



(86) Date de dépôt PCT/PCT Filing Date: 2010/10/13
 (87) Date publication PCT/PCT Publication Date: 2011/04/28
 (85) Entrée phase nationale/National Entry: 2012/04/10
 (86) N° demande PCT/PCT Application No.: IB 2010/054631
 (87) N° publication PCT/PCT Publication No.: 2011/048527
 (30) Priorité/Priority: 2009/10/19 (ZA2009/07285)

(51) Cl.Int./Int.Cl. *C07C 2/32* (2006.01),
C07C 2/36 (2006.01)
 (71) Demandeur/Applicant:
SASOL TECHNOLOGY (PTY) LIMITED, ZA
 (72) Inventeurs/Inventors:
HANTON, MARTIN JOHN, GB;
SMITH, DAVID MATTHEW, GB;
GABRIELLI, WILLIAM FULLARD, GB;
KELLY, MARK WILLIAM, GB
 (74) Agent: SMART & BIGGAR

(54) Titre : OLIGOMERISATION DE COMPOSES OLEFINIQUES AVEC FORMATION REDUITE DE POLYMERE
 (54) Title: OLIGOMERISATION OF OLEFINIC COMPOUNDS WITH REDUCED POLYMER FORMATION

(57) **Abrégé/Abstract:**

The invention relates to a process for producing an oligomeric product by oligomerisation of at least one olefinic compound, the process including a) providing an activated oligomerisation catalyst by combining, in any order, i) a source of chromium, ii) a ligating compound of the formula I $(R^1)_m X^1 (Y) X^2 (R^2)_n \dots$ I wherein X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X^1 and/or X^2 allows for such oxidation, Y is a linking group between X^1 and X^2 , m and n are independently 0, 1 or a larger integer, and R^1 and R^2 are independently hydrogen, a hydrocarbyl group, an organoheteryl group or a heterohydrocarbyl group, and R^1 being the same or different when $m > 1$, and R^2 being the same or different when $n > 1$, iii) a catalyst activator or combination of catalyst activators, b) providing a zinc compound, and c) contacting the at least one olefinic compound with a composition containing the activated oligomerisation catalyst and the zinc compound, the zinc compound being present in a sufficient quantity such that the ratio of the molar amount of zinc in the zinc compound to the molar amount of chromium in the source of chromium is between 1 and 10000 The invention also provides for a process for activating an oligomerisation catalyst to be used to produce an oligomeric product from at least one olefinic compound, as described above



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
28 April 2011 (28.04.2011)

PCT

(10) International Publication Number
WO 2011/048527 A1(51) International Patent Classification:
C07C 2/32 (2006.01) C07C 2/36 (2006.01)(74) Agent: DM KISCH INC.; P O Box 781218, 2146 Sand-
ton (ZA).(21) International Application Number:
PCT/IB2010/054631(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,
NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD,
SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.(22) International Filing Date:
13 October 2010 (13.10.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2009/07285 19 October 2009 (19.10.2009) ZA(71) Applicant (for all designated States except US): SASOL
TECHNOLOGY (PTY) LIMITED [ZA/ZA]; 1 Sturdee
Avenue, Rosebank, 2196 Johannesburg (ZA).(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG,
ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): HANTON, Martin
John [GB/GB]; 20 Osnaburgh Court, Dairsie Fife KY15
4SU (GB). SMITH, David Matthew [GB/GB]; 14
Freuchie Mill, Freuchie Fife KY15 7JL (GB).
GABRIELLI, William Fullard [ZA/GB]; 17 South
Street, St Andrews Fife KY16 9QS (GB). KELLY, Mark
William [GB/GB]; Flat 1R, 3 Gowrie Street, Dundee Fife
DD2 1ES (GB).

Published:

— with international search report (Art. 21(3))

(54) Title: OLIGOMERISATION OF OLEFINIC COMPOUNDS WITH REDUCED POLYMER FORMATION

(57) Abstract: The invention relates to a process for producing an oligomeric product by oligomerisation of at least one olefinic compound, the process including a) providing an activated oligomerisation catalyst by combining, in any order, i) a source of chromium, ii) a ligating compound of the formula I (R¹)_mX¹(Y)X²(R²)_n.....I wherein X¹ and X² are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X¹ and/or X² allows for such oxidation, Y is a linking group between X¹ and X², m and n are independently 0, 1 or a larger integer, and R¹ and R² are independently hydrogen, a hydrocarbyl group, an organoheteryl group or a heterohydrocarbyl group, and R¹ and R² being the same or different when m>1, and R² being the same or different when n>1, iii) a catalyst activator or combination of catalyst activators, b) providing a zinc compound, and c) contacting the at least one olefinic compound with a composition containing the activated oligomerisation catalyst and the zinc compound, the zinc compound being present in a sufficient quantity such that the ratio of the molar amount of zinc in the zinc compound to the molar amount of chromium in the source of chromium is between 1 and 10000 The invention also provides for a process for activating an oligomerisation catalyst to be used to produce an oligomeric product from at least one olefinic compound, as described above

WO 2011/048527 A1

OLIGOMERISATION OF OLEFINIC COMPOUNDS WITH REDUCED POLYMER FORMATION.

5 TECHNICAL FIELD

This invention relates to the oligomerisation of olefinic compounds in the presence of an activated oligomerisation catalyst and relates further to the use of a zinc compound in oligomerisation.

10 BACKGROUND ART

A number of different oligomerisation technologies are known to produce α -olefins. Some of these processes, including the Shell Higher Olefins Process and Ziegler-type technologies, have been summarized in WO 04/056479 A1. The same document also discloses that the prior art (e.g. WO 03/053891 and WO 02/04119) teaches that chromium based catalysts
15 containing heteroaromatic ligands with both phosphorus and nitrogen heteroatoms, selectively catalyse the trimerisation of ethylene to 1-hexene.

Processes wherein transition metals and heteroaromatic ligands are combined to form catalysts for trimerisation, tetramerisation, oligomerisation and polymerisation of olefinic
20 compounds have also been described in different patent applications such as WO 03/053890 A1; WO 03/053891; WO 04/056479 A1; WO 04/056477 A1; WO 04/056480 A1; WO 04/056478 A1; WO 05/123884 A2; WO 05/123633 A1 and USA Patent No. 7,285,607.

The catalysts utilized in the abovementioned trimerisation, tetramerisation, oligomerisation or
25 polymerisation processes all include one or more activators to activate the catalyst. Such an activator is a compound that generates an active catalyst when the activator is combined with the catalyst.

Suitable activators include organoaluminium compounds, organoboron compounds, organic
30 salts, such as methyl lithium and methyl magnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate, sodium hexafluoroantimonate and the like.

A common catalyst activator used in combination with Cr based catalysts for oligomerisation
35 of olefinic compounds is alkylaluminumoxane, particularly methylaluminumoxane (MAO). It is well known that MAO includes significant quantities of alkylaluminum in the form of trimethylaluminum (TMA), and in effect the catalyst activator is a combination of TMA and MAO. The MAO may also be replaced with modified MAO (MMAO), which may contain free trialkylaluminum in the form of TMA and heavier trialkylaluminiums. The use of organoboron
40 compounds as catalyst activators is also known.

Activators containing aluminium compounds are costly to the effect that it impacts significantly on process economics of olefin oligomerisation technologies that utilize this class of activators. For this reason, it is desirable to run commercial oligomerisation processes at low
5 activator concentrations. However, in the case where an aluminium-containing compound was used as an activator for transition metal based oligomerisation catalysts, it was found that at conditions of low starting aluminium concentrations (e.g. <6 mmol/l), low reaction rates and high levels of unwanted solid formation (polyethylene (PE) and waxes) resulted when ethylene was oligomerised.

10

Reduction in the formation of polymer as a by-product in Cr-based ethylene oligomerisation (both tri- and tetramerisation) processes remains an ongoing challenge, as polymer fouling reduces plant run time and necessitates shut-downs due to blockages.

15

The inventors of the present invention have found that reductions in polymer formation levels can be achieved in the chromium catalysed olefin oligomerisation processes by the incorporation of a zinc compound, in particular dialkyl zinc, in the catalyst system in the manner described below.

