CLAIMS

What is claimed is:

1. A catalyst system comprising:

   a) a transition metal compound;

   b) a pyrrole compound comprising independently-selected C_1 to C_{18} organyl groups at the 2- and 5-positions, wherein at least one of the organyl group alpha-carbon atoms attached to the 2- and 5-positions of the pyrrole compound is a secondary carbon atom; and

   c) a metal alkyl.

2. A catalyst system comprising:

   a) a chromium compound;

   b) a pyrrole compound comprising independently-selected C_1 to C_{18} hydrocarbyl groups at the 2- and 5-positions, wherein at least one of the hydrocarbyl group alpha-carbon atoms attached to the 2- and 5-positions of the pyrrole compound is a secondary carbon atom; and

   c) a metal alkyl.

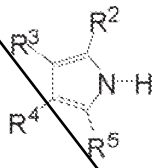
3. A catalyst system according to any one of claims 1-2, wherein the pyrrole compound has independently-selected C_2 to C_{18} alkyl groups at the 2- and 5-positions and wherein the hydrocarbyl group alpha-carbon atoms attached to the 2- and 5-positions of the pyrrole compound are secondary carbon atoms.

4. A catalyst system according to any one of claims 1-3, wherein the pyrrole compound has alkyl groups at the 2- and 5-positions selected independently from methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, or n-octyl.

5. A catalyst system according to any one of claims 1-4, wherein the pyrrole compound is a 2,5-disubstituted pyrrole.

6. A catalyst system according to any one of claims 1-2, wherein the pyrrole compound is 2,5-diethyl pyrrole.

7. A catalyst system according to any one of claims 1-3, wherein the pyrrole has the formula P1:

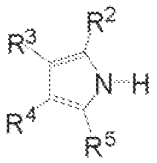


(P1), wherein

a) R^2 and R^5 are selected independently from a C_1 to C_{18} organyl group, wherein at least one the R^2 and R^5 organyl group alpha-carbon atoms attached to the pyrrole ring is a secondary carbon atom; and

b) R^3 and R^4 are selected independently from hydrogen, a C_1 to C_{18} organyl group, a C_1 to C_{18} organyl group comprising inert functional groups, a C_1 to C_{18} hydrocarbyl group, and a C_1 to C_{18} alkyl group.

8. A catalyst system according to any one of claims 1-3, wherein the pyrrole has the formula P1:



(P1), wherein

a) R^2 and R^5 are selected independently from a C_2 to C_{18} organyl group, wherein at least one the R^2 and R^5 organyl group alpha-carbon atoms attached to the pyrrole ring is a secondary carbon atom; and

b) R^3 and R^4 are selected independently from hydrogen, a C_1 to C_{18} organyl group, a C_1 to C_{18} organyl group comprising inert functional groups, a C_1 to C_{18} hydrocarbyl group, and a C_1 to C_{18} alkyl group

9. A catalyst system according to claim 7, wherein each of R^2 and R^5 are selected independently from a C_2 to C_{18} hydrocarbyl group.

10. A catalyst system according to any one of claims 7-9, wherein R^3 and R^4 are hydrogen.

11. A catalyst system according to any one of claims 7-8, wherein R^2 and R^5 are selected independently from an ethyl group, an n-propyl group, an n-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, or an n-octyl group.

12. A catalyst system according to any one of claims 7-8 and 11, wherein R^3 and R^4 are hydrogen and R^2 and R^5 are selected independently from an ethyl group, an n-propyl group, an n-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, or an n-octyl group.

