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(54) **OLIGOMERISATION IN THE PRESENCE OF BOTH A TETRAMERISATION CATALYST AND A FURTHER OLIGOMERISATION CATALYST**

OLIGOMERISATION IN GEGENWART SOWOHL EINES TETRAMERISATIONSKATALYSATORS
ALS AUCH EINES WEITEREN OLIGOMERISATIONSKATALYSATORS

OLIGOMERISATION EN PRESENCE A LA FOIS D'UN CATALYSEUR DE TETRAMERISATION ET
D'UN CATALYSEUR D'OLIGOMERISATION

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Description**TECHNICAL FIELD**

5 **[0001]** This invention relates to the oligomerisation of olefinic compounds In the presence of both a tetramerisation catalyst and a further oligomerisation catalyst to produce a mixture of tetramers and other oligomers.

BACKGROUND TO THE INVENTION

10 **[0002]** Many different processes for the oligomerisation of olefinic compounds are known. The oligomerisation of ethylene and similar processes are described in PCT/ZA20031000187.

[0003] US 2003/0166456 describes an olefin trimerisation catalyst in combination with a further olefin oligomerisation catalyst such as nickel phosphine dimerisation catalysts or Fe and Co pyridyldiimine oligomerisation catalysts.

15 **[0004]** The inventors of the present invention have now found that a tetramerisation reaction as described in PCT/ZA2003/000187 and PCT/ZA2003/000186 can be combined with at least one further oligomerisation reaction to yield a mixture of tetramers and other oligomers, The processes described in PCT/ZA2003/000187 and PCT/ZA2003/000186 also yield a somewhat mixed oligomerised product, the ratios between the oligomer being dependent on and determined by the catalyst system and reaction conditions selected. The current process can now be used to manipulate the ratios of the oligomers in the product stream as may be required by market needs.

20 **[0005]** Most surprisingly it has been found that a tetramerisation reaction as described in this patent application is compatible with a further oligomerisation reaction and accordingly is suitable to manipulate the composition of the oligomerised product stream.

DISCLOSURE OF THE INVENTION

25 **[0006]** According to the present invention there is provided a process for the oligomerisation of at least one olefinic compound in the form of an olefin or a compound including an olefinic moiety by contacting the at least one olefinic compound with at least two different catalysts, namely a tetramerisation catalyst and a further oligomerisation catalyst, wherein the tetramerisation catalyst and the further oligomerisation catalyst are defined according to claim 1.

30 **[0007]** In this specification a substituent is a moiety (excluding H) which is bound to a linear structure or a cyclic structure bound to X¹ and X², but does not form part of the linear or cyclic structure.

[0008] In this specification a polar substituent is a substituent with a permanent electric or induced dipole moment.

Tetramerisation catalyst

35

SOURCE OF TRANSITION METAL

[0009] The source of transition metal is Cr.

40 **[0010]** The Cr transition metal may be an inorganic salt, an organic salt, a coordination compound or an organometallic complex.

[0011] Preferably the source of transition metal is a source of chromium and preferably it is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex; (benzene)tricarbonyl chromium; chromium (III) octanoate; chromium hexacarbonyl; chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate. Preferably it is chromium (III) acetylacetonate.

45

LIGATING COMPOUND

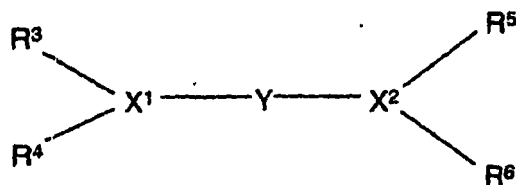
[0012] X¹ and/or X² may be a potential electron donor for coordination with the transition metal.

50 **[0013]** An electron donor is defined as an entity that donates electrons used in chemical, including dative covalent, bond formation.

[0014] X¹ and/or X² are phosphorus.

[0015] The ligating compound is of the formula

55



wherein Y is as defined below; X¹ and X² is as defined above and R³ to R⁶ are the same or different and are each independently a hydrocarbyl group a substituted hydrocarbyl group, or a heterohydrocarbyl group as defined below provided that

- (a) if two or more of R³ to R⁶ are aromatic with a ring atom of the aromatic ring structure bound to either X¹ or X² not more than two of said aromatic R³ to R⁶ have a substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X²; and
- (b) none of R³ to R⁶ are aromatic with a ring atom of the aromatic ring structure bound to X¹ or X² with a polar substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X².

[0016] One or more of R³ to R⁶ may be a substituted hydrocarbyl group or a substituted heterohydrocarbyl group defined below, that is at least one substituent is bound to the hydrocarbyl group or the heterohydrocarbyl group. The term "substituent" is as defined earlier, that is a substituent is a moiety (excluding H) which is bound to a linear structure or a cyclic structure bound to X¹ or X², but does not form part of the linear or cyclic structure.

[0017] The linear or cyclic structure may be selected from the group consisting of a linear hydrocarbyl, a cyclic hydrocarbyl and a cyclic heterohydrocarbyl group defined below. Linear hydrocarbyl may include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl and decynyl. Cyclic hydrocarbyl may include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclopentenyl, cyclohexenyl, cyclo-octenyl, phenyl, cyclopentadienyl, naphthalenyl, norbornyl, adamantyl, phenanthrenyl, anthracenyl, phenalenyl, tetrahydronaphthalenyl, decalinyl, indenyl and tetrahydroindenyl. Cyclic heterohydrocarbyl is tetrahydrofuranyl, tetrahydrothiophenyl, pyrrolidenyl, piperidineyl, pyrrolineyl, oxazolyl, thiazolyl, furanyl, thiophenyl, pyrazolinyl, pyrazolyl, imidazolyl, benzofuranyl, coumaranyl and indolyl. According to the above definition and for the purpose of clarity, benzyl is considered to be methyl linear structure with a phenyl substituent and tolyl is considered as a phenyl cyclic structure with a methyl substituent.

[0018] R³ to R⁶ may also be selected from a group of metallocenes such as a ferrocenyl, zirconocenyl and titanocenyl group.

[0019] In one embodiment of the invention R³ to R⁶ are the same or different and each is a hydrocarbyl group, or a heterohydrocarbyl group which contains no substituent or contains a non-polar substituent. Preferably each of R³ to R⁶ does not have any polar substituent. In one embodiment of the invention at least two of (but preferably all of) R³ to R⁶ are aromatic with a ring atom of the aromatic ring structure bound to X¹ or X², but not more than two of said aromatic R³ to R⁶ having a non-polar substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X². Preferably none of the aromatic R³ to R⁶ have a non-polar substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X². Preferably all of aromatic R³ to R⁶ are non-substituted aromatic compounds. R³ to R⁶ may be independently selected from the group consisting of a non-aromatic compound; an aromatic compound; and a heteroaromatic compound. Preferably each of R³ to R⁶ is an aromatic or heteroaromatic compound, more preferably an aromatic compound (including a substituted aromatic compound). The aromatic compound (or substituted aromatic compound) may comprise phenyl or a substituted phenyl.

[0020] In this specification a non-polar substituent is a substituent without a permanent electric or induced dipole moment.

[0021] Examples of suitable non-polar substituents include, but are not limited to, methyl, ethyl, ethenyl, propyl, isopropyl, cyclopropyl, propenyl, propynyl, butyl, sec-butyl, tertiary-butyl, cyclobutyl, butenyl, butynyl, pentyl, isopentyl, neopentyl, cyclopentyl, pentenyl, pentynyl, hexyl, sec-hexyl, cyclohexyl, 2-methylcyclohexyl, 2-ethylcyclohexyl, 2-isopropylcyclohexyl, cyclohexenyl, hexenyl, hexynyl, octyl, cyclo-octyl, cyclo-octenyl, decyl, benzyl, phenyl, tolyl, xylyl, o-methylphenyl, o-ethylphenyl, o-isopropylphenyl, o-t-butylphenyl, cumyl, mesityl, biphenyl, naphthyl, anthracenyl, and the like.

[0022] Any one of R³ to R⁶ may be independently linked to one or more of each other, or to Y to form a cyclic structure.

[0023] In yet another embodiment of the invention R^3 to R^6 are the same or different and each is a hydrocarbonyl group, or a heterohydrocarbonyl group, provided that at least one of R^3 to R^6 contains a polar substituent on a carbon atom, but not one of R^3 to R^6 contains a polar substituent on a carbon atom of R^3 to R^6 adjacent to a carbon atom bound to X^1 or X^2 . One or more, or all of R^3 to R^6 may be independently selected from the group consisting of a substituted non-aromatic compound; a substituted aromatic compound; and a substituted heteroaromatic compound. Preferably each of R^3 to R^6 is a substituted aromatic or a substituted heteroaromatic compound, more preferably a substituted aromatic compound. The substituted aromatic compound may comprise a substituted phenyl.

[0024] Any polar substituent on one or more of R^3 , R^4 , R^5 and R^6 may be electron donating.