20

The use of a zinc compound in olefin oligomerisation is not unknown, but it has not been disclosed previously that it may be used in the manner of the present invention to achieve a reduction in polymer formation as herein disclosed. Thus the use of chain transfer reagents within the field of polymerisation has long been known. For example the use of triethylaluminium in combination with various 'chain growth' type polymerisation catalysts (e.g. 1,3,7-triazacyclononane) has been previously studied.

25

WO 2008/085659 and US 2008/0058486 both disclose the use of various activators for oligomerisation catalyst systems. Both contain the statement that "(o)ther general activators or compounds useful in an oligomerization reaction may be used. These compounds may be activators in some contexts, but may also serve other functions in the reaction system, such as alkylating a metal center or scavenging impurities. These compounds are within the general definition of "activator," but are not considered herein to be ion-forming activators."

30

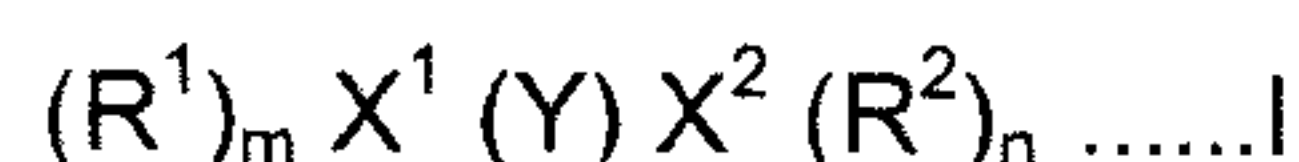
Both these publications broadly identify these "other" components as Group 13 reagents, divalent metal reagents, and alkali metal reagents and names diethyl zinc as one of a large group of reagents said to be "useful as activators for the catalyst compounds" with which the publications are concerned. However, neither of these publications exemplify such use of these "other" components and in particular of diethyl zinc, nor do they disclose any benefit
35 derived from the use of diethyl zinc, or any effect that such use of diethyl zinc might have on the extent of polymer formation in chromium catalysed olefin oligomerisation.

DISCLOSURE OF THE INVENTION

According to the present invention, there is provided a process for producing an oligomeric product by the oligomerisation of at least one olefinic compound, the process including:

a) providing an activated oligomerisation catalyst by combining, in any order,

- 5 i) a source of chromium;
 ii) a ligating compound of the formula I

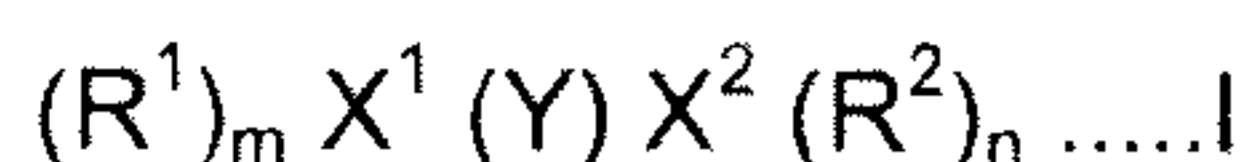


10 wherein: X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X^1 and/or X^2 allows for such oxidation;
 Y is a linking group between X^1 and X^2 ;
 15 m and n are independently 0, 1 or a larger integer; and
 R^1 and R^2 are independently hydrogen, a hydrocarbyl group, an organoheteryl group or a heterohydrocarbyl group, and R^1 being the same or different when $m > 1$, and R^2 being the same or different when $n > 1$;

- 20 iii) a catalyst activator or combination of catalyst activators;
 b) providing a zinc compound; and
 c) contacting the at least one olefinic compound with a composition containing the activated oligomerisation catalyst and the zinc compound, the zinc compound being present in a sufficient quantity such that the ratio of the molar amount of zinc in the
 25 zinc compound to the molar amount of chromium in the source of chromium is between 1 and 10000.

According to the present invention there is also provided a process for activating an oligomerisation catalyst to be used to produce an oligomeric product from at least one olefinic
 30 compound, the process comprising the combination, in any order, of

- i) a source of chromium;
 ii) a ligating compound of the formula I



35 wherein: X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X^1 and/or X^2 allows for such oxidation;
 40 Y is a linking group between X^1 and X^2 ;

m and n are independently 0, 1 or a larger integer; and
R¹ and R² are independently hydrogen, a hydrocarbyl group an
organoheteryl group or a heterohydrocarbyl group, and R¹ being the
same or different when m>1, and R² being the same or different
when n>1;

5

- iii) a catalyst activator or combination of catalyst activators;
- iv) a zinc compound, the zinc compound being present in a sufficient quantity such
that the ratio of the molar amount of zinc in the zinc compound to the molar
amount of chromium in the source of chromium is between 1 and 10000 .

10

In both the above aspects of the invention the zinc compound is present in the reaction of the
invention in a sufficient quantity such that the ratio of the molar amount of zinc in the zinc
compound to the molar amount of chromium in the source of chromium is preferably between
10 and 1000, and more preferably between 50 and 450.

15

The above aspects of the invention further may include the use of a solvent.

In this specification, the following definitions apply:

20

The term olefinic compound denotes an olefin or any compound which includes a carbon to
carbon double bond and olefinic moiety has a corresponding meaning;

A hydrocarbyl group is a univalent group formed by removing one hydrogen atom from a
hydrocarbon;

25

A hydrocarbylene group is a divalent group formed by removing two hydrogen atoms from the
same or different carbon atoms in a hydrocarbon, the resultant free valencies of which are not
engaged in a double bond;

30

A heterohydrocarbyl group is a univalent group formed by removing one hydrogen atom from
a heterohydrocarbon, that is a hydrocarbon compound which includes at least one hetero
atom (that is, not being H or C), and which group binds with other moieties through the
resultant free valency on that carbon atom;

35

A heterohydrocarbylene group is a divalent group formed by removing two hydrogen atoms
from the same or different carbon atoms in a heterohydrocarbon, the free valencies of which
are not engaged in a double bond and which group binds with other moieties through the
resultant free valencies on that or those carbon atoms;

An organoheteryl group is a univalent group containing carbon atoms and at least one hetero atom, and which has its free valence at an atom other than carbon;

A polar substituent is a substituent with a permanent electric or induced dipole moment; and

5 A non-polar substituent is a substituent without a permanent electric or induced dipole moment.

The oligomerisation catalyst of the present invention is preferably a trimerisation catalyst or a tetramerisation catalyst.

10 The oligomerisation process for producing an oligomeric product is preferably a trimerisation process for producing a trimeric product by the utilization of a trimerisation catalyst or a tetramerisation process for producing a tetrameric product by utilization of a tetramerisation catalyst.

15 The inventors of the present invention have surprisingly found that the incorporation of a zinc compound in the process described above, results in a reduction in solids formation, that is, polymer and in particular polyethylene formation relative to processes in which such zinc compound is absent.

Oligomerisation catalyst

20

Source of chromium (i):

The source of chromium may be an inorganic salt, an organic salt, a coordination compound or an organometallic complex.

25 Preferably the source of chromium is selected from the group consisting of chromium trichloride tris-tetrahydrofuran complex; (benzene)tricarbonyl chromium; chromium (III) octanoate; chromium hexacarbonyl; chromium (III) acetylacetonate, chromium (III) naphthenate, chromium (III) 2-ethylhexanoate, chromium (III) acetate, chromium (III) 2,2,6,6-tetramethylheptadionate, chromium (III) chloride. Preferably it is chromium (III)
30 acetylacetonate or chromium (III) 2-ethylhexanoate.

Ligating compound (ii):

X^1 and/or X^2 are preferably independently phosphorus or phosphorus oxidised by S or Se or N or O. Preferably X^1 and X^2 are the same, and most preferably both are P.

