[0033] A modifier can be present in the system, selected from (but not limited to) ammonium or phosphonium salts of the type $[H_4E]X$, $[H_3ER]X$, $[H_2ER_2]X$, $[HER_3]X$, or $[ER_4]X$ wherein E is N or P, X is Cl, Br or I, and R is alkyl, cycloalkyl, acyl, aryl, alkenyl, alkynyl, preferably C_1-C_{22}-alkyl, C_3-C_{10}-cycloalkyl, C_1-C_{22}-acyl, C_6-C_{30}-aryl, C_2-C_{22}-alkenyl, C_2-C_{22}-alkynyl, and the like. For example, dodecyltrimethylammonium chloride can be used, or ~~triphenyphosphonium~~ tetraphenylphosphonium chloride.

[0034] Preferably, R_1, R_2, R_3, R_4, and R_5 are selected from chloro, amino, trimethylsilyl, methyl, ethyl, isopropyl, tert-butyl, phenyl, benzyl, tolyl, and xylyl.

[0035] More preferably, the PNPNH compound is selected from $(Ph)_2$P-N(i-Pr)-P(Ph)-N(i-Pr)-H, $(Ph)_2$P-N(i-Pr)-P(Ph)-N(Ph)-H, $(Ph)_2$P-N(i-Pr)-P(Ph)-N(tert-butyl)-H and $(Ph)_2$P-N(i-Pr)-P(Ph)-N(CH(CH_3)(Ph))-H.

[0036] Preferably, metalating in step (ii) is achieved by adding an organometallic compound, a base, sodium metal, or potassium metal in an amount equivalent to or in excess of the molar concentration of the PNPNH compound into the solution obtained in step (i).

[0037] More preferred, metalation is achieved by adding n-butyl lithium, sec-butyl lithium, tert-butyl lithium, sodium cyclopentadienide, sodium hydride, sodium amide, alkyl- or aryl magnesium halides (Grignard reagents), sodium bis(trimethylsilyl) amide, dialkylmagnesium, diarylmagnesium, trialkylaluminium, dialkylzinc, sodium metal, or potassium metal, preferably n-butyllithium.

[0038] Finally, metalated compounds, obtainable by a method above, are described.

[0039] As used herein, the term PNPNH is to be understood to represent the general structure R_1R_2P-N(R_3)-P(R_4)-N(R_5)-H.

[0040] The metalated ligand disclosed herein may be abbreviated by ñPNPN-M,ò with M being the metal used for metalation. This formula should be understood by a skilled person to comprise any compounds, such as $[PNPN\text{-}M]_2$, $]PNPN]_2M$, PNPNMR or PNPNMRR with R being any suitable alkyl or aryl substituent, clearly depending on the chemical requirements of the metalation reagent used. For example, metalation with lithium would result in a metalated ligand having the formula $[PNPNLi]_2$, or the use of chromium would result in a compound of $[PNPN]_2Cr$, or the use of dialkyl zinc would result in a structure of PNPNM alkyl.

[0041] As is to be understood, any cyclic derivative of the PNPNH compound can be utilized, wherein at least one of the P or N atoms of the PNPN-unit is a ring member, or any cyclic derivative wherein at least one of the P or N atoms of the PNPN-H structure is a member of a ring system, the ring system being formed from one or more constituent

CLAIMS

What is claimed is:

1. A process for oligomerization of ethylene, comprising contacting a catalyst composition with a gas phase of ethylene under conditions effective to oligomerize the ethylene, wherein the catalyst composition comprises

(a) a chromium compound,

(b) a metalated PNPNH compound, wherein the PNPNH compound is of the formula

$$R_1R_2P\text{-}N(R_3)\text{-}P(R_4)\text{-}N(R_5)\text{-}H$$

wherein R_1, R_2, R_3, R_4 and R_5 are independently selected from halogen, amino, trimethylsilyl, C_1-C_{10}-alkyl, substituted C_1-C_{10}-alkyl, C_6-C_{20}-aryl and substituted C_6-C_{20}-aryl, or any cyclic derivative wherein at least one of the P or N atoms of the PNPN-H structure is a member of a ring system, the ring system being formed from one or more constituent compounds of the PNPNH-structure by substitution, and

(c) an activator or cocatalyst~~.~~, and

~~2.~~ (d) ~~The catalyst composition of claim 1, further comprising~~ an ammonium or phosphonium salt of the formula $[H_4E]X$, $[H_3ER]X$, $[H_2ER_2]X$, $[HER_3]X$, or $[ER_4]X$ wherein E is N or P, X is Cl, Br or I, and each R is independently C_1-C_{22}-alkyl, C_3-C_{10}-cycloalkyl, C_1-C_{22}-acyl, C_6-C_{30}-aryl, C_2-C_{22}-alkenyl, or C_2-C_{22}-alkynyl~~.~~, preferably dodecyltrimethylammonium chloride or tetraphenylphosphonium chloride.

~~3.~~2. The process according to claim 1, wherein the oligomerization is carried out a pressure of 1 to 200 bar, preferably 10 to 50 bar.

