMe_3$-Cp)$_2HfMe_2$; Ph_2Si(3-CH_2-$SiMe_3$-Cp)$_2HfMe_2$; PhMeSi(3-CH_2-SiMe3-Cp)$_2HfMe_2$; $SiMe_2(Me_4Cp)$(3-nPrCp)$HfMe_2$; $SiPh_2$(Me4Cp)(3-nPrCp)$HfMe_2$; $Me_2Ge(Me_4Cp)$(3-nPrCp)$HfMe_2$; $Ph_2Ge(Me_4Cp)$(3-nPrCp)$HfMe_2$; $PhMeSi(Me_4Cp)$(3-nPrCp)$HfMe_2$; Et2Si(Me4Cp)(3-nPrCp)$HfMe_2$; $SiMe_2$(EtMe_3Cp)(3-nPrCp)$HfMe_2$; $SiMe_2$(Me4Cp)(3-nBuCp)$HfMe_2$; $SiPh_2(Me_4Cp)$(3-nBuCp)$HfMe_2$; $Me_2Ge(Me_4Cp)$(3-nBuCp)$HfMe_2$; $Ph_2Ge(Me_4Cp)$(3-nBuCp)$HfMe_2$; $PhMeSi(Me_4Cp)$(3-nBuCp)$HfMe_2$; Et_2Si(Me4Cp)(3-nBuCp)$HfMe_2$; $SiMe_2$(EtMe_3Cp)(3-nBuCp)$HfMe_2$; $SiMe_2$(Me4Cp)(3-CH2-$SiMe_3$-Cp)$HfMe_2$; $SiPh_2(Me_4Cp)$(3-CH_2-$SiMe_3$-Cp)$HfMe_2$; $Me_2Ge(Me_4Cp)$(3-CH_2-$SiMe_3$-Cp)$HfMe_2$; $Ph_2Ge(Me_4Cp)$(3-CH2-$SiMe_3$-Cp)$HfMe_2$; $PhMeSi(Me_4Cp)$(3-CH2-$SiMe_3$-Cp)$HfMe_2$; $Et_2Si(Me_4Cp)$(3-CH2-$SiMe_3$-Cp)$HfMe_2$; $SiMe_2$(EtMe_3Cp)(3-CH2-$SiMe_3$-Cp)$HfMe_2$; $SiMe_2(Me_4Cp)$(3-CH_2-SiPhMe_2-Cp)$HfMe_2$; $SiPh_2(Me_4Cp)$(3-CH_2-SiPhMe_2-Cp)$HfMe_2$; $Me_2Ge(Me_4Cp)$(3-CH2-SiPhMe_2)$HfMe_2$; $Ph_2Ge(Me_4Cp)$(3-CH_2-SiPhMe_2)$HfMe_2$; $PhMeSi(Me_4Cp)$(3-CH2-SiPhMe_2-Cp)$HfMe_2$; $Et_2Si(Me_4Cp)$(3-CH_2-SiPhMe_2-Cp)$HfMe_2$; $SiMe_2$(EtMe_3Cp)(3-CH_2-$SiPh_3$-Cp)$HfMe_2$; $SiMe_2(Me_4Cp)$(3-CH_2-$SiPh_3$-Cp)$HfMe_2$; $SiPh_2(Me_4Cp)$(3-CH_2-$SiPh_3$-Cp)$HfMe_2$; $Me_2Ge(Me_4Cp)$(3-CH_2-$SiPh_3$)$HfMe_2$; $Ph_2Ge(Me_4Cp)$(3-CH_2-$SiPh_3$)$HfMe_2$;

$PhMeSi(Me_4Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; $Et_2Si(Me4Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; $SiMe_2(EtMe_3Cp)(3\text{-}CH_2\text{-}SiPh_3\text{-}Cp)HfMe_2$; and the versions thereof where the Me_2 is replaced with Et_2, Cl_2, Br_2, I_2, or Ph_2.