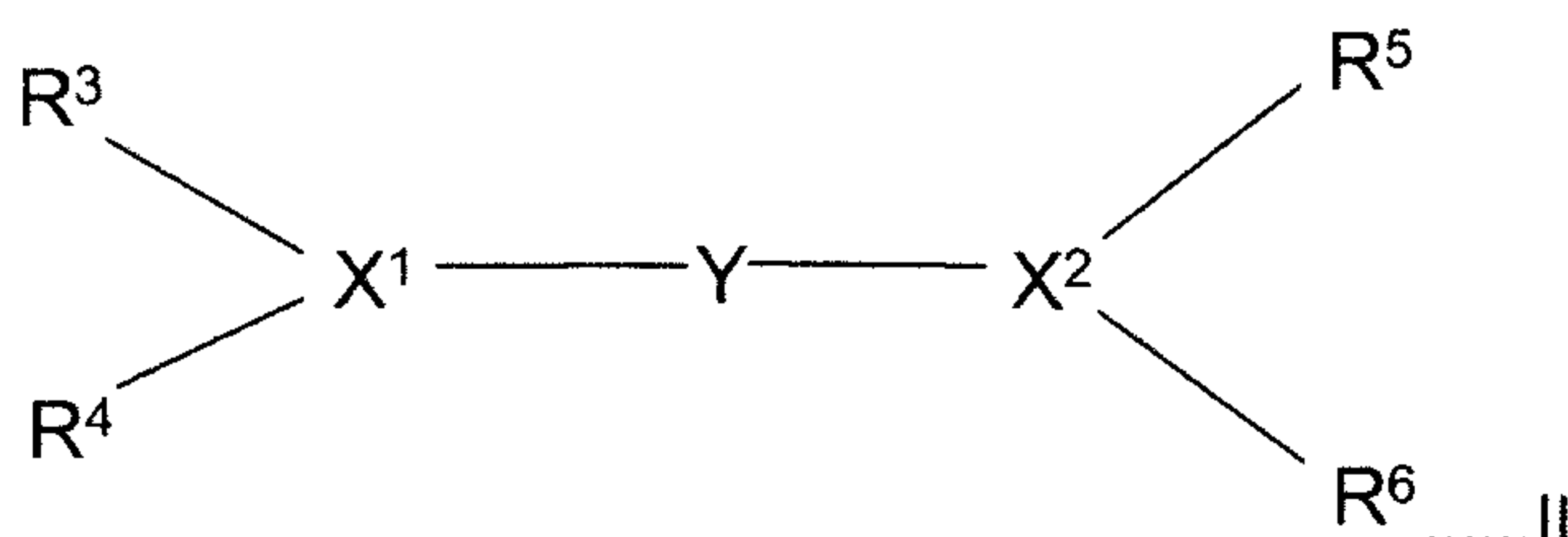
35

It will be appreciated that m and n are dependent on factors such as the valence and oxidation state of X^1 and X^2 , bond formation of Y with X^1 and X^2 respectively, and bond formation of R^1 and R^2 with X^1 and X^2 respectively. Preferably both m and n are not 0.

Preferably the ligating compound is a bidentate ligand.

Preferably the ligating compound is of the formula II

5



wherein Y is as defined herein, X¹ and X² are independently selected from the group consisting of nitrogen, phosphorus, arsenic, antimony and bismuth and R³ to R⁶ are each independently a hydrocarbyl group or a heterohydrocarbyl group.

10

Preferably X¹ and X² are independently selected from the group consisting of phosphorus and nitrogen. More preferably X¹ and X² are the same. Most preferably both X¹ and X² are phosphorus.

15

R³ to R⁶ may be independently selected from the group consisting of a non-aromatic moiety; an aromatic moiety; and a heteroaromatic moiety. Preferably each of R³ to R⁶ is an aromatic or heteroaromatic moiety, more preferably an aromatic moiety (including a substituted aromatic moiety). The aromatic moiety (or substituted aromatic moiety) may comprise phenyl or a substituted phenyl.

20

One or more of R³ to R⁶ may be a substituted hydrocarbyl group or a substituted heterohydrocarbyl group, of which at least one substituent is bound to a hydrocarbyl group or a heterohydrocarbyl group.

25

In this specification, a substituent with reference to moieties bound to X¹ and/or X² is a moiety (excluding H) that is bound to a linear structure or a cyclic structure bound to X¹ and/or X², but the substituent does not form part of the linear or cyclic structure.

30

The linear or cyclic structure may be selected from the group consisting of a linear hydrocarbyl, a linear heterohydrocarbyl, a cyclic hydrocarbyl and a cyclic heterohydrocarbyl group. Linear hydrocarbyl may include methyl, 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.

35

Linear heterohydrocarbyl may include methoxy, ethoxy, thiomethoxy, thioethoxy, methylsilyl, ethylsilyl, methylamino, methylphosphino, methoxymethyl and thiomethoxymethyl. 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 may include tetrahydrofuranyl, tetrahydrothiophenyl, pyrrolidenyl, piperidineyl, pyrrolineyl, oxazolyl, thiazolyl, furanyl, thiophenyl, pyrazolinyl, pyrazolyl, imidazolyl, benzofuranyl, coumaranyl and indolyl.

10

R^3 to R^6 may also be selected from a group of metallocenes such as a ferrocenyl, zirconocenyl and titanocenyl group.

15

Preferably R^3 to R^6 are aromatic moieties of which a ring atom of the aromatic ring structure is bound to either X^1 or X^2 and with a polar substituent bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X^1 or X^2 .

20

Preferably, if two or more of R^3 to R^6 are aromatic moieties with a ring atom of the aromatic ring structure bound to either X^1 and X^2 not more than two of said aromatic moieties R^3 and R^6 have a substituent bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X^1 or X^2 .

25

In one embodiment of the invention, R^3 to R^6 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 R^3 to R^6 does not include any polar substituent. In one embodiment of the invention at least two of (but preferably all of) R^3 to R^6 are aromatic moieties with a ring atom of the aromatic ring structure bound to X^1 or X^2 , but preferably not more than two of said aromatic moieties R^3 to R^6 have a non-polar substituent other than H bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X^1 or X^2 .

30

Preferably none of the aromatic moieties R^3 to R^6 have a non-polar substituent bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X^1 or X^2 . Preferably all of aromatic moieties R^3 to R^6 are non-substituted aromatic moieties.

35

Examples of suitable non-polar substituents include, but are not limited to, methyl, ethyl, ethenyl, propyl, iso-propyl, 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,

40

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.

- 5 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.

R³ and R⁴ may be the same and R⁵ and R⁶ may be the same. R³ to R⁶ may all be the same.

- 10 In another embodiment of the invention, R³ to R⁶ are the same or different and each is a hydrocarbyl group, or a heterohydrocarbyl group (preferably an organyl 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. One or more or all of R³ to R⁶ may be independently selected from the group
15 consisting of a substituted non-aromatic moiety; a substituted aromatic moiety; and a substituted heteroaromatic moiety. Preferably each of R³ to R⁶ is a substituted aromatic or a substituted heteroaromatic moiety, more preferably a substituted aromatic moiety. The substituted aromatic moiety may comprise a substituted phenyl. 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
20 aromatic ring structure bound to X¹ or X², but preferably not more than two of said aromatic moieties R³ to R⁶ have a substituent bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X¹ or X².

Any polar substituent on one or more of R³, R⁴, R⁵ and R⁶ may be electron donating.

- 25 Suitable polar substituents may be a methoxy, ethoxy, isopropoxy, C₃-C₂₀ alkoxy, phenoxy, methoxymethyl, methylthiomethyl, 1,3-oxazolyl, methoxymethoxy, hydroxyl, amino, pentafluorophenoxy, tosyl, methylsulfanyl, trimethylsiloxy, dimethylamino, sulphate, nitro, halides or the like.

- 30 Y may be selected from the group consisting of an organic linking group such as a hydrocarbylene, substituted hydrocarbylene, heterohydrocarbylene and a substituted heterohydrocarbylene; an inorganic linking group comprising either a single- or two-atom linker spacer; and a group comprising methylene; dimethylmethylene; ethylene; ethene-1,2-
35 diyl; propane-1,2-diyl, propane-1,3-diyl; cyclopropane-1,1-diyl; cyclopropane-1,2-diyl; cyclobutane-1,2-diyl, cyclopentane-1,2-diyl, cyclohexane-1,2-diyl, cyclohexane-1,1-diyl; 1,2-phenylene; naphthalene-1,8-diyl; phenanthrene-9,10-diyl, phenanthrene-4,5-diyl, 1,2-catecholate, 1,2-diarylhydrazine-1,2-diyl (-N(Ar)-N(Ar)-) where Ar is an aryl group; 1,2-dialkylhydrazine-1,2-diyl (-N(Alk)-N(Alk)-) where Alk is an alkyl group; -B(R⁷)-, -Si(R⁷)₂-, -
40 P(R⁷)- and -N(R⁷)- where R⁷ is hydrogen, a hydrocarbyl or heterocarbyl or halogen.

