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 comprising a metalated ligand of the formula PNPN-M, 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, wherein the substitution is by formally eliminating per constituent compound either two whole groups R_1-R_5 or H, one atom from each of two groups R_1-R_5 or a whole group R_1-R_5 or H and an atom from another group R_1-R_5, and joining the formally so created valence-unsaturated sites by one covalent bond per constituent compound to provide the same valence as initially present at a given site, and

wherein M is Li, Mg, Na, K, Cr, Al, or a combination comprising at least one of the foregoing,

(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.

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.

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.

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.

5. A catalyst composition for oligomerization of ethylene comprising

(a) a chromium compound,

(b) a metalated PNPNH compound comprising a metalated ligand of the formula PNPN-M, 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, wherein the substitution is by formally eliminating per constituent compound either two whole groups R_1-R_5 or H, one atom from each of two groups R_1-R_5 or a whole group R_1-R_5 or H and an atom from another group R_1-R_5, and joining the formally so created valence-unsaturated sites by one covalent bond per constituent compound to provide the same valence as initially present at a given site, and

wherein M is Li, Mg, Na, K, Cr, Al, or a combination comprising at least one of the foregoing,

(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.

6. The catalyst composition according to claim 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.

7. The catalyst composition according to claim 5 or 6, 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.

8. The catalyst composition according to any of the claims 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.