[0025] Suitable polar substituents may be a methoxy, ethoxy, isopropoxy, C_3 - C_{20} alkoxy, phenoxy, methoxymethyl, methylthiomethyl, 1,3-oxazolyl, methoxymethoxy, hydroxyl, amino, pentafluorophenoxy, tosyl, methylsulfanyl, trimethylsiloxy, dimethylamino, sulphate, nitro or the like.

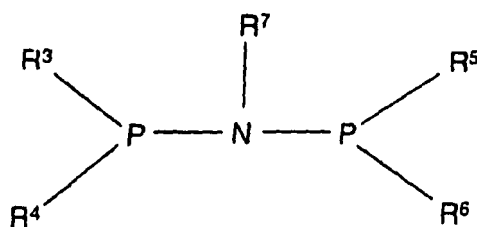
[0026] R^3 and R^4 may be the same, and R^5 and R^6 may be the same. R^3 to R^6 may all be the same.

[0027] Y is selected from the group consisting of 1,2-ethane; 1,2-ethene; 1,1-cyclopropane; 1,1-cyclobutane; 1,1-cyclohexane; 1,1-cyclopentane; 1,2-cyclopentane; 1,2-cyclohexane; 1,2-phenylene; 1,8-naphthyl; 9,10-phenanthrene; 4,5-phenanthrene; 1,3-propane; 1,2-catechol; 1,2-dialkylhydrazine; and $-N(R^7)$, where R^7 is selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents. R^7 may be methyl, ethyl, propyl, isopropyl, cyclopropyl, allyl, butyl, tertiary-butyl, sec-butyl, cyclobutyl, pentyl, isopentyl, neopentyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclo-octyl; decyl, cyclodecyl, 1,5-dimethylheptyl, 2-naphthylethyl, 1-naphthylmethyl, adamantylmethyl, adamantyl, 2-isopropylcyclohexyl, 2,6-dimethylcyclohexyl, cyclododecyl, 2-methylcyclohexyl, 3-methylcyclohexyl, 4-methylcyclohexyl, 2-ethylcyclohexyl, 2-isopropylcyclohexyl, 2,6-dimethyl-cyclohexyl, exo-2-norbornanyl, isopinocampheyl, dimethylamino, phthalimido, pyrrolyl, trimethylsilyl, dimethyl-tertiary-butylsilyl, 3-trimethoxysilane-propyl, indanyl, cyclohexanemethyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 4-tertiary-butylphenyl, 4-nitrophenyl, (1,1'-bis(cyclohexyl)-4,4'-methylene), 1,6-hexylene, 1-naphthyl, 2-naphthyl, N-morpholine, diphenylmethyl, 1,2-diphenyl-ethyl, phenylethyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2,6-dimethyl-phenyl, 1,2,3,4-tetrahydronaphthyl, or a 2-octyl group.

[0028] Y may include a first atom bound to X^1 and a different atom bound to X^2 .

[0029] Preferably Y includes or is a single atom bound to both X^1 and X^2 .

[0030] Preferably the ligating compound is of the formula



with R^3 to R^7 as defined above.

[0031] The ligating compound is a bidentate ligand.

[0032] Non limiting examples of the ligating compound are

(phenyl)₂PN(methyl)P(phenyl)₂; (phenyl)₂PN(ethyl)P(phenyl)₂;
 (phenyl)₂PN(propyl)P(phenyl)₂; (phenyl)₂PN(butyl)P(phenyl)₂;
 (phenyl)₂PN(pentyl)P(phenyl)₂; (phenyl)₂PN(hexyl)P(phenyl)₂;
 (phenyl)₂PN(heptyl)P(phenyl)₂; (phenyl)₂PN(octyl)P(phenyl)₂;
 (phenyl)₂PN(nonyl)P(phenyl)₂; (phenyl)₂PN(decyl)P(phenyl)₂;
 (phenyl)₂PN(cyclopropyl)P(phenyl)₂; (phenyl)₂PN(cyclobutyl)P(phenyl)₂;
 (phenyl)₂PN(cyclopentyl)P(phenyl)₂; (phenyl)₂PN(cyclohexyl)P(phenyl)₂;
 (phenyl)₂PN(cycloheptyl)P(phenyl)₂; (phenyl)₂PN(cyclooctyl)P(phenyl)₂;
 (phenyl)₂PN(cyclodecyl)P(phenyl)₂; (phenyl)₂PN(cyclododecyl)P(phenyl)₂;
 (phenyl)₂PN(isopropyl)P(phenyl)₂; (phenyl)₂PN(isobutyl)P(phenyl)₂;
 (phenyl)₂PN(secbutyl)P(phenyl)₂; (phenyl)₂PN(tertiarybutyl)P(phenyl)₂;
 (phenyl)₂PN(neopentyl)P(phenyl)₂; (phenyl)₂PN(1,2-dimethyl-propyl)P(phenyl)₂;
 (phenyl)₂PN(allyl)P(phenyl)₂; (phenyl)₂PN(methylheptyl)P(phenyl)₂;
 (phenyl)₂PN(1,5-dimethyl-heptyl)P(phenyl)₂; (phenyl)₂PN(2-ethylhexyl)P(phenyl)₂;

- (phenyl)₂PN(3-trimethoxysilane-propyl)P(phenyl)₂;
 (phenyl)₂PN(indanyl)P(phenyl)₂; (phenyl)₂PN(cyclohexylethyl)P(phenyl)₂;
 (phenyl)₂PN(2-methylcyclohexyl)P(phenyl)₂; (phenyl)₂PN(adamantyl)P(phenyl)₂;
 (phenyl)₂PN(adamantylmethyl)P(phenyl)₂;
 5 (phenyl)₂PN(cyclohexanemethyl)P(phenyl)₂; (phenyl)₂PN(benzyl)P(phenyl)₂;
 (phenyl)₂PN(phenyl)P(phenyl)₂; (phenyl)₂PN((4-methoxy)-phenyl)P(phenyl)₂;
 (phenyl)₂PN((3-methoxy)-phenyl)P(phenyl)₂;
 (phenyl)₂PN((2-methoxy)phenyl)P(phenyl)₂;
 (phenyl)₂PN((4-t-butyl)-phenyl)P(phenyl)₂;
 10 (phenyl)₂PN((4-nitro)-phenyl)P(phenyl)₂; (phenyl)₂PN(1-naphthyl)P(phenyl)₂;
 (phenyl)₂PN(2-naphthyl)P(phenyl)₂; (phenyl)₂PN(4-pyridyl)P(phenyl)₂;
 (phenyl)₂PN(3-(N-morpholine)-propyl)P(phenyl)₂;
 (phenyl)₂PN(2-naphthyl-ethyl)P(phenyl)₂; (phenyl)₂PN(1-naphthylmethyl)P(phenyl)₂;
 (phenyl)₂PN(diphenylmethyl)P(phenyl)₂;
 15 (phenyl)₂PN(1,2-diphenyl-ethyl)P(phenyl)₂; (phenyl)₂PN(phenylethyl)P(phenyl)₂;
 (phenyl)₂PN((2-methyl)phenyl)P(phenyl)₂;
 (phenyl)₂PN((3-methyl)phenyl)P(phenyl)₂;
 (phenyl)₂PN((4-methyl)phenyl)P(phenyl)₂;
 (phenyl)₂PN((2,6-dimethyl)phenyl)P(phenyl)₂;
 20 (phenyl)₂PN((2-ethyl)-phenyl)P(phenyl)₂;
 (phenyl)₂PN(1,2,3,4-Tetrahydronaphthyl)P(phenyl)₂;
 (phenyl)₂PN((2-methyl)cyclohexyl)P(phenyl)₂;
 (phenyl)₂PN((3-methyl)cyclohexyl)P(phenyl)₂;
 (phenyl)₂PN((4-methyl)cyclohexyl)P(phenyl)₂;
 25 (phenyl)₂PN((2-ethyl)cyclohexyl)P(phenyl)₂;
 (phenyl)₂PN((2-isopropyl)cyclohexyl)P(phenyl)₂;
 (phenyl)₂PN((2,6-dimethyl)cyclohexyl)P(phenyl)₂;
 (phenyl)₂PN(exo-2-norbornanyl)P(phenyl)₂;
 (phenyl)₂PN(isopinocampheyl)P(phenyl)₂;
 30 (phenyl)₂PN(dimethylamino)P(phenyl)₂; (phenyl)₂PN(phthalimido)P(phenyl)₂;
 (phenyl)₂PN(pyrrolyl)P(phenyl)₂; (phenyl)₂PN(trimethylsilyl)P(phenyl)₂;
 (phenyl)₂PN(dimethyltertiarybutylsilyl)P(phenyl)₂;
 (4-biphenyl)PN(methyl)P(4-biphenyl)₂;
 (2-naphthyl)₂PN(methyl)P(2-naphthyl)₂;
 35 (4-methylphenyl)₂PN(methyl)P(4-methylphenyl)₂;
 (3-methylphenyl)₂PN(methyl)P(3-methylphenyl)₂;
 (2-naphthyl)₂PN(methyl)P(phenyl)₂;
 (2-naphthyl)(phenyl)PN(methyl)P(2-naphthyl)(phenyl);
 (2-naphthyl)₂PN(methyl)P(2-naphthyl)(phenyl);
 40 (2-naphthyl)(phenyl)PN(methyl)P(phenyl)₂;
 (2-methylphenyl)(phenyl)PN(isopropyl)P(2-methylphenyl)(phenyl);
 (2-methylphenyl)₂PN(methyl)P(phenyl)₂;
 (2-methylphenyl)(phenyl)PN(isopropyl)P(phenyl)₂;
 (ethyl)₂PN(methyl)P(ethyl)₂; (ethyl)₂PN(isopropyl)P(ethyl)₂;
 45 (ethyl)₂PN(tert(arybutyl)P(ethyl)₂; (methyl)₂PN(isopropyl)P(methyl)₂;
 (isopropyl)₂PN(methyl)P(isopropyl)₂; (ethyl)₂PN(isopropyl)P(ethyl)(phenyl);
 (ethyl)(phenyl)PN(isopropyl)P(ethyl)(phenyl); (ethyl)₂PN(isopropyl)P(phenyl)₂;
 (ethyl)(phenyl)PN(isopropyl)P(phenyl)₂;
 (2-thiophenyl)₂PN(isopropyl)P(2-thiophenyl)₂;
 50 (phenyl)₂PN(methyl)N(methyl)P(phenyl)₂; (phenyl)₂PN(ethyl)N(ethyl)P(phenyl)₂;
 (phenyl)₂PN(isopropyl)N(isopropyl)P(phenyl)₂;
 (phenyl)₂PN(isopropyl)N(methyl)P(phenyl)₂;
 (phenyl)₂PN(isopropyl)N(methyl)P(phenyl)₂;
 (4-methylphenyl)₂P-N(CH₃)N(CH₃)-P(4-methylphenyl)₂;
 55 (3-methylphenyl)₂P-N(CH₃)N(CH₃)-P(3-methylphenyl)₂;
 (2-methylphenyl)₂P-N(CH₃)N(CH₃)-P(phenyl)₂; (ethyl)₂P-N(CH₃)N(CH₃)-P(ethyl)₂;
 (methyl)₂P-N(CH₃)N(CH₃)-P(methyl)₂; (isopropyl)₂P-N(CH₃)N(CH₃)-P(isopropyl)₂;
 (ethyl)₂P-N(CH₃)N(CH₃)-P(ethyl)(phenyl);