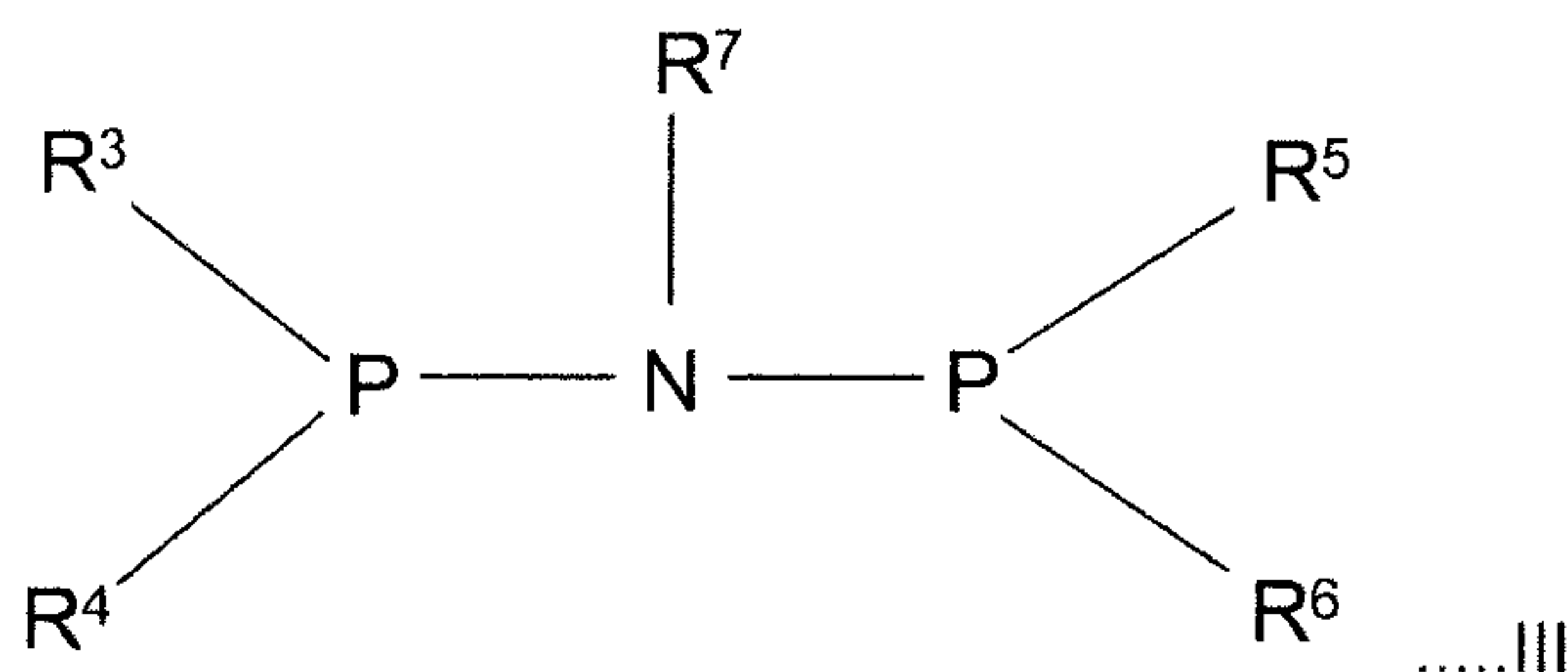
Preferably, Y may be $-N(R^7)-$ and R^7 may be selected from the group consisting of hydrogen, alkyl, substituted alkyl, aryl, substituted aryl, aryloxy, substituted aryloxy, halogen, alkoxy, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents. Preferably

5 R^7 may be a hydrocarbyl or a heterohydrocarbyl or an organoheteryl group. R^7 may be methyl, ethyl, propyl, isopropyl, cyclopropyl, allyl, butyl, tertiary-butyl, sec-butyl, cyclobutyl, pentyl, isopentyl, 1,2-dimethylpropyl (3-methyl-2-butyl), 1,2,2-trimethylpropyl (*R/S*-3,3-dimethyl-2-butyl), 1-(1-methylcyclopropyl)-ethyl, neopentyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclo-octyl, decyl, cyclodecyl, 1,5-dimethylheptyl, 1-methylheptyl, 2-naphthylethyl,

10 1-naphthylmethyl, adamantylmethyl, 1-adamantyl, 2-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,

15 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, or a 1,2,3,4-tetrahydronaphthyl.

20 Preferably the ligating compound is of the formula III



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

25

Preferably each of R^3 to R^6 is an alkyl (preferably methyl, ethyl or isopropyl) or aromatic (preferably phenyl or substituted phenyl).

30

The ligating compound may include a polymeric moiety to render the reaction product of the source of chromium 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 re-use 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 chromium 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.

The ligating compound may include multiple ligating units or derivatives thereof. Non-limiting
 5 examples of such ligands include dendrimeric ligands as well as ligands where the individual
 ligating units are coupled either *via* one or more of the R groups or *via* the linking group Y.
 More specific, but not limiting, examples of such ligands may include 1,2-di-(N(P(phenyl)₂)₂)-
 benzene, 1,4-di-(N(P(phenyl)₂)₂)-benzene, N(CH₂CH₂N(P(phenyl)₂)₂)₃, 1,4-di-
 (P(phenyl)N(methyl)P(phenyl)₂)-benzene, 1,2-di-(N(P(*p*-methoxyphenyl)₂)₂)-benzene, 1,4-di-
 10 (N(P(*p*-methoxyphenyl)₂)₂)-benzene, N(CH₂CH₂N(P(*p*-methoxyphenyl)₂)₂)₃ and 1,4-di-(P(*p*-
 methoxyphenyl)N(methyl)P(*p*-methoxyphenyl)₂)-benzene.

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.

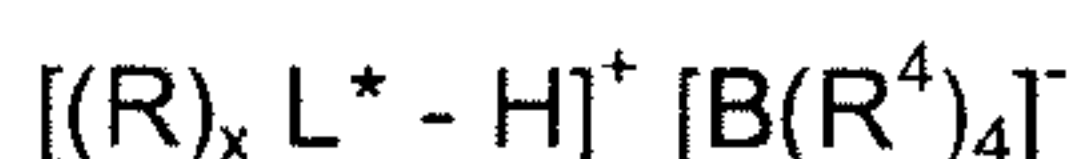
15 The oligomerisation catalyst may be prepared *in situ*, that is in the reaction mixture in which
 the oligomerisation reaction is to take place. Often the oligomerisation catalyst will be
 prepared *in situ*. Alternatively the catalyst may be pre-formed or partly pre-formed.

20 Activation

Activator (iii)

The catalyst activator may be a compound that generates an active catalyst when the
 activator is combined with the source of chromium and the ligating compound.

25 In one form of the invention the activator is an organoboron compound that includes a cation
 and a non-coordinating anion of the general formula



30 wherein:

L* is an atom selected from the group consisting of N, S and P;

the cation [(R)_x L* - H]⁺ is a Bronsted acid;

x is an integer 1, 2 or 3;

each R is the same or different and each is a -H, hydrocarbyl group
 35 or a heterohydrocarbyl group;

provided that at least one of R comprises at least 6 carbon atoms
 and provided further that the total number of carbon atoms in (R)_x
 collectively is greater than 12;

40 R⁴ independently at each occurrence is selected from the group
 consisting of hydride, dialkylamido, halide, alkoxide, aryloxyde,

hydrocarbyl, halosubstituted-hydrocarbyl radicals, halosubstituted-alkoxide, halosubstituted-aryloxide and a halosubstituted aromatic moiety with at least one halide substituent on the aromatic moiety.

5 $[(R)_x L^* - H]^+$ is a cation. More particularly, $[(R)_x L^* - H]^+$ is a Bronsted acid. A Bronsted acid is any compound that is capable of donating a hydrogen ion (proton).