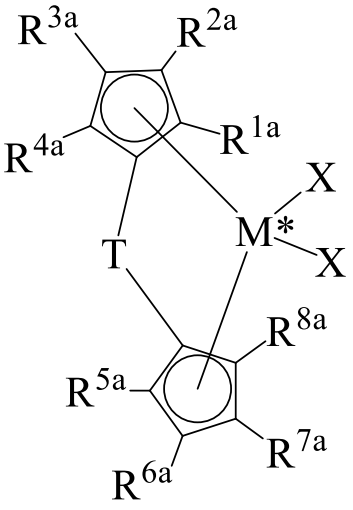
5. A supported catalyst system comprising:

a bridged group 4 metallocene catalyst;

an iron catalyst;

a support material; and

an activator; wherein the bridged group 4 metallocene compound is represented by the formula (A):



(A)

where

M* is a group 4 metal;

each of R^{1a}, R^{2a}, and R^{4a} is independently hydrogen, alkoxide or C_1 to C_{40} substituted or unsubstituted hydrocarbyl;

R^{3a} is independently hydrogen, a substituted C_1 to C_{12} hydrocarbyl group, an unsubstituted C_1 to C_{12} hydrocarbyl group, or is $-R^{20}\text{-}SiR'_3$ or is $-R^{20}\text{-}CR'_3$ 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, provided that at least one R' is not H, alternatively 2 R' are not H, alternatively 3 R' are not H;

each of R^{5a}, R^{6a}, and R^{8a} is independently hydrogen, halide, alkoxide or C_1 to C_{40} substituted or unsubstituted hydrocarbyl;

R^{7a} is $-R^{9a}\text{-}SiR'_3$ or $-R^{9a}\text{-}CR'_3$ where R^{9a} is C_1 to C_4 hydrocarbyl, and each R' is independently C_1 to C_{20} substituted or unsubstituted hydrocarbyl, and at least one R' is H;

T is a bridging group; and

each X is independently a univalent anionic ligand, a diene ligand, an alkylidene ligand, or two Xs are joined to form a metallocyclic ring; and

wherein the iron complex is at least one of: bis(2,6-[1-(2,6-dimethylphenylimino)ethyl])pyridineiron dichloride, bis(2,6-[1-(2,4,6-trimethylphenylimino)ethyl)])pyridineiron dichloride, bis(2,6-[1-(2,6-dimethylphenylimino)ethyl]- ethyl])pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2,4-dichloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-bromo-4,6-dimethylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-bromo-4,6-dimethylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride, and the dibromides or tribromides thereof where dichloride in the list above is replaced with dibromide or tribromide.

6. The supported catalyst system of claim 1, wherein the support material has a specific surface area in the range of from 10 m^2/g to 700 m^2/g and an average particle diameter in the range of from 10 μm to 500 μm.

7. The supported catalyst system of claim 1, wherein the support material is selected from the group consisting of silica, alumina, silica-alumina, and combinations thereof.

8. The supported catalyst system of claim 1, wherein the support material is a silica aluminate treated with fluoride or sulfate anions and is activated with an aluminum alkyl and is substantially void of alumoxane and non-coordinating anion activators.

9. The supported catalyst system of claim 8, wherein the support material has a fluorine concentration in the range of 0.6 to 3.5 wt%, based upon the weight of the support material.

10. The supported catalyst system of claim 1, wherein the activator comprises alumoxane and/or a non-coordinating anion.

11. The supported catalyst system of claim 1, wherein the bridged metallocene compound represented by formula A is present in the catalyst system as at least two isomers.

12. The supported catalyst system of claim 1, wherein the activator comprises one or more of: N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, $[Me_3NH^+][B(C_6F_5)^{4-}]$, 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl) pyrrolidinium; 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl) pyrrolidinium, sodium tetrakis(pentafluorophenyl)borate, potassium tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridinium, sodium tetrakis(perfluorophenyl)aluminate, potassium tetrakis(pentafluorophenyl), and N,N-dimethylanilinium tetrakis(perfluorophenyl)aluminate.