- (ethyl)(phenyl)P-N(CH₃)N(CH₃)-P(ethyl)(phenyl);
 (ethyl)₂P-N(CH₃)N(CH₃)-P(phenyl)₂; (ethyl)(phenyl)P-N(CH₃)N(CH₃)-P(phenyl)₂;
 (2-thiophenyl)₂P-N(CH₃)N(CH₃)-P(2-thiophenyl)₂;
 (2-naphthyl)₂P-N(CH₃)N(CH₃)-P(2-naphthyl)₂;
 5 (4-biphenyl)₂P-N(CH₃)N(CH₃)-P(4-biphenyl)₂; (phenyl)₂P-1,8-naphthy(-P(phenyl)₂);
 (phenyl)₂P-9,10-phenanthrene-P(phenyl)₂;
 (phenyl)₂P-4,5-phenanthrene-P(phenyl)₂;
 (phenyl)₂P-C(CH₂)₂-P(phenyl)₂; (phenyl)₂P-1,2-benzene-P(phenyl)₂;
 (4-methylphenyl)₂P-1,2-benzene-P(4-methylphenyl)₂;
 10 (3-methylphenyl)₂P-1,2-benzene-P(3-methylphenyl)₂;
 (2-methylphenyl)₂P-1,2-benzene-P(phenyl)₂; (ethyl)₂P-1,2-benzene-P(ethyl)₂;
 (methyl)₂P-1,2-benzene-P(methyl)₂; (isopropyl)₂P-1,2-benzene-P(isopropyl)₂;
 (ethyl)₂P-1,2-benzene-P(ethyl)(phenyl);
 (ethyl)(phenyl)P-1,2-benzene-P(ethyl)(phenyl);
 15 (ethyl)₂P-1,2-benzene-P(phenyl)₂; (ethyl)(phenyl)P-1,2-benzene-P(phenyl)₂;
 (2-thiophenyl)₂P-1,2-benzene-P(2-thiophenyl)₂;
 (2-naphthyl)₂P-1,2-benzene-P(2-naphthyl)₂;
 (4-biphenyl)₂P-1,2-benzene-P(4-biphenyl)₂; (phenyl)₂P-CH₂CH₂-P(phenyl)₂;
 (4-methylphenyl)₂P-CH₂CH₂-P(4-methylphenyl)₂;
 20 (3-methylphenyl)₂P-CH₂CH₂-P(3-methylphenyl)₂;
 (4-methylphenyl)₂P-CH₂CH₂-P(4-methylphenyl)(phenyl);
 (4-methylphenyl)(phenyl)P-CH₂CH₂-P(4-methylphenyl)(phenyl);
 (4-methylphenyl)₂P-CH₂CH₂-P(phenyl)₂;
 (4-methylphenyl)(phenyl)P-CH₂CH₂-P(phenyl)₂;
 25 (2-methylphenyl)₂P-CH₂CH₂-P(phenyl)₂; (ethyl)₂P-CH₂CH₂-P(ethyl)₂;
 (methyl)₂P-CH₂CH₂-P(methyl)₂; (isopropyl)₂P-CH₂CH₂-P(isopropyl)₂;
 (ethyl)₂P-CH₂CH₂-P(ethyl)(phenyl); (ethyl)(phenyl)P-CH₂CH₂-P(ethyl)(phenyl);
 (ethyl)₂P-CH₂CH₂-P(phenyl)₂; (ethyl)(phenyl)P-CH₂CH₂-P(phenyl)₂;
 (2-thiophenyl)₂P-CH₂CH₂-P(2-thiophenyl)₂;
 30 (4-trifluoromethylphenyl)₂PN(isopropyl)P(4-trifluoromethylphenyl)₂;
 (4-chlorophenyl)₂PN(isopropyl)P(4-chlorophenyl)₂;
 (4-methoxyphenyl)₂PN(methyl)P(4-methoxyphenyl)₂;
 (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)₂;
 (3-methoxyphenyl)₂PN(methyl)P(3-methoxyphenyl)₂;
 35 (4-methoxyphenyl)₂PN(isopropyl)P(4-methoxyphenyl)(phenyl);
 (4-methoxyphenyl)(phenyl)PN(isopropyl)P(4-methoxyphenyl)(phenyl);
 (4-methoxyphenyl)₂PN(isopropyl)P(phenyl)₂;
 (4-methoxyphenyl)(phenyl)PN(isopropyl)P(phenyl)₂;
 (4-methoxyphenyl)₂P-N(CH₃)N(CH₃)-P(4-methoxyphenyl)₂;
 40 (3-methoxyphenyl)₂P-N(CH₃)N(CH₃)-P(3-methoxyphenyl)₂;
 (4-methoxyphenyl)₂P-N(CH₃)N(CH₃)-P(4-methoxyphenyl)(phenyl);
 (4-methoxyphenyl)(phenyl)P-N(CH₃)N(CH₃)-P(4-methoxyphenyl)(phenyl);
 (4-methoxyphenyl)₂P-N(CH₃)N(CH₃)-P(phenyl)₂;
 (4-methoxyphenyl)(phenyl)P-N(CH₃)N(CH₃)-P(phenyl)₂;
 45 (4-methoxyphenyl)₂P-1,2-benzene-P(4-methoxyphenyl)₂;
 (3-methoxyphenyl)₂P-1,2-benzene-P(3-methoxyphenyl)₂;
 (4-methoxyphenyl)₂P-1,2-benzene-P(4-methoxyphenyl)(phenyl);
 (4-methoxyphenyl)(phenyl)P-1,2-benzene-P(4-methoxyphenyl)(phenyl);
 (4-methoxyphenyl)₂P-1,2-benzene-P(phenyl)₂;
 50 (4-methoxyphenyl)(phenyl)P-1,2-benzene-P(phenyl)₂;
 (3-methoxyphenyl)₂P(CH₂CH₂)P(3-methoxyphenyl)₂;
 (3-methoxyphenyl)₂P(CH₂CH₂)P(3-methoxyphenyl)(phenyl);
 (3-methoxyphenyl)(phenyl)P(CH₂CH₂CH₂)P(3-methoxyphenyl)(phenyl);
 (3-methoxyphenyl)(phenyl)P(CH₂CH₂)P(3-methoxyphenyl)(phenyl);
 55 (3-methoxyphenyl)₂P(CH₂CH₂)P(phenyl)₂;
 (3-methoxyphenyl)(phenyl)P(CH₂CH₂)P(phenyl)₂;
 (4-methoxyphenyl)₂P(CH₂CH₂)P(4-methoxyphenyl)₂;
 (4-methoxyphenyl)₂P(CH₂CH₂)P(4-methoxyphenyl)(phenyl);

(4-methoxyphenyl)(phenyl)P(CH₂CH₂CH₂)P(4-methoxyphenyl)(phenyl);
 (4-methoxyphenyl)(phenyl)P(CH₂CH₂)P(4-methoxyphenyl)(phenyl);
 (4-methoxyphenyl)₂P(CH₂CH₂)P(phenyl)₂ and
 (4-methoxyphenyl)(phenyl)P(CH₂CH₂)P(phenyl)₂.