Where L^* is an atom selected from the group consisting of N or P, the cation $[(R)_x L^* - H]^+$ may be represented by the formula



wherein:

$L_1 = N$ or P ;

R^1 , R^2 and R^3 are the same or different and each is a $-H$, hydrocarbyl group or a heterohydrocarbyl group; and

15 provided that at least one of R^1 , R^2 and R^3 comprises at least 6 carbon atoms and provided further that the total number of carbon atoms in R^1 , R^2 and R^3 collectively is greater than 12.

Where L^* is S, the cation $[(R)_x L^* - H]^+$ may be represented by the formula



wherein:

$L_2 = S$;

R^1 and R^2 are the same or different and each is a $-H$, hydrocarbyl group or a heterohydrocarbyl group; and

25 provided that at least one of R^1 and R^2 comprises at least 6 carbon atoms and provided further that the total number of carbon atoms in R^1 and R^2 collectively is greater than 12.

30 R^1 , R^2 and R^3 are each independently an aliphatic hydrocarbyl or an aliphatic heterohydrocarbyl group, preferably a saturated aliphatic hydrocarbyl or a saturated aliphatic heterohydrocarbyl, more preferably a substituted hydrocarbyl or a substituted heterohydrocarbyl where the substituents may be non-polar groups.

35 Suitable examples of R^1 , R^2 and R^3 include, but are not limited to, methyl, ethyl, ethylenyl, propyl, propenyl, propynyl, butyl, pentyl, hexyl, cyclohexyl, 2-methylcyclohexyl, 2-ethylcyclohexyl, octyl, 2-ethylhexyl, iso-octyl, decyl, dodecyl, tetradecyl, octadecyl, 2-isopropylcyclohexyl, benzyl, phenyl, tolyl, xylyl, o-methylphenyl, o-ethylphenyl, o-isopropylphenyl, o-t-butylphenyl, biphenyl, naphthyl and the like.

40

Examples of suitable non-polar substituents include, but are not limited to, butyl, pentyl, hexyl, sec-hexyl, cyclohexyl, 2-methylcyclohexyl, 2-ethylcyclohexyl, 2-isopropylcyclohexyl, cyclohexenyl, hexenyl, hexynyl, octyl, cyclo-octyl, cyclo-octenyl, 2-ethylhexyl, iso-octyl, decyl, benzyl, phenyl, tolyl, xylyl, o-methylphenyl, o-ethylphenyl, o-isopropylphenyl, o-*t*-butylphenyl, cumyl, mesityl, biphenyl, naphthyl, anthracenyl, and the like.

In one embodiment of the invention, at least one of R comprises 6 to 40 carbon atoms with a total of from 13 to 100 carbons. Preferably, at least one of R comprises 6 to 40 carbon atoms with a total of from 21 to 90 total carbons.

10

It is believed that the presence of long chain hydrocarbon substituents, that is hydrocarbon substituents having at least 6 carbon atoms, renders the activator more soluble in aliphatic solutions thereby facilitating activation of the catalyst. Moreover, it is believed that where the total number of carbon atoms in the hydrocarbyl substituents that R¹, R² and R³ have is greater than 12, the solubility of the catalyst activator in aliphatic compounds will be increased thereby resulting in improved olefin oligomerisation with low solid formation.

15

As discussed herein above, R⁴ may be a halosubstituted aromatic moiety with at least one halide substituent on the aromatic ring. In a preferred embodiment of the invention, the halosubstituted aromatic moiety is pentafluorophenyl.

20

Illustrative, but non-limiting examples of organoboron compounds having a cation and a non-coordinating anion of the formula of the present invention, set out herein above, include

dihexyl(methyl)ammonium tetrakis(pentafluorophenyl) borate;
dioctyl(methyl)ammonium tetrakis(pentafluorophenyl) borate;
methyldi(octyl)ammonium tetrakis(pentafluorophenyl) borate;
decyldi(methyl)ammonium tetrakis(pentafluorophenyl) borate;
dodecyldi(methyl)ammonium tetrakis(pentafluorophenyl) borate;
tetradecyldi(methyl)ammonium tetrakis(pentafluorophenyl) borate;
hexaadecyldi(methyl)ammonium tetrakis(pentafluorophenyl) borate;
octadecyldi(methyl)ammonium tetrakis(pentafluorophenyl) borate;
eicosyldi(methyl)ammonium tetrakis(pentafluorophenyl) borate;
methyldi(decyl)ammonium tetrakis(pentafluorophenyl) borate;
methyldi(dodecyl)ammonium tetrakis(pentafluorophenyl) borate;
methyldi(tetradecyl)ammonium tetrakis(pentafluorophenyl) borate;
methyldi(hexadecyl)ammonium tetrakis(pentafluorophenyl) borate;
methyldi(octadecyl)ammonium tetrakis(pentafluorophenyl) borate;
methyldi(eicosyl)ammonium tetrakis(pentafluorophenyl) borate;
trihexylammonium tetrakis(pentafluorophenyl) borate;
trioctylammonium tetrakis(pentafluorophenyl) borate;

40

- tri(2-ethylhexyl)ammonium tetrakis(pentafluorophenyl) borate;
 tri(iso-octyl)ammonium tetrakis(pentafluorophenyl) borate;
 tridecylammonium tetrakis(pentafluorophenyl) borate;
 tridodecylammonium tetrakis(pentafluorophenyl) borate;
 5 tritetradecylammonium tetrakis(pentafluorophenyl) borate;
 trihexadecylammonium tetrakis(pentafluorophenyl) borate;
 trioctadecylammonium tetrakis(pentafluorophenyl) borate;
 trieicosylammonium tetrakis(pentafluorophenyl) borate;
 hexyldi(n-butyl)ammonium tetrakis(pentafluorophenyl) borate;
 10 octyldi(n-butyl)ammonium tetrakis(pentafluorophenyl) borate;
 decyldi(n-butyl)ammonium tetrakis(pentafluorophenyl) borate;
 dodecyldi(n-butyl)ammonium tetrakis(pentafluorophenyl) borate;
 octadecyldi(n-butyl)ammonium tetrakis(pentafluorophenyl) borate;
 N,N-dihexylanilinium tetrakis(pentafluorophenyl) borate;
 15 N,N-dioctylanilinium tetrakis(pentafluorophenyl) borate;
 N,N-didodecylanilinium tetrakis(pentafluorophenyl) borate;
 N-methyl-N-dodecylanilinium tetrakis(pentafluorophenyl) borate;
 N,N-di(octadecyl)(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl) borate;
 cyclohexyldi(dodecyl)ammonium tetrakis(pentafluorophenyl) borate;
 20 methyl(di(dodecyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate;
 trioctylphosphonium tetrakis(pentafluorophenyl) borate;
 trihexylphosphonium tetrakis(pentafluorophenyl) borate;
 tributylphosphonium tetrakis(pentafluorophenyl) borate;
 dioctyl(methyl)phosphonium tetrakis(pentafluorophenyl) borate;
 25 dimethyl(octyl)phosphonium tetrakis(pentafluorophenyl) borate;
 bis(dihexylsulfide)onium tetrakis(pentafluorophenyl) borate, $[\{(C_6H_{13})_2S\}_2H][B(C_6F_5)_4]$;
 bis(dioctylsulfide)onium tetrakis(pentafluorophenyl) borate, $[\{(C_8H_{17})_2S\}_2H][B(C_6F_5)_4]$;
 bis(didecylsulfide)onium tetrakis(pentafluorophenyl) borate, $[\{(C_{10}H_{21})_2S\}_2H][B(C_6F_5)_4]$;
 and
 30 bis(didodecylsulfide)onium tetrakis(pentafluorophenyl) borate, $[\{(C_{12}H_{25})_2S\}_2H][B(C_6F_5)_4]$.