~~4.~~3. The process according to claim 1 or 2, wherein the oligomerization is carried out at a temperature of from 10 to 200°C, preferably 20 to 100°C.

~~5.~~4. The process according to any of the preceding claims, wherein the mean residence time is from 20 minutes to 20 hours, preferably 1 to 4 hours.

~~6.~~5. A catalyst composition for oligomerization of ethylene comprising

(a) a chromium compound,

(b) a metalated PNPNH compound, wherein the PNPNH compound is of the formula

$$R_1R_2P\text{-}N(R_3)\text{-}P(R_4)\text{-}N(R_5)\text{-}H$$

wherein R_1, R_2, R_3, R_4 and R_5 are independently selected from halogen, amino, trimethylsilyl, C_1-C_{10}-alkyl, substituted C_1-C_{10}-alkyl, C_6-C_{20}-aryl and substituted C_6-C_{20}-aryl, or any cyclic derivative wherein at least one of the P or N atoms of the PNPN-H structure is a member of a ring system, the ring system being formed from one or more constituent compounds of the PNPNH-structure by substitution, and

(c) an activator or cocatalyst~~.~~, and

(d) an ammonium or phosphonium salt of the formula $[H_4E]X$, $[H_3ER]X$, $[H_2ER_2]X$, $[HER_3]X$, or $[ER_4]X$ wherein E is N or P, X is Cl, Br or I, and each R is independently C_1-C_{22}-alkyl, C_3-C_{10}-cycloalkyl, C_1-C_{22}-acyl, C_6-C_{30}-aryl, C_2-C_{22}-alkenyl, or C_2-C_{22}-alkynyl, preferably dodecyltrimethylammonium chloride or tetraphenylphosphonium chloride.

~~7.~~6. The catalyst composition according to claim ~~6~~5, wherein the chromium compound is selected from organic or inorganic salts, coordination complexes, organometallic complexes of Cr(II) or Cr(III), or a combination comprising at least one of the foregoing.

~~8.~~7. The catalyst composition according to claim 5 or ~~6 6 or 7~~, wherein the chromium compound is $CrCl_3(THF)_3$, Cr(III)acetyl acetonate, Cr(III)octanoate, chromium hexacarbonyl, Cr(III)-2-ethyl-hexanoate and (benzene)tricarbonyl-chromium, or a combination comprising at least one of the foregoing.

~~9.~~8. The catalyst composition according to any of the claims ~~6-8~~5-7, wherein the activator or co-catalyst is selected from trimethyl aluminum, triethyl aluminum, triisopropyl aluminum, triisobutyl aluminum, ethyl aluminum sesquichloride, diethyl aluminum chloride, ethyl aluminum dichloride, methyl aluminoxane, or a combination comprising at least one of the foregoing.

~~10. A method for metalating a compound of the general formula~~

~~$R_1R_2P\text{-}N(R_3)\text{-}P(R_4)\text{-}N(R_5)\text{-}H$~~

wherein R_1, R_2, R_3, R_4 and R_5 are independently selected from halogen, amino, trimethylsilyl, C_1-C_{10} alkyl, or any cyclic derivative wherein at least one of the P or N atoms of the PNPN-H structure is a member of a ring system, the ring system being formed from one or more constituent compounds of the PNPNH-structure by substitution, the method comprising the steps of:

(i) dissolving the PNPNH compound in a solvent to obtain a solution;

(ii) metalating the PNPNH compound in the solution, and

(iii) precipitating the metalated compound, separating from the solvent and optionally washing with the solvent.

11. The method according to claim 10, wherein R_1, R_2, R_3, R_4 and R_5 are selected from chloro, amino, trimethylsilyl, methyl, ethyl, isopropyl, tert-butyl, phenyl, benzyl, tolyl and xylyl.

12. The method according to claim 10 or 11, wherein the PNPNH compound is $(Ph)_2$P-N(i-Pr)-P(Ph)-N(i-Pr)-H, $(Ph)_2$P-N(i-Pr)-P(Ph)-N(Ph)-H, $(Ph)_2$P-N(i-Pr)-P(Ph)-N(tert-butyl)-H, $(Ph)_2$P-N(i-Pr)-P(Ph)-N($CH(CH_3)$(Ph))-H, or a combination comprising at least one of the foregoing.

13. The method according to any of the preceding claims 10-12, wherein the metalating in step (ii) is by adding, into the solution obtained in step (i), an organometallic compound, a metal-containing base, sodium metal, or potassium metal, in an amount equivalent to or in excess of the molar concentration of the PNPNH compound.

14. The method according to claim 13, wherein metalation is achieved by adding n-butyl lithium, sec-butyl lithium, tert-butyl lithium, sodium cyclopentadienide, sodium hydride, sodium amide, alkyl- or aryl magnesium halides (Grignard reagents), sodium bis(trimethylsilyl) amide, dialkylmagnesium, diarylmagnesium, trialkylaluminium, dialkylzinc, sodium metal, or potassium metal, preferably n-butyllithium, or a combination comprising at least one of the foregoing.

15. A metalated compound, obtained by a method according to claim 10.