[0033] The ligating compound may include a polymeric moiety to render the reaction product of the source of transition metal and the said ligating compound to be soluble at higher temperatures and insoluble at lower temperatures e.g. 25°C. This approach may enable the recovery of the complex from the reaction mixture *for reuse and has been used for other catalyst as described by* D.E. Bergbreiter et al., J. Am. Chem. Soc., 1987, 109, 177-179. In a similar vein these transition metal catalysts can also be immobilised by binding the ligating compound to silica, silica gel, polysiloxane or alumina backbone as, for example, demonstrated by C. Yuanyin et al., Chinese J. React. Pol., 1992, 1(2), 152-159 for immobilising platinum complexes.

[0034] The ligating compounds may be prepared using procedures known to one skilled in the art and procedures forming part of the state of the art.

[0035] The tetramerisation catalyst may be prepared in situ, that is in the reaction mixture in which the oligomerisation reaction is to take place. Reaction mixture will be understood to include a reaction medium, reactants (olefinic compounds), reaction products and catalyst components. Typically the oligomerisation catalyst will be prepared in situ. However it is foreseen that the catalyst may be pre-formed or partly pre-formed.

[0036] The source of transition metal and ligating compound may be combined (in situ or ex situ) to provide any suitable molar ratio, preferably a transition metal to ligand compound molar ratio, from about 0.01 : 100 to 10 000 : 1, preferably from about 0.1 : 1 to 10:1.

[0037] The process may also include combining one or more different sources of transition metal with one or more different ligating compounds.

[0038] The tetramerisation catalyst or its individual components, in accordance with the invention, may also be immobilised by supporting it on a support material, for example, silica, alumina, MgCl₂, zirconia, artificial hectorite or smectonite clays such as Laponite™ RD or mixtures thereof, or on a polymer, for example polyethylene, polypropylene, polystyrene, or poly(aminostyrene). The catalyst can be formed *in situ* in the presence of the support material, or the support can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components or the oligomerisation catalyst. In some cases, the support material can also act as a component of the activator. This approach would also facilitate the recovery of the catalyst from the reaction mixture for reuse.

ACTIVATION

[0039] The catalyst may also include one or more activators. Such an activator may be a compound that generates an active catalyst when the activator is combined with the source of transition metal and the ligating compound.

[0040] Suitable activators include aluminium compounds (including organoaluminium compounds), organoboron compounds, organic salts such as methyl lithium and methylmagnesium bromide, inorganic acids and salts such as tetrafluoroboric acid etherate, silver tetrafluoroborate, sodium hexafluoroantimonate, and the like. Suitable aluminium compounds include compounds of the formula Al(R⁹)₃ (R⁹ being the same or different), where each R⁹ is independently a C₁-C₁₂ alkyl, an oxygen containing moiety or a halide, aluminosilanes, and compounds such as LiAlH₄ and the like. Aluminosilanes are well known in the art as typically oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic, cages or mixtures thereof. Examples of suitable organoaluminium activators include trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, aluminium isopropoxide, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, methylaluminosilane (MAO), ethylaluminosilane (EAO), isobutylaluminosilane (iBuAO), modified alkylaluminosilanes such as modified methylaluminosilane (MMAO) and mixture thereof.

[0041] Examples of suitable organoboron compounds are boroxines, NaBH₄, triethylborane, tris(pentafluorophenyl) borane, trityl tetrakis(pentafluorophenyl) borate, dimethylaniliumtetrakis(pentafluorophenyl) borate, tributyl borate and the like.

[0042] The activator may also be or contain a compound that acts as a reducing or oxidising agent, such as sodium or zinc metal and the like, or hydrogen or oxygen and the like.

[0043] The activator may be selected from alkylaluminosilanes such as methylaluminosilane (MAO), high stability methylaluminosilane (MAO HS), ethylaluminosilane (EAO), isobutylaluminosilane (iBuAO) well as modified alkylaluminosilanes such as modified methylaluminosilane (MMAO). Modified methylaluminosilane (a commercial product from Akzo-Nobel) contains modifier groups such as isobutyl or n-octyl groups, in addition to methyl groups.

[0044] The transition metal source and the aluminosilane may be combined in proportions to provide Al/transition metal molar ratios from about 1:1 to 10 000:1, preferably from about 1:1 to 1000: 1, and more preferably from 1:1 to 500:1.

[0045] The process may include the step of adding to the catalyst system a trialkylaluminium compound in amounts

of between 0.01 to 1000 mol per mol of alkylaluminumoxane.

[0046] It should be noted that aluminosiloxanes generally also contain considerable quantities of the corresponding trialkylaluminum compounds used in their preparation. The presence of these trialkylaluminum compounds in aluminosiloxanes can be attributed to their incomplete hydrolysis with water. Any quantity of a trialkylaluminum compound quoted in this disclosure is additional to alkylaluminum compounds contained within the aluminosiloxanes.

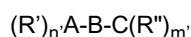
Further oligomerisation catalyst

[0047] The further oligomerisation catalyst may comprise a conventional oligomerisation catalyst (e.g. as described in US 6555723, US 6683187 and US 20030144514), a dimerisation catalyst (e.g. as described in US 2003/0149198), but preferably it comprises a trimerisation catalyst. Preferably it comprises a trimerisation catalyst as described in any one of US 5811618, WO 02/04119, WO 03/053890, WO 03/053891 and PCT/ZA2003/000185. Preferably it comprises a catalyst as described in WO 03/053890 or PCT/ZA2003/000185.

Tetramerisation catalyst and further oligomerisation catalyst

[0048] In a preferred embodiment of the invention the further oligomerisation catalyst is a catalyst comprising the combination of

- i) a source of transition metal; and
- ii) a ligating compound, preferably of the formula



where

A and C are independently selected from the group consisting of N, P, As, Sb, Bi, O, S and Se;

B is a linking group between A and C;

m' and n' are independently 0, 1 or a larger integer;

R' and R'' are independently hydrogen or hydrocarbyl group;

and R' being the same or different when n > 1, and R'' being the same or different when n > 1.

[0049] Preferably the oligomerisation catalyst is a trimerisation catalyst and the source of transition metal and ligating compound is as described in US 5811618, WO 02/04119, WO/053890 or WO 031053891 or PCT/ZA2003/000185.

[0050] Preferably the source of transition metal of the tetramerisation catalyst and the further oligomerisation catalyst as described above is the same source. Preferably it is a source of Cr in both cases.

[0051] In one embodiment of the invention both the tetramerisation catalyst and the further oligomerisation catalyst may be prepared in the same medium (preferably *in situ*). The preparation may be carried out by combining

- i) a source of transition metal for both the tetramerisation catalyst and the further oligomerisation catalyst;
- ii) a ligating compound for the tetramerisation catalyst as defined above;
- iii) a different ligating compound for the oligomerisation (preferably trimerisation) catalyst; and
- iv) optionally an activator.

[0052] The oligomerisation catalyst, may be a trimerisation catalyst, and preferably it is as described in US 5811618, WO 02/04119, WO/053890 or WO 03/053891 or PCT/ZA2003/000185.

[0053] The molar ratio of the ligating compound for the tetramerisation catalyst to the ligating compound for the other oligomerisation catalyst may be varied as required and may for example be 0.05:1 or 1:1 or 1:2 or 1:3.

[0054] According to another aspect of the present invention there is provided an oligomerisation catalyst comprising the combination of

- i) source of transition metal for both a tetramerisation catalyst and a trimerisation catalyst;
- ii) a ligating compound for a tetramerisation catalyst as defined above;
- iii) a different ligating compound for a trimerisation catalyst; and
- iv) optionally an activator.

Oligomeric product

[0055] The oligomeric product may include a mixture of at least one tetramer and at least one other oligomer. Both the at least one tetramer and the at least one other oligomer may comprise olefins or compounds including an olefinic moiety. Preferably both are olefins, preferably olefins containing a single carbon-carbon double bond, and preferably both comprise α -olefins. The at least one tetramer may comprise octene, preferably 1-octene. The at least one other oligomer may comprise a trimer, preferably hexene, preferably 1-hexene.

[0056] The at least one tetramer and the at least one other oligomer may be branched, but preferably they are non-branched.

Olefinic compound

[0057] The at least one olefinic compound may comprise a single olefinic compound or mixture of olefinic compounds. In one embodiment of the invention it may comprise a single olefin.