13. A process for polymerization of olefin monomers comprising contacting one or more monomers with the supported catalyst system of claim 1.

14. A process to produce linear low density polyethylene comprising contacting one or more monomers with the supported catalyst system of claim 1.

15. A process for the production of an ethylene alpha-olefin copolymer comprising: polymerizing ethylene and at least one C_3-C_{20} alpha-olefin by contacting the ethylene and the at least one C_3-C_{20} alpha-olefin with the supported catalyst of claim 1 in at least one gas phase reactor at a reactor pressure of from 0.7 to 70 bar and a reactor temperature of from 20°C to 150°C to form an ethylene alpha-olefin copolymer.

16. A process for the production of an ethylene alpha-olefin copolymer comprising: polymerizing ethylene and at least one C_3-C_{20} alpha-olefin by contacting the ethylene and the at least one C_3-C_{20} alpha-olefin with the supported catalyst of claim 1 in at least one slurry phase

reactor at a reactor pressure of from 0.7 to 70 bar and a reactor temperature of from 20°C to 150°C to form an ethylene alpha-olefin copolymer.

17. The supported catalyst system of claim 3, wherein M* of formula (A) is Hf or Zr, each R^{1a}, R^{2a}, R^{3a}, and R^{4a} is a C_1 to C_{20} alkyl group and R^{7a} is $–CH_2SiR'_3$ or $–CH_2CR'_3$ where R' is C_1 to C_{20} alkyl or aryl.

18. The supported catalyst system of claim 4, wherein the iron catalyst is at least one of: bis(2,6-[1-(2,6-dimethylphenylimino)ethyl])pyridineiron dichloride, bis(2,6-[1-(2,4,6-trimethylphenylimino)ethyl)])pyridineiron dichloride, bis(2,6-[1-(2,6-dimethylphenylimino)ethyl]-ethyl])pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2,4-dichloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-bromo-4,6-dimethylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-bromo-4,6-dimethylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride and 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride and the dibromides or tribromides thereof where dichloride in the list above is replaced with dibromide or tribromide.

19. A process for polymerization of olefin monomers comprising contacting one or more monomers with a supported catalyst system of claim 17.

20. A process for polymerization of olefin monomers comprising contacting one or more monomers with a supported catalyst system of claim 18.

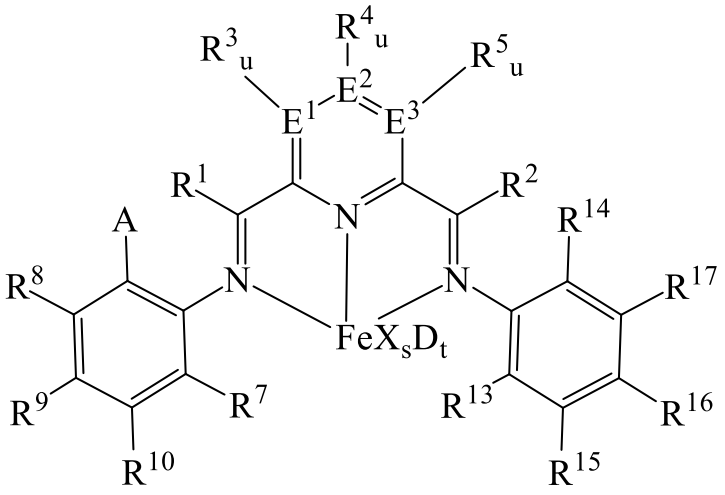
21. A supported catalyst system comprising:
a bridged group 4 metallocene catalyst;

an iron catalyst;