13. A catalyst system according to any one of claims 1-2, wherein the pyrrole is selected from 2,5-diethylpyrrrole, 2,5-dipropylpyrrole, 2,5-dibutylpyrrole, 2,5-hexylpyrrole, 2,5-diheptylpyrrole, 2,5-dioctylpyrrole, 2,3,5-trimethylpyrrole, 2,3,5-triethylpyrrrole, 2,3,5-tributylpyrrrole, 2,3,5-trihexylpyrrrole, 2,3,5-triheptylpyrrrole, 2,3,5-trioctylpyrrrole, 2,3,4,5-tetramethylpyrrole, 2,3,4,5-tetraethylpyrrole, 2,3,4,5-tetrabutylpyrrole, 2,3,4,5-tetrahexylpyrrole, 2,5-bis(2',2',2'-trifluoroethyl) pyrrole, 2,5-bis(2'-methoxymethyl) pyrrole, or any combination thereof.

14. A catalyst system according to any one of claims 1-13, wherein the transition metal compound comprises an inorganic or organometallic compound of a group 5, 6, 7, 8, 9, 10, or 11 metal, or any combination thereof.

15. A catalyst system according to any one of claims 1-13, wherein the transition metal compound is a chromium (II) or chromium (III) halide, 1,3-diketonate, or carboxylate.

16. The catalyst system according to any one of claims 1-13, transition metal compound is a chromium(II) or chromium(III) carboxylate wherein each carboxylate is a C_4 to C_{19} carboxylate

17. A catalyst system according to any one of claims 1-13, wherein the transition metal compound is selected from chromium (III) 2-ethylhexanoate, chromium (III) octanoate, chromium(III) 2,2,6,6,-tetramethylheptanedionate, chromium(III) naphthenate, chromium(III) acetate, chromium(III) propionate, chromium(III) butyrate, chromium(III) neopentanoate, chromium(III) laurate, chromium(III) stearate, chromium(III) oxalate, chromium(II) bis(2-ethylhexanoate), chromium(II) acetate, chromium(II) propionate, chromium(II) butyrate, chromium(II) neopentanoate, chromium(II) laurate, chromium(II) stearate, chromium(II) oxalate, or any combination thereof.

18. A catalyst system according to any one of claims 1-17, wherein the metal alkyl comprises a group 1, 2, 11, 12, 13, or 14 metal alkyl compound.

19. A catalyst system according to any one of claims 1-18, further comprising a halogen-containing compound selected from a metal halide, and alkyl metal halide, or an organic halide.

20. The catalyst system according to claim 1, wherein the transition metal compound is a chromium is a chromium(II) or chromium(III) carboxylate wherein each

carboxylate is a C_4 to C_{19} carboxylate; the pyrrole compound is a 2,5-disubstituted pyrrole and the substituents at the 2- and 5-positions selected independently from ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, or n-octyl; and the metal alkyl comprises a mixture of a triethylaluminum and a diethylaluminum chloride

21. An oligomerization process comprising:

a) contacting a feedstock olefin with the catalyst system of any one of claim 1-19; and

b) oligomerizing the olefin under oligomerization conditions to form an oligomerization product.

22. The oligomerization process of claim 20, wherein the feedstock olefin is ethylene the oligomerization product comprises 1-hexene, the transition metal compound is a chromium(II) or chromium(III) carboxylate wherein each carboxylate is a C_4 to C_{19} carboxylate; the pyrrole compound is a 2,5-disubstituted pyrrole and the substituents at the 2- and 5-positions selected independently from ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, or n-octyl; and the metal alkyl comprises a mixture of a triethylaluminum and a diethylaluminum chloride.

23. The oligomerization process of claim 22, wherein the process provides a higher selectivity to 1-hexene than the process using 2,5-dimethylpyrrole as the pyrrole compound.

24. The oligomerization process of claim 22, wherein the process provides a higher purity 1-hexene product than the process using 2,5-dimethylpyrrole as the pyrrole compound.

25. A process for preparing a catalyst system of any one of claim 1-20, comprising contacting:

a) the transition metal compound;

b) the pyrrole compound; and

c) the metal alkyl.

26. The process of claim 25, wherein the transition metal compound, the pyrrole, and the metal alkyl are contacted in the presence of an unsaturated compound.

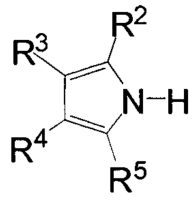
27. The process of claim 26, wherein the unsaturated compound is a C_6 to C_{18} aromatic compound.