[0058] The at least one olefinic compound preferably comprises an olefin and the olefin may include multiple carbon-carbon double bonds, but preferably it comprises a single carbon-carbon double bond. The olefin may comprise an α -olefin with 2 to 30 carbon atoms, preferably 2 to 10 carbon atoms. The olefinic compound may be selected from the group consisting of ethene, propene, 1-butene, 1-pentene, 1-hexene, styrene, 1-heptene, and 1-octene, 1-nonene, 1-decene, 3-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, p-methyl styrene, 1-dodecene or combinations thereof. Preferably it comprises ethene or propene, preferably ethene. The ethene may be used to produce octene (preferably 1-octene) and other oligomers, preferably hexene (preferably 1-hexene).

Process

[0059] The molar ratio of the tetramerisation catalyst to the further oligomerisation catalyst may be 0.01:1 to 100:1, preferably 0.1:1 to 10:1.

[0060] The olefinic compound or mixture thereof to be oligomerised according to this invention can be introduced into the process in a continuous or batch fashion.

[0061] The olefinic compound or mixture of olefinic compounds may be contacted with the oligomerisation catalysts at a pressure of 100 kPa or higher, preferably greater than 1000 kPa, more preferably greater than 3000 kPa. Preferred pressure ranges are from 1000 to 30000 kPa, more preferably from 3000 to 10000 kPa.

[0062] The process may be carried out at temperatures from -100 °C to 250 °C. Temperatures in the range of 15-150 °C are preferred. Particularly preferred temperatures range from 40-120°C.

[0063] The oligomerisation process may include the step of mixing the components of the catalysts at any temperature between -20 °C and 250 °C in the presence or absence of an olefinic compound or mixture thereof. The preferred temperature range being from 20 °C to 150 °C. The components of the catalysts may also be added separately and at different temperatures to allow for selective and controlled contact between the components.

[0064] The individual components constituting the tetramerisation catalyst or further oligomerisation catalyst described herein may be combined simultaneously or sequentially in any order, and in the presence or absence of a solvent, in order to give an active and selective catalyst. The presence of an olefinic compound during the mixing of the catalyst components generally provides a protective effect which may result in improved catalyst performance.

[0065] The reaction products derived from the oligomerisation reaction as described herein, may be prepared using the disclosed catalysts by a homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalysts and the oligomeric product is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

[0066] The oligomerisation reaction may also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, heptane, methylcyclohexane, methylcyclopentane, cyclohexane, Isopar C, ionic liquids as well as the product formed during the reaction in a liquid state and the like.

[0067] The oligomerisation reaction may be carried out in a plant which includes reactor types known in the art. Examples of such reactors include, but are not limited to, batch reactors, semi-batch reactors and continuous reactors. The plant may include, in combination a) a stirred or fluidised bed reactor system, b) at least one inlet line into this reactor for olefin reactant and the catalyst system, c) effluent lines from this reactor for oligomerisation reaction products, and d) at least one separator to separate the desired oligomerisation reaction products which may include a recycle loop for solvents and/or reactants and/or products which may also serve as temperature control mechanism.

[0068] The invention will now be further described by means of the following non-limiting examples.

Examples**Example 1: Combined ethylene tetra- and trimerisation reaction using Cr(acetylacetonate)₃, (phenyl)₂PN(*i*-propyl)P(phenyl)₂, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO**

[0069] A solution of 9.4 mg of (phenyl)₂PN(*i*-propyl)P(phenyl)₂ (0.022 mmol) and (tetramerisation ligand) 11.3 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (0.022 mmol) (trimerisation ligand) in 10 ml of toluene was added to a solution of 7.4 mg Cr(acetylacetonate)₃ (0.022 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml) and MAO (methylaluminoxane, 9.9 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa. The reaction was terminated after 12 min by discontinuing the ethylene feed to the reactor and cooling the reactor to below 10°C. After releasing the excess ethylene from the autoclave, the liquid contained in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid products. These solid products were dried overnight in an oven at 100°C and then weighed. The mass of total product was 111.66 g. The product distribution of this example is summarised in Table 1.

Example 2: Combined ethylene tetra- and trimerisation reaction using Cr(acetylacetonate)₃, (phenyl)₂PN(*i*-propyl)P(phenyl)₂, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO

[0070] A solution of 6.4 mg of (phenyl)₂PN(*i*-propyl)P(phenyl)₂ (0.015 mmol) (tetramerisation ligand) and 7.7 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (0.015 mmol) (trimerisation ligand) in 10 ml of toluene was added to a solution of 7 mg Cr(acetylacetonate)₃ (0.02 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml) and MAO (methylaluminoxane, 4 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa. The reaction was terminated after 13.5 min, and the procedure of Example 1 above was employed. The product mass was 68.58 g. The product distribution of this example is summarised in Table 1.

Example 3: Combined ethylene tetra- and trimerisation reaction using Cr(acetylacetonate)₃, (phenyl)₂PN(propyl)P(phenyl)₂, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO

[0071] A solution of 4.3 mg of (phenyl)₂PN(propyl)P(phenyl)₂ (0.01 mmol) (tetramerisation ligand) and 10.2 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (0.02 mmol) (trimerisation ligand) in 10 ml of toluene was added to a solution of 7 mg Cr(acetylacetonate)₃ (0.02 mmol) in 10 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml) and MAO (methylaluminoxane, 4 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa. The reaction was terminated after 15 min, and the procedure of Example 1 above was employed. The product mass was 84.35 g. The product distribution of this example is summarised in Table 1.

Example 4: Combined ethylene tetra- and trimerisation reaction using Cr(acetylacetonate)₃, (phenyl)₂PN(*i*-propyl)P(phenyl)₂, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO

[0072] A solution of 3.2 mg of (phenyl)₂PN(*i*-propyl)P(phenyl)₂ (0.0075 mmol) (tetramerisation ligand) and 11.5 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (0.0225 mmol) (trimerisation ligand) in 10 ml of toluene was added to a solution of 7 mg Cr(acetylacetonate)₃ (0.02 mmol) in 10 ml toluene in a Schlenk vessel.

[0073] The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80 ml) and MAO (methylaluminoxane, 4 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa. The reaction was terminated after 19 min, and the procedure of Example 1 above was employed. The product mass was 99.05 g. The product distribution of this example is summarised in Table 1.

Example 5: Combined ethylene tetra- and trimerisation reaction using Cr(acetylacetonate)₃, (phenyl)₂PN(*i*-propyl)P(phenyl)₂, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO

[0074] A solution of 3.2 mg of (phenyl)₂PN(*i*-propyl)P(phenyl)₂ (0.0075 mmol) (tetramerisation ligand) and 11.5 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (0.0225 mmol) (trimerisation ligand) in 10 ml of methylcyclohexane was added to a solution of 7 mg Cr(acetylacetonate)₃ (0.02 mmol) in 10 ml methylcyclohexane in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of methylcyclohexane (80 ml) and MAO (methylaluminoxane in toluene, 4 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa. The reaction was terminated after 19 min, and the procedure of Example 1 above was employed. The product mass was 91.11 g. The product distribution of this example is summarised in Table 1.

Example 6: Combined ethylene tetra- and trimerisation reaction using Cr(acetylacetonate)₃, (phenyl)₂PN(*i*-propyl)P(phenyl)₂, (o-methoxyphenyl)₂PN(Me)P(o-methoxyphenyl)₂ and MMAO

[0075] A solution of 4.3 mg of (phenyl)₂PN(*i*-propyl)P(phenyl)₂ (0.01 mmol) (tetramerisation ligand) and 5.1 mg of (o-methoxyphenyl)₂PN(Me)P(o-methoxyphenyl)₂ (0.01 mmol) (trimerisation ligand) in 5 ml of methylcyclohexane was added to a solution of 7 mg Cr(acetylacetonate)₃ (0.02 mmol) in 5 ml methylcyclohexane in a Schlenk vessel. MMAO-3A (modified methylaluminoxane, 5.1 mmol) was added and the mixture was immediately transferred to a 300 ml pressure reactor (autoclave) containing methylcyclohexane (80 ml) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa. The reaction was terminated after 7 min, and the procedure of Example 1 above was employed. The product mass was 84.2 g. The product distribution of this example is summarised in Table 1.

Example 7: Combined ethylene tetra- and trimerisation reaction using Cr(acetylacetonate)₃, (p-methoxyphenyl)₂PN(Me)P(p-methoxyphenyl)₂, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MMAO

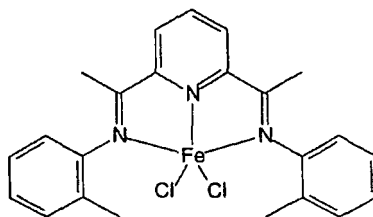
[0076] A solution of 0.5 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (trimerisation ligand) (0.001 mmol) and 4.7 mg of (p-methoxyphenyl)₂PN(Me)P(p-methoxyphenyl)₂ (0.009 mmol) (tetramerisation ligand) in 5 ml of methylcyclohexane was added to a solution of 3.5 mg Cr(acetylacetonate)₃ (0.01 mmol) in 5 ml methylcyclohexane in a Schlenk vessel. MMAO-3A (modified methylaluminoxane, 1.3 mmol) was added and the mixture was immediately transferred to a 300 ml pressure reactor (autoclave) containing methylcyclohexane (90 ml) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa. The reaction was terminated after 23 min, and the procedure of Example 1 above was employed. The product mass was 47.9 g. The product distribution of this example is summarised in Table 1.