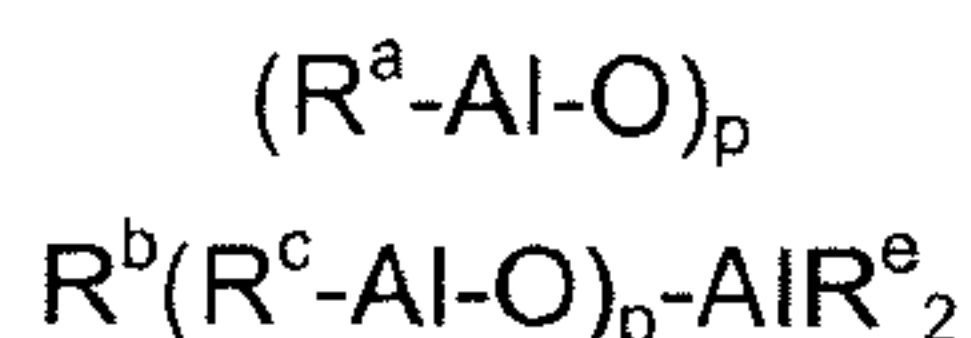
The source of chromium and the organoboron compound may be combined in proportions to
 provide organoboron compound /chromium molar ratios from about 0.1 to 50 organoboron to
 1 chromium, preferably from about 0.8 to 20 organoboron to 1 chromium, and more preferably
 35 from 1 to 10 organoboron to 1 chromium.

Preferably the concentration of the boron in the activated catalyst prior to dilution is at least 0.01 mmol/l. Preferably, the concentration of the boron is 0.1 - 100 mmol/l, and most preferably the concentration is 0.1 - 10 mmol/l.

5

Further non-limiting examples of activators, include alumoxanes, aluminum alkyls, other metal or main group alkyl or aryl compounds, ionizing activators, which may be neutral or ionic, Lewis acids, reducing agents, oxidizing agents, and combinations thereof. In one embodiment, aluminoxane activators are utilized as an activator in the compositions useful in the invention. Aluminoxanes are generally oligomeric compounds containing -Al(R*)-O- sub-
 10 units, where R* is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), ethylalumoxane, isobutylalumoxane, and modified methylalumoxanes (MMAO), which include alkyl groups other than methyl such as ethyl, isobutyl, and n-octyl. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the
 15 abstractable ligand of the catalyst is a halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. The activator compounds comprising Lewis-acid activators and in particular alumoxanes are specifically characterized by the following general formulae:

20



where R^a, R^b, R^c and R^e are, independently a C₁-C₃₀ alkyl radical, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, and "p" is an integer from 1 to about 50.

25

Most specifically, R^a, R^b, R^c and R^d are each methyl and "p" is a least 4. When an alkyl aluminum halide or alkoxide is employed in the preparation of the alumoxane, one or more R^a, R^b, R^c or R^e are groups may be halide or alkoxide.

30

It is recognized that alumoxane is not a discrete material. An alumoxane is generally a mixture of both the linear and cyclic compounds. A typical alumoxane will contain free trisubstituted or trialkyl aluminum, bound trisubstituted or trialkyl aluminum, and alumoxane molecules of varying degree of oligomerisation. For some embodiments, it is preferred that methylalumoxanes contain lower levels of trimethylaluminum. Lower levels of trimethylaluminum can be achieved by reaction of the trimethylaluminum with a Lewis base or
 35 by vacuum distillation of the trimethylaluminum or by any other means known in the art.

40

For further descriptions, see U.S. Pat. Nos. 4,665,208, 4,952,540, 5,041,584, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031 and EP 0561476A1, EP 0279586B1, EP 0516476A1, EP 0594218A1 and WO 94/10180.

When the activator is an alumoxane (modified or unmodified), some embodiments select the maximum amount of activator at a 5000-fold molar excess Al/Cr over the catalyst precursor.

5 The minimum preferred activator-to-catalyst-precursor is a 1:1 molar ratio. More specifically, the Al/Cr ratio is from 1000:1 to 100:1.

Alumoxanes may be produced by the hydrolysis of the respective trialkylaluminum compound. MMAO may be produced by the hydrolysis of trimethylaluminum and a higher
10 trialkylaluminum such as triisobutylaluminum.

There are a variety of methods for preparing alumoxane and modified alumoxanes, non-limiting examples of which are described in U.S. Pat. Nos. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032,
15 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838, 5,731,253, 5,731,451, 5,744,656, 5,847,177, 5,854,166, 5,856,256 and 5,939,346 and European publications EP 0561476A1, EP 0279586B1, EP 0594218A1 and EP 0586665B1, and PCT publications WO 94/1 0180 and WO 99/15534, all of which are herein fully incorporated by reference.

20 Aluminum alkyl or organoaluminum compounds which may be utilized as activators (or scavengers) include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, ethylaluminum dichloride, diethylaluminum chloride, diethylaluminum ethoxide and the like.

25 Ionizing Activators

In some embodiments, the activator includes compounds that may abstract a ligand making the metal complex cationic and providing a charge-balancing non-coordinating or weakly
30 coordinating anion. The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to said cation or which is only weakly coordinated to said cation thereby remaining sufficiently labile to be displaced by a Lewis base (for example, a neutral Lewis base).

35 It is within the scope of this invention to use an ionizing or stoichiometric activator, neutral or ionic, such as tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, a tris(pentafluorophenyl)boron metalloid precursor or a tris(heptafluoronaphthyl)boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (U.S. Pat. No. 5,942,459) or combination thereof. It is also within the scope of this invention to use neutral or

ionic activators alone or in combination with alumoxane or modified alumoxane activators.

Examples of neutral stoichiometric activators include tri-substituted boron, tellurium, aluminum, gallium and indium or mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogen, substituted alkyls, aryls, arylhalides, alkoxy and halides. In some embodiments, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds and mixtures thereof, preferred are alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls). In other embodiments, the three groups are alkyls having 1 to 4 carbon groups, phenyl, naphthyl or mixtures thereof. In further embodiments, the three groups are halogenated, specifically fluorinated, aryl groups. In even further embodiments, the neutral stoichiometric activator is tris(perfluorophenyl) boron or tris(perfluoronaphthyl) boron.

Ionic stoichiometric activator compounds may contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP 0570982A1, EP 0520732A1, EP 0495375A1, EP 0500944B1, EP 0277003A1 and EP 0277004A1, and U.S. Pat. Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,384,299 and 5,502,124 and U.S. Pat. App. No. 08.285,380, filed August 3, 1994, all of which are herein fully incorporated by reference.

Ionic catalysts can be prepared by reacting a Cr compound with some neutral Lewis acids, such as $B(C_6F_5)_3$, which upon reaction with the abstractable ligand (X) of the Cr compound forms an anion, such as $[B(C_6F_5)_3(X)]^-$, which stabilizes the cationic Cr species generated by the reaction. The catalysts can be prepared with activator components, which are ionic compounds or compositions.

In some embodiments, compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which is optionally a Brønsted acid capable of donating a proton, and a compatible non-coordinating anion which is capable of stabilizing the active catalyst species which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic substrates or other neutral Lewis bases such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions useful herein have been disclosed in EP 0277003A1 and EP 0277004A1 published 1988: anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core; and, anions comprising a plurality of boron atoms such as carboranes, metallocarboranes and boranes.

In one preferred embodiment, the stoichiometric activators include a cation and an anion component, and may be represented by the following formula:



where L is a neutral Lewis base; H is hydrogen; $(L-H)^+$ is a Bronsted acid; A^{d-} is a non-coordinating anion having the charge d^- ; and d is an integer from 1 to 3.

The cation component, $(L-H)^{d+}$ may include Brönsted acids such as protons or protonated Lewis bases or reducible Lewis acids capable of protonating or abstracting a moiety, such as an alkyl or aryl, from the bulky ligand chromium catalyst precursor, resulting in a cationic transition metal species.

The activating cation $(L-H)^{d+}$ may be a Brönsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, specifically ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo-N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from diethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers such as dimethyl ether diethyl ether, tetrahydrofuran and dioxane, sulfoniums from thioethers, such as diethyl thioethers and tetrahydrothiophene, and mixtures thereof. The activating cation $(L-H)_d^+$ may also be a moiety such as silver, tropylium, carbeniums, ferroceniums and mixtures, specifically carboniums and ferroceniums. In one embodiment $(L-H)^{d+}$ can be triphenyl carbonium.