a support material; and

an activator; wherein the bridged group 4 metallocene compound is one or more of: $SiMe_2$(2-Me,3-n-Pr-Ind)$_2HfMe_2$; $SiPh_2$(2-Me,3-n-Pr-Ind)$_2HfMe_2$; $GeMe_2$(2-Me,3-n-Pr-Ind)$_2HfMe_2$; $GePh_2$(2-Me,3-n-Pr-Ind)$_2HfMe_2$; SiPhMe(2-Me,3-n-Pr-Ind)$_2HfMe_2$; Et_2Si(2-Me,3- n-Pr-Ind)$_2HfMe_2$; $SiMe_2$(2-Me,3-n-Bu-Ind)$_2HfMe_2$; $SiPh_2$(2-Me,3-n-Bu-Ind)$_2HfMe_2$; $GeMe_2$(2-Me,3-n-Bu-Ind)$_2HfMe_2$; $GePh_2$(2-Me,3-n-Bu-Ind)$_2HfMe_2$; SiPhMe(2-Me,3-n-Bu-Ind)$_2HfMe_2$; Et_2Si(2-Me,3-n-Bu-Ind)$_2HfMe_2$; $SiMe_2$(2-Me,3-CH_2-$SiMe_3$-Ind)$_2HfMe_2$; $SiPh_2$(2-Me,3-CH_2-$SiMe_3$-Ind)$_2HfMe_2$; $GeMe_2$(2-Me,3-CH_2-$SiMe_3$-Ind)$_2HfMe_2$; $GePh_2$(2-Me,3-CH_2-$SiMe_3$-Ind)$_2HfMe_2$; SiPhMe(2-Me,3-CH_2-$SiMe_3$-Ind)$_2HfMe_2$; Et_2Si(2-Me,3-CH_2-$SiMe_3$-Ind)$_2HfMe_2$; $SiMe_2$(2-Me,3-CH_2-SiPhMe$_2$-Ind)$_2HfMe_2$; $SiPh_2$(2-Me,3-CH_2-SiPhMe$_2$-Ind)$_2HfMe_2$; $GeMe_2$(2-Me,3-CH_2-SiPhMe$_2$-Ind)$_2HfMe_2$; $GePh_2$(2-Me,3-CH_2-SiPhMe$_2$-Ind)$_2HfMe_2$; SiPhMe(2-Me,3-CH_2-SiPhMe$_2$-Ind)$_2HfMe_2$; Et_2Si(2-Me,3-CH_2-SiPhMe$_2$-Ind)$_2HfMe_2$; $SiMe_2$(2-Me,3-CH_2-$SiPh_3$-Ind)$_2HfMe_2$; $SiPh_2$(2-Me,3-CH_2-$SiPh_3$-Ind)$_2HfMe_2$; $GeMe_2$(2-Me,3-CH_2-$SiPh_3$-Ind)$_2HfMe_2$; $GePh_2$(2-Me,3-CH_2-$SiPh_3$-Ind)$_2HfMe_2$; SiPhMe(2-Me,3-CH_2-$SiPh_3$-Ind)$_2HfMe_2$; Et_2Si(2-Me,3-CH_2-$SiPh_3$-Ind)$_2HfMe_2$, and the versions thereof where the Me_2 is replaced with Et_2, Cl_2, Br_2, I_2, or Ph_2;

and the iron catalyst is represented by formula (B):



(B)

wherein:

A is chlorine, bromine, iodine, $-CF_3$ or $-OR^{11}$;

each of R^1 and R^2 is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms,

or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O and S;

wherein each of R^1 and R^2 is optionally substituted by halogen, $-NR^{11}_2$, $-OR^{11}$ or $-SiR^{12}_3$;

wherein R^1 optionally bonds with R^3, and R^2 optionally bonds with R^5, in each case to independently form a five-, six- or seven-membered ring;