Example 8: Combined ethylene tetra- and trimerisation reaction using Cr(acetylacetonate)₃, Ph₂PN(Me)N(Me)PPh₂, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MMAO

[0077] A solution of 3.9 mg of Ph₂PN(Me)N(Me)PPh₂ (0.009 mmol) (tetramerisation ligand) and 0.5 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (0.001 mmol) (trimerisation ligand) in 5 ml of methylcyclohexane was added to a solution of 3.5 mg Cr(acetylacetonate)₃ (0.01 mmol) in 10 ml methylcyclohexane in a Schlenk vessel. MMAO-3A (modified methylaluminoxane, 2.5 mmol) was added and the mixture was immediately transferred to a 300 ml pressure reactor (autoclave) containing methylcyclohexane (80 ml) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 4500 kPa. The reaction was terminated after 5 min, and the procedure of Example 1 above was employed. The product mass was 52.47 g. The product distribution of this example is summarised in Table 1.

Example 9: Combined ethylene tetra- and oligomerisation reaction using Cr(acetylacetonate)₃, (phenyl)₂PN(*i*-propyl)P(phenyl)₂, Fe-bis(iminopyridyl) (1) and MMAO

[0078] A solution of 6.5 mg of (phenyl)₂PN(*i*-propyl)P(phenyl)₂ (0.016 mmol) (tetramerisation ligand) and 5.25 mg Cr(acetylacetonate)₃ (0.015 mmol) in 5 ml toluene was added to a suspension of 1.64 mg (0.0035 mmol) of (1) (ethylene oligomerisation catalyst^{1a}) in 5 ml toluene in a Schlenk vessel. The mixture was transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (90 ml) and MAO (methylaluminoxane in toluene, 9.5 mmol) at 40°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 45°C, while the ethylene pressure was maintained at 3000 kPa. The reaction was terminated after 30 min, and the procedure of Example 1 above was employed. The product mass was 34.6 g. The product distribution of this example is summarised in Table 2.



(1)

1a) B. L. Small, M. Brookhart, J. Am. Chem. Soc., 1998, 120, 7143. 1b) G. J. P. Britovsek, S. Mastroianni, G. A. Solan, S. P. D. Baugh, C. Redshaw, V. C. Gibson, A. J. P. White, D. J. Williams and M. R. J. Elsegood, Chemistry - A European Journal, 2000, 6, 2221.

Example 10: Ethylene oligomerisation reaction using Fe-bisiminopyridyl (1) and MAO (comparative example)

[0079] A suspension of 2.34 mg (0.005 mmol) of (1) (see example 9, ethylene oligomerisation catalyst) in 10 ml toluene was added to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (90 ml) and MAO (methylaluminoxane in toluene, 2.5 mmol) at 90°C. The pressure reactor was charged with ethylene after which the reactor temperature was controlled at 90°C, while the ethylene pressure was maintained at 3000 kPa. The reaction was terminated after 6 min, and the procedure of Example 1 above was employed. The product mass was 109.4 g. The product distribution and the k-value for the Schulz-Flory distribution of this example are summarised in Table 2.

Table 1: Combined Tri- and Tetramerisation

Example	activity	C-6	1-hex.	C-8	1-oct.
	g/g Cr	%	%	%	%
1	97600	43	87.6	52.8	98.9
2	65800	38.7	98.3	51.4	98.8
3	81000	52.9	94.2	38.2	98.9
4	95100	58.5	93.1	36	98.9
5	87500	62.2	96.5	25.7	99
6	81000	47.3	93.9	40.5	98.9
7	92100	78.7*	96.4	12.2*	93.2
8	100900	56.9	94.1	34.4	99.2
*Liquid fraction (i.o.w. selectivities excluding the polymeric side products) Percentages are expressed as weight % (of total product)					

Table 2: Combined Oligomerisation and Tetramerisation

Example	activity	C-6	1-hex.	C-8	1-oct.	C-10	C-12	C-14	k-value
	g/g metal	%	%	%	%	%	%	%	
9	35300	18.0	82.0	33.3	96.0	7.0	4.9	3.5	n/a

(continued)

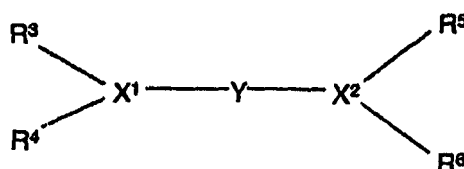
Example	activity	C-6	1-hex.	C-8	1-oct.	C-10	C-12	C-14	k-value
	g/g metal	%	%	%	%	%	%	%	
10	391900	10.6	98.0	9.5	97.0	11.2	9.2	5.7	0.73
Percentages are expressed as weight % (of total product).									

Claims

1. A process for the oligomerisation of at least one olefinic compound in the form of an olefin or a compound including an olefinic moiety by contacting the at least one olefinic compound with at least two different catalysts, namely, a tetramerisation catalyst and a further oligomerisation catalyst, thus producing an oligomeric product which includes a mixture of at least one tetramer and at claim 1

least one other oligomer wherein the tetramerisation catalyst comprises a combination of

- i) a source of a transition metal which transition metal is Cr; and
- ii) a ligating compound of the formula



wherein: X¹ X² are P;

R³ to R⁶ are the same or different and are each independently selected from the group consisting of a hydrocarbonyl group, a substituted hydrocarbonyl group, and a group selected from tetrahydrofuranyl, tetrahydrothiophenyl, pyrrolidenyl, piperidineyl, pyrrolinyl, oxazolyl, thiazolyl, furanyl, thiophenyl, pyrazolinyl, pyrazolyl, imidazolyl, benzofuranyl, coumaranyl and indolyl;

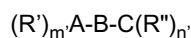
Y is a linking group between X¹ and X² and selected from the group consisting of 1,2-ethane; 1,2-ethene; 1,1-cyclopropane; 1,1-cyclobutane; 1,1-cyclohexane; 1,1-cyclopentane; 1,2-cyclopentane; 1,2-cyclohexane; 1,2-phenylene; 1,8-naphthyl; 9,10-phenanthrene; 4,5-phenanthrene; 1,3-propane; 1,2-catechol; 1,2-dialkylhydrazine, -N(R⁷)- where R⁷ is selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents; provided that

(a) if two or more of R³ to R⁶ are aromatic with a ring atom of the aromatic ring structure bound to either X¹ or X², not more than two of said aromatic R¹ and R² have a substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X²; and

(b) none of R³ to R⁶ are aromatic with a ring atom of the aromatic ring structure bound to either X¹ and X² and with a polar substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X²;

and wherein the further oligomerisation catalyst is a catalyst comprising the combination of

- i) a source of transition metal; and
- ii) a ligating compound of the formula



where

A and C are independently selected from the group consisting of N, P, As, Sb, Bi, O, S and Se;

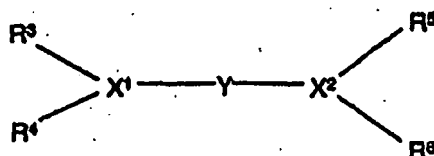
B is a linking group between A and C;
 m' and n' are independently 1 or a larger integer;
 R' and R'' are independently selected from the group comprising hydrogen, or a hydrocarbyl group;
 and R' being the same or different when m' > 1, and R'' being the same or different when n' > 1.

2. The process of claim 1 wherein the source of Cr is selected from the group of compounds consisting of an inorganic salt, an organic salt, a coordination compound and an organometallic complex.
3. The process of claim 2 wherein the source of Cr is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex; (benzene)tricarbonyl chromium; chromium (III) octanoate; chromium hexacarbonyl; chromium (III) acetylacetonate and chromium (III) 2-ethylhexanoate.
4. The process of any one of the preceding claims wherein R³ to R⁶ are the same or different and each is a hydrocarbyl group, which contains no substituent or contains a non-polar substituent.
5. The process of claim 4 wherein each of R³ to R⁶ does not have any polar substituent.
6. The process of claim 5 wherein at least two of R³ to R⁶ are aromatic with a ring atom of the aromatic ring structure bound to X¹ or X², but not more than two of said aromatic R³ to R⁶ have a non-polar substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X².
7. The process of claim 6 wherein all of R³ to R⁶ are aromatic and none of the aromatic R³ to R⁶ have a non-polar substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X².
8. The process of any one of the preceding claims 1 to 5 wherein R³ to R⁶ are the same or different and each is a hydrocarbyl group, provided that at least one of R³ to R⁶ contains a polar substituent on a carbon atom, but not one of R³ to R⁶ contains a polar substituent on a carbon atom of R³ to R⁶ adjacent to a carbon atom bound to X¹ or X².
9. The process of any one of the preceding claims wherein the catalyst includes one or more activators.
10. The process of claim 9 wherein the one or more activators are one or more organoaluminum compounds.
11. The process of claim 1 wherein the further oligomerisation catalyst is a trimerisation catalyst.
12. The process of any of the preceding claims wherein both the tetramerisation catalyst and the further oligomerisation catalyst are prepared in the same medium and in situ, the preparation being carried out by combining
 - i) chromium as the transition metal for both the tetramerisation catalyst and the further oligomerisation catalyst;
 - ii) a ligating compound for the tetramerisation catalyst as defined in claim 1;
 - iii) a different ligating compound for the further oligomerisation catalyst as defined in claim 1; and
 - iv) optionally an activator.
13. The process of any one of the preceding claims wherein the at least one olefinic compound comprises a single olefinic compound.
14. The process of claim 13 wherein the single olefinic compound is ethene.
15. The process of any one of the preceding claims which is carried out in an inert solvent.
16. An oligomerisation catalyst comprising the combination of
 - i) source of Cr for both a tetramerisation catalyst and a trimerisation catalyst as a further oligomerisation catalyst;
 - ii) a ligating compound for a tetramerisation catalyst as defined in claim 1;
 - iii) a different ligating compound for a trimerisation catalyst as said further oligomerisation catalyst as defined in claim 1; and
 - iv) optionally an activator.

