CLAIMS

1. A catalyst composition comprising:

(a) a chromium compound;

(b) a ligand of the general structure

(A) $R_1R_2P\text{-}N(R_3)\text{-}P(R_4)\text{-}NR_5R_6$ or

(B) $R_1R_2P\text{-}N(R_3)\text{-}P(XR_7)R_8$ or $R_1R_2P\text{-}N(R_3)\text{-}P(XR_7)_2$, with X = O or S, wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are independently C_1-C_{10}-alkyl, C_6-C_{20}-aryl, C_3-C_{10}-cycloalkyl, aralkyl, alkylaryl, or trialkylsilyl, or any cyclic derivatives of (A) and (B), wherein at least one of the P or N atoms of the PNPN-unit or PNP-unit is a member of the ring system, the ring system being formed from one or more constituent compounds of structures (A) or (B) by substitution; and

(c) an activator or co-catalyst.

2. A catalyst composition according to claim 1, wherein the chromium compound is an organic salt, an inorganic salt, a coordination complex, an organometallic complexes of Cr(II), or Cr(III), or a combination comprising at least one of the foregoing.

3. A catalyst composition according to claim 2, wherein the chromium compound is $CrCl_3(THF)_3$, Cr(III)acetylacetonate, Cr(III)octanoate, chromium hexacarbonyl, Cr(III)-2-ethylhexanoate, (benzene)tricarbonyl-chromium, or a combination comprising at least one of the foregoing.

4. A catalyst composition according to any of the preceding claims 1 to 3, wherein R_1, R_2, R_3, R_4, R_5, R_6, R_7, and R_8 are each independently methyl, ethyl, isopropyl, tert-butyl, cyclohexyl, phenyl, benzyl, tolyl, or xylyl.

5. A catalyst composition according to any of the preceding claims 1 to 4, wherein the activator or co-catalyst is trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, ethylaluminumsesquichloride, diethylaluminum chloride, ethylaluminumdichloride, methylaluminoxane (MAO), modified methylaminoxane (MMAO), or a combination comprising at least one of the foregoing.

6. A catalyst composition according to any of the preceding claims 1 to 5, wherein the ligand is Ph_2P-N(i-Pr)-P(Ph)-N(i-Pr)Ph, Ph_2P-N(i-Pr)-P(Ph)-N(Me)C_6H_6, Ph_2P-N(i-Pr)-P(Ph)S(i-Pr), Ph_2P-N(i-Pr)-P(Ph)OC_2H_5, Ph_2P-N(i-Pr)P(Ph)OCH_3, or a combination comprising at least one of the foregoing.

7. A catalyst composition according to any of the preceding claims 1 to 6, additionally comprising a solvent, preferably aromatic hydrocarbons, straight-chain aliphatic hydrocarbons, cyclic aliphatic hydrocarbons, straight-chain olefins, ethers, or a combination comprising at least one of the foregoing, preferably toluene, benzene, ethylbenzene, cumene, xylenes, mesitylene, hexane, octane, cyclohexane, methylcyclohexane, hexene, heptene, octene, diethylether, tetrahydrofuran, chlorobenzene, or a combination comprising at least one of the foregoing, most preferably toluene or chlorobenzene.

8. A catalyst composition according to claim 7, wherein the concentration of the chromium compound is from 0.01 to 100 mmol/l, preferably 0.1 to 10 mmol/l.

9. A catalyst composition according to any of the preceding claims 1 to 8, wherein the ligand/Cr molar ratio is from 0.5 to 50, preferably 0.8 to 2.0.

10. A catalyst composition according to any of the preceding claims 5 to 9, wherein the Al/Cr molar ratio is from 1:1 to 1000:1, preferably 10:1 to 200:1.