R^7 is a C_1-C_{20} alkyl;

each of R^3_u, R^4_u, R^5_u, R^8, R^9, R^{10}, R^{15}, R^{16}, and R^{17} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, $-NR^{11}_2$, $-OR^{11}$, halogen, $-SiR^{12}_3$ or five-, six- or seven-membered heterocyclyl comprising at least one atom selected from the group consisting of N, P, O, and S;

wherein R^3_u, R^4_u, R^5_u, R^7, R^8, R^9, R^{10}, R^{15}, R^{16}, and R^{17} are optionally substituted by halogen, $-NR^{11}_2$, $-OR^{11}$ or $-SiR^{12}_3$;

wherein R^3 optionally bonds with R^4, R^4 optionally bonds with R^5, R^7 optionally bonds with R^{10}, R^{10} optionally bonds with R^9, R^9 optionally bonds with R^8, R^{17} optionally bonds with R^{16}, and R^{16} optionally bonds with R^{15}, in each case to independently form a five-, six- or seven-membered carbocyclic or heterocyclic ring, the heterocyclic ring comprising at least one atom from the group consisting of N, P, O and S;

R^{13} is C_1-C_{20}-alkyl bonded with the aryl ring via a primary or secondary carbon atom;

R^{14} is chlorine, bromine, iodine, $-CF_3$ or $-OR^{11}$, or C_1-C_{20}-alkyl bonded with the aryl ring;

each R^{11} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or $-SiR^{12}_3$, wherein R^{11} is optionally substituted by halogen, or two R^{11} radicals optionally bond to form a five- or six-membered ring;

each R^{12} is independently hydrogen, C_1-C_{22}-alkyl, C_2-C_{22}-alkenyl, C_6-C_{22}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or two R^{12} radicals optionally bond to form a five- or six-membered ring;

each of E^1, E^2, and E^3 is independently carbon, nitrogen or phosphorus;

each u is independently 0 if E^1, E^2, and/or E^3 is nitrogen or phosphorus and is 1 if E^1, E^2, and/or E^3 is carbon;

each X is independently fluorine, chlorine, bromine, iodine, hydrogen, C_1-C_{20}-alkyl, C_2-C_{10}-alkenyl, C_6-C_{20}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, $-NR^{18}_2$, $-OR^{18}$, $-SR^{18}$, $-SO_3R^{18}$, $-OC(O)R^{18}$, -CN, -SCN,

β-diketonate, -CO, $-BF_4^-$, $-PF_6^-$ or bulky non-coordinating anions, and the radicals X can be bonded with one another;

each R^{18} is independently hydrogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{20}-aryl, arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, or $-SiR^{19}_3$, wherein R^{18} can be substituted by halogen or nitrogen- or oxygen-containing groups and two R^{18} radicals optionally bond to form a five- or six-membered ring;

each R^{19} is independently hydrogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{20}-aryl or arylalkyl where alkyl has from 1 to 10 carbon atoms and aryl has from 6 to 20 carbon atoms, wherein R^{19} can be substituted by halogen or nitrogen- or oxygen-containing groups or two R^{19} radicals optionally bond to form a five- or six-membered ring;

s is 1, 2, or 3;

D is a neutral donor; and

t is 0 to 2.

22. The supported catalyst system of claim 21, wherein the iron catalyst is at least one of: bis(2,6-[1-(2,6-dimethylphenylimino)ethyl])pyridineiron dichloride, bis(2,6-[1-(2,4,6-trimethylphenylimino)ethyl)])pyridineiron dichloride, bis(2,6-[1-(2,6-dimethylphenylimino)ethyl]- ethyl])pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2,4-dichloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-chloro-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-bromo-4,6-dimethylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-bromo-4,6-dimethylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,6-dimethylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride, 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride and 2-[1-(2,6-diisopropylphenylimino)ethyl]-6-[1-(2-bromo-6-methylphenylimino)ethyl]pyridineiron dichloride and the dibromides or tribromides thereof where dichloride in the list above is replaced with dibromide or tribromide.