Patentansprüche

1. Verfahren zum Oligomerisieren von zumindest einer olefinischen Verbindung in Form eines Olefins oder einer Verbindung, die eine olefinische Einheit aufweist, durch Inkontaktbringen der zumindest einen olefinischen Verbindung mit mindestens zwei unterschiedlichen Katalysatoren, d.h. einem Tetramerisierungskatalysator und einem weiteren Oligomerisierungskatalysator, womit ein oligomeres Produkt erzeugt wird, das ein Gemisch von zumindest einem Tetramer und zumindest einem anderen Oligomer einschließt, wobei der Tetramerisierungskatalysator eine Kombination von folgendem umfaßt:

- i) eine Quelle eines Übergangsmetalls, wobei das Übergangsmetall Cr ist; und
 ii) eine sich als Ligand koordinativ anlagernde Verbindung der Formel



worin

X¹ und X² gleich P sind;

R³ bis R⁶ gleich oder verschieden sind und jeweils unabhängig voneinander aus der Gruppe ausgewählt sind, bestehend aus einem Kohlenwasserstoffrest, einem substituierten Kohlenwasserstoffrest und einer Gruppe, die aus Tetrahydrofuranyl, Tetrahydrothiophenyl, Pyrrolidenyl, Piperidiny, Pyrrolinyl, Oxazolyl, Thiazolyl, Furanyl, Thiophenyl, Pyrazolinyl, Pyrazolyl, Imidazolyl, Benzofuranyl, Cumaranyl und Indolyl ausgewählt ist;

Y ein Brückenrest zwischen X¹ und X² ist und aus der Gruppe ausgewählt ist, bestehend aus: 1,2-Ethan, 1,2-Ethen, 1,1-Cyclopropan, 1,1-Cyclobutan, 1,1-Cyclohexan, 1,1-Cyclopentan, 1,2-Cyclopentan, 1,2-Cyclohexan, 1,2-Phenylen, 1,8-Naphthyl, 9,10-Phenanthren, 4,5-Phenanthren, 1,3-Propan, 1,2-Catechin, 1,2-Dialkylhydrazin, -N(R⁷)-, wobei R⁷ ausgewählt ist aus der Gruppe, bestehend aus Wasserstoff, einer Alkyl-, substituierten Alkyl-, Aryl-, substituierten Aryl-, Aryloxy-, substituierten Aryloxygruppe, einem Halogen, einer Nitro-, Alkoxy-carbonyl-, Carbonyloxy-, Alkoxy-, Aminocarbonyl-, Carbonylamino-, Dialkylamino-, Silylgruppe oder Derivaten davon, und einem mit irgendeinem dieser Substituenten substituierten Aryl;

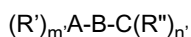
mit der Maßgabe, daß

(a) wenn zwei oder mehr der Reste R³ bis R⁶ aromatisch sind, wobei ein Ringatom der aromatischen Ringstruktur entweder an X¹ oder X² gebunden ist, nicht mehr als zwei dieser aromatischen Reste R¹ und R² einen Substituenten als ein nicht zum Ring gehörendes Atom aufweisen, das an ein Ringatom der aromatischen Ringstruktur gebunden ist, das an das Ringatom angrenzt, das an X¹ oder X² gebunden ist; und

(b) keiner der Reste R³ bis R⁶ aromatisch ist, wobei ein Ringatom der aromatischen Ringstruktur jeweils an X¹ und X² gebunden ist, und mit einem polaren Substituenten als nicht zum Ring gehörendes Atom, das an ein Ringatom der aromatischen Ringstruktur gebunden ist, das an das Ringatom angrenzt, das an X¹ oder X² gebunden ist;

und wobei der weitere Oligomerisierungskatalysator ein Katalysator ist, der eine Kombination von folgendem umfaßt:

- (i) eine Quelle eines Übergangsmetalls; und
 (ii) eine sich als Ligand koordinativ anlagernde Verbindung der Formel



worin

A und C unabhängig voneinander aus der Gruppe ausgewählt sind, die aus N, P, As, Sb, Bi, O, S und Se besteht; B ein Brückenrest zwischen A und C ist;

m' und n' unabhängig voneinander 1 oder eine höhere ganze Zahl sind;

R' und R'' unabhängig voneinander aus der Gruppe ausgewählt sind, die Wasserstoff oder einen Kohlenwasserstoffrest umfaßt;

und R' gleich oder verschieden ist, wenn $m' > 1$ ist, und R" gleich oder verschieden ist, wenn $n' > 1$ ist.

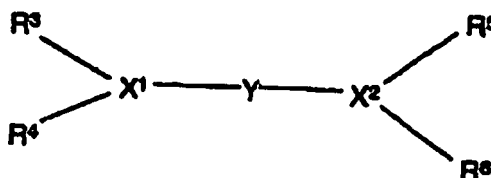
2. Verfahren nach Anspruch 1, wobei die Quelle von Cr aus der Gruppe von Verbindungen ausgewählt ist, die aus einem anorganischen Salz, einem organischen Salz, einer Koordinationsverbindung und einem Organometallkomplex besteht.
3. Verfahren nach Anspruch 2, wobei die Quelle von Cr aus der Gruppe ausgewählt ist, die aus Chromtrichlorid, einem Tristetrahydrofuran-Komplex, (Benzol)tricarbonylchrom, Chrom(III)-ac-tanoat, Chromhexacarbonyl, Chrom(III)-acetylacetonat und Chrom(III)2-ethylhexanoat besteht.
4. Verfahren nach einem der vorstehenden Ansprüche, wobei R^3 bis R^6 gleich oder verschieden und jeweils ein Kohlenwasserstoff sind, der keinen Substituenten oder einen nichtpolaren Substituenten enthält.
5. Verfahren nach Anspruch 4, wobei R^3 bis R^6 jeweils keinen polaren Substituenten aufweisen.
6. Verfahren nach Anspruch 5, wobei zumindest zwei der Reste R^3 bis R^6 aromatisch sind, wobei ein Ringatom der aromatischen Ringstruktur an X^1 oder X^2 gebunden ist, jedoch nicht mehr als zwei der aromatischen Reste R^3 bis R^6 einen nichtpolaren Substituenten als nicht zum Ring gehörendes Atom haben, das an ein Ringatom der aromatischen Ringstruktur gebunden ist, das an das Ringatom angrenzt, das an X^1 oder X^2 gebunden ist.
7. Verfahren nach Anspruch 6, wobei R^3 bis R^6 jeweils aromatisch sind und keiner der aromatischen Reste R^3 bis R^6 einen nichtpolaren Substituenten als nicht zum Ring gehörendes Atom aufweist, das an ein Ringatom der aromatischen Ringstruktur gebunden ist, das an das Ringatom angrenzt, das an X^1 oder X^2 gebunden ist.
8. Verfahren nach einem der vorstehenden Ansprüche 1 bis 5, wobei R^3 bis R^6 gleich oder verschieden und jeweils ein Kohlenwasserstoffrest sind, mit der Maßgabe, daß zumindest einer der Reste R^3 bis R^6 einen polaren Substituenten an einem Kohlenstoffatom enthält, jedoch keiner der Reste R^3 bis R^6 einen polaren Substituenten an einem Kohlenstoffatom von R^3 bis R^6 enthält, das an ein Kohlenstoffatom angrenzt, das an X^1 oder X^2 gebunden ist.
9. Verfahren nach einem der vorstehenden Ansprüche, wobei der Katalysator einen oder mehrere Aktivatoren einschließt.
10. Verfahren nach Anspruch 9, wobei der eine oder die mehreren Aktivatoren eine oder mehrere Organoaluminiumverbindungen sind.
11. Verfahren nach Anspruch 1, wobei der weitere Oligomerisierungskatalysator ein Trimerisierungskatalysator ist.
12. Verfahren nach einem der vorstehenden Ansprüche, wobei der Tetramerisierungskatalysator und der weitere Oligomerisierungskatalysator jeweils im gleichen Medium und in situ hergestellt werden, wobei die Herstellung durch Kombinieren von folgendem durchgeführt wird:
 - i) Chrom als das Übergangsmetall für den Tetramerisierungskatalysator und auch den weiteren Oligomerisierungskatalysator;
 - ii) eine sich als Ligand koordinativ anlagernde Verbindung für den Tetramerisierungskatalysator nach Anspruch 1;
 - iii) eine andere sich als Ligand koordinativ anlagernde Verbindung für den weiteren Oligomerisierungskatalysator nach Anspruch 1; und
 - iv) gegebenenfalls ein Aktivator.
13. Verfahren nach einem der vorstehenden Ansprüche, wobei die zumindest eine olefinische Verbindung eine einzige olefinische Verbindung umfaßt.
14. Verfahren nach Anspruch 13, wobei die einzige olefinische Verbindung Ethen ist.
15. Verfahren nach einem der vorstehenden Ansprüche, das in einem inerten Lösungsmittel durchgeführt wird.
16. Oligomerisierungskatalysator, umfassend die Kombination von:

- i) einer Quelle von Cr für den Tetramerisierungskatalysator und auch den Trimerisierungskatalysator als einen weiteren Oligomerisierungskatalysator;
 ii) eine sich als Ligand koordinativ anlagernde Verbindung für einen Tetramerisierungskatalysator nach Anspruch 1;
 iii) eine andere sich als Ligand koordinativ anlagernde Verbindung für einen Trimerisierungskatalysator als den weiteren Oligomerisierungskatalysator nach Anspruch 1; und
 iv) gegebenenfalls einem Aktivator.

Revendications

1. Procédé pour l'oligomérisation d'au moins un composé oléfinique sous la forme d'une oléfine ou un composé comprenant un fragment oléfinique par mise en contact de l'au moins un composé oléfinique avec au moins deux catalyseurs différents, à savoir un catalyseur de tétramérisation et un autre catalyseur d'oligomérisation, de manière à produire un produit oligomère qui comprend un mélange d'au moins un tétramère et au moins un autre oligomère où le catalyseur de tétramérisation comprend une combinaison de

- i) une source d'un métal de transition, ledit métal de transition étant Cr; et
 ii) un composé de ligature de formule



dans laquelle X¹ et X² sont P;

R³ à R⁶ sont identiques ou différents et sont chacun indépendamment choisis dans le groupe constitué d'un groupe hydrocarbyle, un groupe hydrocarbyle substitué, et un groupe choisi parmi le tétrahydrofuranyle, le tétrahydrothiophényle, le pyrrolidinyle, le pipéridinyle, le pyrrolinyle, l'oxazolyle, le thiazolyle, le furanyle, le thiophényle, le pyrazolinyle, le pyrazolyle, l'imidazolyle, le benzofuranyle, le coumaranyle et l'indolyle ;

Y est un groupe de liaison entre X¹ et X² et choisi dans le groupe constitué des 1,2-éthane ; 1,2-éthène ; 1,1-cyclopropane ; 1,1-cyclobutane ; 1,1-cyclohexane ; 1,1-cyclopentane ; 1,2-cyclopentane ; 1,2-cyclohexane ; 1,2-phénylène ; 1,8-naphtyle ; 9,10-phénanthrène ; 4,5-phénanthrène ; 1,2-propane ; 1,2-catéchol ; 1,2-dialkylhydrazine ; N(R⁷)-où R⁷ est choisi dans le groupe constitué de groupes hydrogène, alkyle, alkyle substitué, aryle, aryle substitué, aryloxy, aryloxy substitué, halogène, nitro, alcoxycarbonyl, carbonyloxy, alcoxy, aminocarbonyl, carbonylamino, dialkylamino, silyle et des dérivés de ceux-ci, et un aryle substitué par l'un quelconque de ces substituants ;

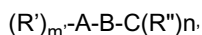
à condition que

(a) si deux ou plus de R³ à R⁶ sont aromatiques avec un atome cyclique de la structure cyclique aromatique lié à X¹ ou X², pas plus de deux desdits R¹ et R² aromatiques ont un substituant en tant qu'atome non cyclique lié à un atome cyclique de la structure cyclique aromatique adjacent à l'atome cyclique lié à X¹ ou X² ; et

(b) aucun de R³ à R⁶ n'est aromatique avec un atome cyclique de la structure cyclique aromatique liée à X¹ et X² et avec un substituant polaire en tant qu'atome non cyclique lié à un atome cyclique de la structure cyclique aromatique adjacent à l'atome cyclique lié à X¹ ou X²;

et où le catalyseur d'oligomérisation supplémentaire est un catalyseur comprenant la combinaison de

- i) une source de métal de transition ; et
 ii) un composé de ligature de formule



où

A et C sont indépendamment choisis dans le groupe constitué de N, P, As, Sb, Bi, O, S et Se ;
 B est un groupe de liaison entre A et C ;
 m' et n' sont indépendamment 1 ou un grand entier ;
 R' et R'' sont indépendamment choisis dans le groupe comprenant un hydrogène, ou un groupe hydrocarbyle ;
 et R' étant identique ou différent lorsque m' > 1 et R'' étant identique ou différent lorsque n' > 1.

2. Procédé de la revendication 1 dans lequel la source de Cr est choisie dans le groupe de composés constitué d'un sel inorganique, un sel organique, un composé de coordination et un complexe organométallique.
3. Procédé de la revendication 2 dans lequel la source de Cr est choisi dans le groupe constitué des complexe trichlorure de chrome-tris-tétrahydrofurane ; (benzène)tricarbonyl-chrome ; octanoate de chrome (III) ; hexacarbonyl-chrome ; acétylacétonate de chrome (III) et 2-éthylhexanoate de chrome (III).
4. Procédé de l'une quelconque des revendications précédentes dans lequel R³ à R⁶ sont identiques ou différents et chacun est un groupe hydrocarbyle, qui ne contient pas de substituants ou contient un substituant non polaire.
5. Procédé de la revendication 4 dans lequel chacun de R³ à R⁶ n'a aucun substituant polaire.
6. Procédé de la revendication 5 dans lequel au moins deux de R³ à R⁶ sont aromatiques avec un atome cyclique de la structure cyclique aromatique lié à X¹ ou X², mais pas plus de deux desdits R³ à R⁶ aromatiques ont un substituant non polaire en tant qu'atome non cyclique lié à un atome cyclique de la structure cyclique aromatique adjacent à l'atome cyclique lié à X¹ ou X².
7. Procédé de la revendication 6 dans lequel l'ensemble de R³ à R⁶ sont aromatiques et aucun des R³ à R⁶ aromatiques n'a un substituant non polaire en tant qu'atome non cyclique lié à un atome cyclique de la structure cyclique aromatique adjacent à l'atome cyclique lié à X¹ ou X².
8. Procédé de l'une quelconque des revendications précédentes 1 à 5 dans lequel R³ à R⁶ sont identiques ou différents et chacun est un groupe hydrocarbyle, à condition qu'au moins l'un de R³ à R⁶ contienne un substituant polaire sur un atome de carbone, mais qu'aucun de R³ à R⁶ ne contienne un substituant polaire sur un atome de carbone de R³ à R⁶ adjacent à un atome de carbone lié à X¹ ou X².
9. Procédé de l'une quelconque des revendications précédentes dans lequel le catalyseur comprend un ou plusieurs activateurs.
10. Procédé de la revendication 9 dans lequel les un ou plusieurs activateurs sont un ou plusieurs composés organoaluminium.
11. Procédé de la revendication 1 dans lequel le catalyseur d'oligomérisation supplémentaire est un catalyseur de trimérisation.
12. Procédé de l'une quelconque des revendications précédentes dans lequel le catalyseur de trimérisation et l'autre catalyseur d'oligomérisation sont préparés dans le même milieu et *in situ*, la préparation étant conduite par combinaison de
 - i) chrome en tant que métal de transition pour le catalyseur de tétramérisation et l'autre catalyseur d'oligomérisation ;
 - ii) un composé de ligature pour le catalyseur de tétramérisation tel que défini dans la revendication 1 ;
 - iii) un composé de ligature différent pour l'autre catalyseur d'oligomérisation tel que défini dans la revendication 1 ; et
 - iv) facultativement en tant qu'activateur.
13. Procédé de l'une quelconque des revendications précédentes dans lequel l'au moins un composé oléfinique comprend un composé oléfinique unique.
14. Procédé de la revendication 13 dans lequel le composé oléfinique unique est l'éthène.
15. Procédé de l'une quelconque des revendications précédentes qui est conduit dans un solvant inerte.

16. Catalyseur d'oligomérisation comprenant la combinaison de

- i) une source de Cr pour un catalyseur de tétramérisation et un catalyseur de trimérisation en tant qu'autre catalyseur d'oligomérisation;
- ii) un composé de ligature pour un catalyseur de tétramérisation tel que défini dans la revendication 1;
- iii) un composé de ligature différent pour un catalyseur de trimérisation en tant que ledit autre catalyseur d'oligomérisation tel que défini dans la revendication 1 ; et
- iv) facultativement un activateur.

REFERENCES CITED IN THE DESCRIPTION

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