11. A catalyst composition, obtainable by combining at least:

(a) a chromium compound;

(b) a ligand of the general structure

(A) R_1R_2P-N(R_3)-P(R_4)-NR_5R_6 or

(B) R_1R_2P-N(R_3)-P(XR_7)R_8 or R_1R_2P-N(R_3)-P(XR_7)$_2$,

wherein

X = O or S, and

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are independently C_1-C_{10}-alkyl, C_6-C_{20}-aryl, C_3-C_{10}-cycloalkyl, aralkyl, alkylaryl, or trialkylsilyl, or any cyclic derivatives of (A) and (B), wherein at least one of the P or N atoms of the PNPN-unit or PNP-unit is a member of the

ring system, the ring system being formed from one or more constituent compounds of structures (A) or (B) by substitution; and

(c) an activator or co-catalyst.

12. A process for tri- and/or tetramerization of ethylene, comprising subjecting a catalyst composition according to any of the claims 1 to 11 to a gas phase of ethylene in a reactor and conducting an oligomerization.

13. A process according to claim 12, wherein the oligomerization is carried out at a pressure of 1 to 200 bar, preferably 10 to 50 bar.

14. A process according to claim 12 or 13, wherein the oligomerization is carried out at a temperature of from 10 to 200°C, preferably 20 to 100°C.

15. A process according to any of the claims 12 to 14, wherein the mean residence time is from 10 minutes to 20 hours, preferably 1 to 4 hours.

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2. A catalyst composition according to claim 1, wherein the chromium compound is an organic salt, an inorganic salt, a coordination complex, an organometallic complexes of Cr(II), or Cr(III), or a combination comprising at least one of the foregoing.

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modified methylaminoxane (MMAO), or a combination comprising at least one of the foregoing.

6. A catalyst composition according to any of the preceding claims 1 to 5, wherein the ligand is $Ph_2PN(i\text{-}Pr)P(Ph)NMe_2$, $Ph_2P\text{-}N(i\text{-}Pr)\text{-}P(Ph)\text{-}N(i\text{-}Pr)Ph$, $Ph_2P\text{-}N(i\text{-}Pr)\text{-}P(Ph)\text{-}N(Me)C_6H_{11}$, $Ph_2P\text{-}N(i\text{-}Pr)\text{-}P(Ph)S(i\text{-}Pr)$, $Ph_2P\text{-}N(i\text{-}Pr)\text{-}P(Ph)OC_2H_5$, $Ph_2P\text{-}N(i\text{-}Pr)P(Ph)OCH_3$, $Ph_2P\text{-}N(i\text{-}Pr)\text{-}P(OC_2H_5)_2$, or a combination comprising at least one of the foregoing.

7. A catalyst composition according to any of the preceding claims 1 to 6, additionally comprising a solvent, preferably aromatic hydrocarbons, straight-chain aliphatic hydrocarbons, cyclic aliphatic hydrocarbons, straight-chain olefins, ethers, or a combination comprising at least one of the foregoing, preferably toluene, benzene, ethylbenzene, cumene, xylenes, mesitylene, hexane, octane, cyclohexane, methylcyclohexane, hexene, heptene, octene, diethylether, tetrahydrofuran, chlorobenzene, or a combination comprising at least one of the foregoing, most preferably toluene or chlorobenzene.

8. A catalyst composition according to claim 7, wherein the concentration of the chromium compound is from 0.01 to 100 mmol/l, preferably 0.1 to 10 mmol/l.

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wherein

X = O or S, and

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are independently C_1-C_{10}-alkyl, C_6-C_{20}-aryl, C_3-C_{10}-cycloalkyl, aralkyl, alkylaryl, or trialkylsilyl, or any cyclic derivatives of (A) and (B), wherein at least one of the P or N atoms of the PNPN-unit or PNP-unit is a member of the ring system, the ring system being formed from one or more constituent compounds of structures (A) or (B) by substitution; and

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12. A process for tri- and/or tetramerization of ethylene, comprising subjecting a catalyst composition according to any of the claims 1 to 11 to a gas phase of ethylene in a reactor and conducting an oligomerization.

13. A process according to claim 12, wherein the oligomerization is carried out at a pressure of 1 to 200 bar, preferably 10 to 50 bar.

14. A process according to claim 12 or 13, wherein the oligomerization is carried out at a temperature of from 10 to 200°C, preferably 20 to 100°C.

15. A process according to any of the claims 12 to 14, wherein the mean residence time is from 10 minutes to 20 hours, preferably 1 to 4 hours.