Claims

1. A catalyst system comprising:

a) a chromium compound;

b) a pyrrole compound having the formula



(P1),

wherein

i) R^2 and R^5 are selected independently from a C_2 to Cg hydrocarbyl group, wherein the R^2 and R^5 hydrocarbyl group alpha-carbon atoms attached to the pyrrole ring are secondary carbon atoms; and

ii) R^3 and R^4 are hydrogen; and

c) a metal alkyl.

2. A catalyst system according to claim 1, wherein R^2 and R^5 are selected independently from C_2 to C_8 alkyl groups.

3. A catalyst system according to claim 1, wherein R^2 and R^5 are selected independently from an ethyl group, an n-propyl group, an n-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, or an n-octyl group.

4. A catalyst system according to claim 1, wherein the pyrrole compound is selected from 2,5-diethylpyrrole, 2,5-dipropylpyrrole, 2,5-dibutylpyrrole, 2,5-hexylpyrrole, 2,5-diheptylpyrrole or 2,5-dioctylpyrrole.

5. A catalyst system according to claim 1, wherein the pyrrole compound is 2,5-diethyl pyrrole.

6. A catalyst system according to any one of claims 1-5, wherein the chromium compound is a chromium (II) or chromium (III) halide, 1,3-diketonate, or carboxylate.

7. A catalyst system according to any one of claims 1-5, wherein the chromium compound is selected from chromium (III) 2-ethylhexanoate, chromium (III) octanoate, chromium(III) 2,2,6,6, -tetramethylheptanedionate, chromium(III) naphthenate, chromium(III) acetate, chromium (III) propionate, chromium (III) butyrate, chromium(III) neopentanoate, chromium (III) laurate, chromium (III) stearate, chromium (III) oxalate, chromium(II) bis(2-ethylhexanoate), chromium(II) acetate, chromium(II) propionate, chromium(II) butyrate, chromium(II) neopentanoate, chromium(II) laurate, chromium(II) stearate, chromium(II) oxalate, or any combination thereof.

8. A catalyst system according to any one of claims 1-7, wherein the metal alkyl comprises a group 1, 2, 11, 12, 13, or 14 metal alkyl compound.

9. A catalyst system according to any one of claims 1-8, further comprising a halogen-containing compound selected from a metal halide, and alkyl metal halide, or an organic halide.

10. The catalyst system according to claim 1, wherein the chromium compound is a chromium(II) or chromium(III) carboxylate wherein each carboxylate is a C_4 to C_{19} carboxylate; R^2 and R^5 are selected independently from an ethyl group, an n-propyl group, an n-butyl group, an n-pentyl group , an n-hexyl group, an n-heptyl group, or an n-octyl group; and the metal alkyl comprises a mixture of a triethylaluminum and a diethylalumimum chloride.

11. An oligomerization process comprising:

a) contacting a feedstock olefin with the catalyst system of any one of claim 1-10; and
b) oligomerizing the olefin under oligomerization conditions to form an oligomerization product.

12. The oligomerization process of claim 11, wherein the feedstock olefin is ethylene; the oligomerization product comprises 1-hexene; the chromium compound is a chromium(II) or chromium(III) carboxylate wherein each carboxylate is a C_4 to C_{19} carboxylate; R^2 and R^5 are selected independently from an ethyl group, an n-propyl group, an n-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, or an n-octyl group; and the metal alkyl comprises a mixture of a triethylaluminum and a diethylaluminum chloride.

13. A process for preparing a catalyst system of any one of claim 1-10, comprising contacting:
a) the chromium compound;
b) the pyrrole compound; and
c) the metal alkyl.

14. The process of claim 13, wherein the chromium compound, the pyrrole, and the metal alkyl are contacted in the presence of an unsaturated compound.

15. The process of claim 14, wherein the unsaturated compound is a C_6 to C_{18} aromatic compound