The anion component A^{d-} includes those having the formula $(M^{k+}Q_n)^{d-}$ wherein k is an integer from 1 to 5; n is an integer from 2-6; $n - k = d$; M is an element selected from Group 13 of the Periodic Table of the Elements, specifically boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q a halide. Specifically, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more specifically each Q is a fluorinated aryl group, and most specifically each Q is a pentafluoryl aryl group. Examples of suitable A^{d-} also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

In one embodiment of the invention $(M^{k+}Q_n)^{d-}$ may be selected from the group containing the anion $[Al(OR)_4]^-$, a compound including a moiety $Al(OR)_3$ and a salt containing the anion $[Ta(OR)_6]^-$ wherein R is defined as above.

In one embodiment of the invention $(M^{k+}Q_n)^{d-}$ may be selected from the group consisting of $Al(OC_6F_5)_3$; $[Al\{OC(CF_3)_3\}_4]^-$; $[Al(OC_6F_5)_4]^-$; $[Al(C_6F_4O_2)_2]^-$; $[Al\{OC(CF_3)_2C(CF_3)_2O\}_2]^-$; $[AlF\{OC(CF_3)_3\}_3]^-$; $[Al_2F\{OC(CF_3)_3\}_6]^-$; $(Z)Al\{OCH(C_6F_5)_2\}_3$; $(Z)Al\{OC(CF_3)_3\}_3$ and $[Ta(OC_6F_5)_6]^-$ which moiety Z is not -AR as defined above.

Illustrative, but not limiting examples of boron compounds which may be used as a catalyst activator in the preparation of the improved catalysts of this invention are tri-substituted ammonium salts such as:

- 10 trimethylammonium tetraphenyl borate,
triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,
15 N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate,
tropyllium tetraphenylborate,
triphenylcarbenium tetraphenylborate,
20 triphenylphosphonium tetraphenylborate,
triethylsilylium tetraphenylborate,
benzene(diazonium)tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl)borate,
triethylammonium tetrakis(pentafluorophenyl)borate,
25 tripropylammonium tetrakis(pentafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl)borate,
30 N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate,
tropyllium tetrakis(pentafluorophenyl)borate,
triphenylcarbenium tetrakis(pentafluorophenyl)borate,
triphenylphosphonium tetrakis(pentafluorophenyl)borate,
triethylsilylium tetrakis(pentafluorophenyl)borate,
35 benzene(diazonium) tetrakis(pentafluorophenyl)borate,
trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate,
triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate,
40 dimethyl(t-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,

- N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
5 triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
trimethylammonium tetrakis(perfluoronaphthyl)borate,
10 triethylammonium tetrakis(perfluoronaphthyl)borate,
tripropylammonium tetrakis(perfluoronaphthyl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
15 N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate,
tropillium tetrakis(perfluoronaphthyl)borate,
triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
triphenylphosphonium tetrakis(perfluoronaphthyl)borate,
20 triethylsilylium tetrakis(perfluoronaphthyl)borate,
benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
trimethylammonium tetrakis(perfluorobiphenyl)borate,
triethylammonium tetrakis(perfluorobiphenyl)borate,
tripropylammonium tetrakis(perfluorobiphenyl)borate,
25 tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
tri(t-butyl)ammonium tetrakis(perfluorobiphenyl)borate,
N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate,
30 tropillium tetrakis(perfluorobiphenyl)borate,
triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
triphenylphosphonium tetrakis(perfluorobiphenyl)borate,
triethylsilylium tetrakis(perfluorobiphenyl)borate,
benzene(diazonium) tetrakis(perfluorobiphenyl)borate,
35 trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
tri(t-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
40 N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,

- N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tropillium
 tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylphosphonium
 5 tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 and dialkyl ammonium salts such as:
 di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, and dicyclohexylammonium
 10 tetrakis(pentafluorophenyl)borate;
 and additional tri-substituted phosphonium salts such as
 tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate, and
 tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate.
- 15 Most specifically, the ionic stoichiometric activator $(L-H)^{d+} (A^{d-})$ is
 N,N-dimethylanilinium tetra(perfluorophenyl)borate,
 N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
 N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
 N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 20 triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
 triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
 triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, or
 triphenylcarbenium tetra(perfluorophenyl)borate.
- 25 Other examples of preferred ionizing activators include, $[HNMe(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$;
 $[HNPh(C_{18}H_{37})_2]^+[B(C_6F_5)_4]^-$ and $[((4-n-Bu-C_6H_4)NH(n-hexyl)_2)^+[B(C_6F_5)_4]^-]$ and $[((4-n-Bu-$
 $C_6H_4)NH(n-decyl)_2)^+[B(C_6F_5)_4]^-]$. Specific preferred $(L-H)^+$ cations are N,N-dialkylanilinium
 cations, such as $HNMe_2Ph^+$, substituted N,N-dialkylanilinium cations, such as $(4-n-Bu-$
 $C_6H_4)NH(n-C_6H_{13})_2^+$ and $(4-n-Bu-C_6H_4)NH(n-C_{10}H_{21})_2^+$ and $HNMe(C_{18}H_{37})_2^+$. Specific
 30 examples of anions are tetrakis(3,5-bis(trifluoromethyl)phenyl)borate and
 tetrakis(pentafluorophenyl)borate.

In one embodiment, activation methods using ionizing ionic compounds not containing an
 active proton but capable of producing an active oligomerization catalyst are also
 35 contemplated. Such methods are described in relation to metallocene catalyst compounds in
 EP 0426637A1, EP 0573403A1 and U.S. Patent No. 5,387,568, which are all herein
 incorporated by reference.

The process can also employ activator compounds that are initially neutral Lewis acids but
 40 form a cationic metal complex and a noncoordinating anion, or a zwitterionic complex upon

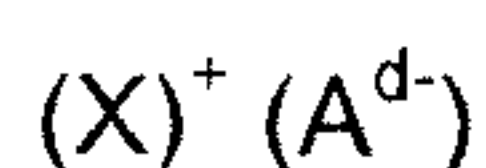
reaction with the compounds of this invention. For example, tris(pentafluorophenyl) boron or aluminum may act to abstract a hydrocarbyl or hydride ligand to yield a cationic metal complex and stabilizing noncoordinating anion.

- 5 In another embodiment, the aforementioned activator compounds can also react with the compounds of the present invention to produce a neutral, uncharged catalyst capable of selective ethylene oligomerization. For example, Lewis acidic reagents such as, for example, alkyl or aryl aluminum or boron compounds, can abstract a Lewis basic ligand such as, for example, THF or Et₂O, from a compound yielding a coordinatively unsaturated catalyst
10 capable of selective ethylene oligomerization.

- When the cations of noncoordinating anion precursors are Brønsted acids such as protons or protonated Lewis bases (excluding water), or reducible Lewis acids such as ferrocenium or silver cations, or alkali or alkaline earth metal cations such as those of sodium, magnesium or
15 lithium, the activator-to-catalyst-precursor molar ratio may be any ratio, however, useful ratios can be from 1000:1 to 1:1.

Combinations of two or more activators may also be used in the practice of this invention.

- 20 Another suitable ion forming, activator compounds comprise a salt of a cationic agent and a noncoordinating, compatible anion characterized by the general formula:



- 25 X⁺ is a cationic agent capable of accepting/abstracting an anionic group; A^{d-} is a non-coordinating anion having the charge d-; and d is an integer from 1 to 3.

Specific examples of (X)⁺ include R₃C⁺, R₃Si⁺, R₂Al⁺, where R is hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals.

- 30 Specific examples include but are not limited to Ph₃C⁺, Et₃Si⁺, (C₁₈H₃₇)₂MeSi⁺, Cp₂Al⁺.

- Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion characterized by the general formula: (OX^{e+})_d(A^{d-})_e where OX^{e+} is a cationic oxidizing agent having a charge of e+; e is an integer
35 from 1 to 3; d is an integer from 1 to 3, and A^{d-} is as previously defined. Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, ammoniumyl (R₃N⁺), Ag⁺, or Pb²⁺. Preferred embodiments of A^{d-} are those anions previously defined with respect to the Bronsted acid containing activators, especially tetrakis(pentafluorophenyl)borate.

Specific examples of ammoniumyl groups include (p-Br-C₆H₄)₃N⁺, (p-NO₂-C₆H₄)₃N⁺, (p-F-C₆H₄)₃N⁺, (p-Me-C₆H₄)₃N⁺, (p-OMe-C₆H₄)₃N⁺.

5 Group 13 Reagents, Divalent Metal Reagents, and Alkali Metal Reagents

Other general activators or compounds useful in an oligomerization reaction may be used. These compounds may be activators in some contexts, but may also serve other functions in the reaction system, such as alkylating a metal center or scavenging impurities. These
 10 compounds are within the general definition of "activator," but are not considered herein to be ion-forming activators. These compounds include a group 13 reagent that may be characterized by the formula G¹³R⁵⁰_{3-p}D_p where G¹³ is selected from the group consisting of B, Al, Ga, In, and combinations thereof, p is 0, 1 or 2, each R⁵⁰ is independently selected from the group consisting of hydrogen, halogen, and optionally substituted alkyl, alkenyl, alkynyl,
 15 heteroalkyl, heteroalkenyl, heteroalkynyl, aryl, heteroaryl, and combinations thereof, and each D is independently selected from the group consisting of halogen, hydrogen, alkoxy, aryloxy, amino, mercapto, alkylthio, arylthio, phosphino and combinations thereof.

In other embodiments, the group 13 activator is an oligomeric or polymeric alumoxane
 20 compound, such as methylalumoxane and the known modifications thereof. See, for example, Barron, "Alkylalumoxanes, Synthesis, Structure and Reactivity", pp. 33-67 in Metallocene-Based Polyolefins: Preparation, Properties and Technology, J. Schiers and W. Kaminsky (eds.), Wiley Series in Polymer Science, John Wiley & Sons Ltd., Chichester, England, 2000, and references cited therein.

25 In other embodiments, a divalent metal reagent may be used that is characterized by the general formula M'R⁵⁰_{2-p'}D_{p'} and p' is 0 or 1 in this embodiment and R⁵⁰ and D are as defined above. M' is the metal and is selected from the group consisting of Mg, Ca, Sr, Ba, Zn, Cd, Cu and combinations thereof.

30 In still other embodiments, an alkali metal reagent may be used that is defined by the general formula M^{iv}R⁵⁰ and in this embodiment R⁵⁰ is as defined above, and M^{iv} is the alkali metal and is selected from the group consisting of Li, Na, K, Rb, Cs and combinations thereof. Additionally, hydrogen and/or silanes may be used in the catalytic composition or added to
 35 the polymerization system. Silanes may be characterized by the formula SiR⁵⁰_{4-q}D_q where R⁵⁰ is defined as above, q is 1, 2, 3 or 4 and D is as defined above, with the proviso that at least one D is hydrogen.

40 Non-limiting examples of Group 13 reagents, divalent metal reagents, and alkali metal reagents useful as activators for the catalyst compounds described above include methyl

lithium, butyl lithium, phenyl lithium, dihexylmercury, butylmagnesium, diethylcadmium, benzylpotassium, tri-n-butyl aluminum, diisobutyl ethylboron, diethylcadmium, and tri-n-amyl boron, and, in particular, the aluminum alkyls, such as hexyl-aluminum, ethylaluminum, methylaluminum, and isobutyl aluminum, diisobutyl aluminum bromide, diethylaluminum chloride, ethylaluminum dichloride, isobutyl boron dichloride, methyl magnesium chloride, ethyl beryllium chloride, ethyl calcium bromide, diisobutyl aluminum hydride, methyl cadmium hydride, diethyl boron hydride, hexylberyllium hydride, dipropylboron hydride, octylmagnesium hydride, dichloroboron hydride, di-bromo-aluminum hydride and bromocadmium hydride. Other Group 13 reagents, divalent metal reagents, and alkali metal reagents useful as activators for the catalyst compounds described above are known to those in the art, and a more complete discussion of these compounds may be found in U.S. Pat. Nos. 3,221,002 and 5,093,415, which are herein fully incorporated by reference.

Other activators include those described in PCT publication WO 98/0751 such as tris(2,2',2''-nonafluorobiphenyl) fluoroaluminate, which publication is fully incorporated herein by reference. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, EP 0573120B1, PCT publications WO 94/07928 and WO 95/14044 and U.S. Pat. Nos. 5,153,157 and 5,453,410, all of which are herein fully incorporated by reference.

Other suitable activators are disclosed in WO 98/09996, incorporated herein by reference, which describes activating bulky ligand metallocene catalyst compounds with perchlorates, periodates and iodates including their hydrates. WO 98/30602 and WO 98/30603, incorporated by reference, describe the use of lithium (2,2'-bisphenyl-ditrimethylsilicate)•4THF as an activator for a bulky ligand metallocene catalyst compound.

WO 99/18135, incorporated herein by reference, describes the use of organo-boron-aluminum activators. EP 0781299B1 describes using a silylium salt in combination with a non-coordinating compatible anion. Also, methods of activation such as using radiation (see EP 0615981B1 herein incorporated by reference), electro-chemical oxidation, and the like are also contemplated as activating methods for the purposes of rendering the chromium complexes or compositions active for the selective oligomerization of olefins. Other activators or methods are described in for example in U.S. Pat. Nos. 5,849,852, 5,859,653 and 5,869,723 and in WO 98/32775 and WO 99/42467 (dioctadecylmethylammonium-bis(tri(pentafluorophenyl)borane) benzimidazolide), which are herein incorporated by reference.

Additional optional activators include metal salts of noncoordinating or weakly coordinating anions, for example where the metal is selected from Li, Na, K, Ag, Ti, Zn, Mg, Cs, and Ba.

Co-activator

5

Preferably the co-activator is an organoaluminium compound and/or an organoboron compound. Alternatively it may be an organic salt such as methyl lithium and/or methyl magnesium bromide, or an inorganic acid or salt such as tetrafluoroboric acid etherate, silver tetrafluoroborate, sodium hexafluoroantimonate, and the like.

10

Examples of suitable organoboron compounds are boroxines, triethylborane, tris(pentafluorophenyl)borane, tributyl borane and the like.

15

Suitable organoaluminium compounds include compounds of the formula $Al(R^9)_3$ (R^9 being the same or different), where each R^9 is independently an organyl group, a halogenated organyl group or a halide, with at least one of R^9 being an organyl group or a halogenated organyl group. Examples include trimethylaluminium (TMA), triethylaluminium (TEA), triisobutylaluminium (TIBA), tri-*n*-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, aluminium isopropoxide, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and aluminoxanes.

20

Aluminoxanes 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.

25

Mixtures of different aluminoxanes may also be used in the process.

In an embodiment of the invention the co-activator may comprise a compound of the formula



30

wherein M' is selected from the group consisting of a group 3A atom, a group 4A atom and a metal atom, including an alkali metal atom and an alkaline earth metal atom;

n is 1 or a larger integer; and

35

R' is an organic group, R' being the same or different when n is larger than 1.

Preferably M' is selected from the group consisting of a group 3A atom, a group 4A atom, and a transition metal atom. Preferably the R group is bound to a group 3A atom. Preferably the group 3A atom is selected from the group consisting of Al and B, preferably it is Al.

40

The organic group R may be an organyl group, and preferably it comprises a hydrocarbyl group, preferably it comprises an alkyl group, preferably methyl, ethyl or a larger alkyl group.

5 In one embodiment of the invention the co-activator comprises AlR''_3 wherein R'' is an alkyl group.

The co-catalyst may be selected from the group consisting of trimethylaluminium (TMA); triethylaluminium (TEA), tributylaluminium, tri-isobutylaluminium (TIBA) and tri-n-octylaluminium.

10

It will be appreciated that TMA is relatively expensive and accordingly the use thereof may be wished to be avoided. It has been found that by using an activator as defined in the present invention in combination with a co-activator as defined above (but excluding MAO) the use of TMA can be avoided as a co-catalyst.

15

It is foreseen that a co-activator as defined hereinabove will usually be used in combination with an activator as defined above.

20

In use, where both an activator and a co-activator are used, the co-activator may be added first and the activator may be added subsequently.

Zinc compound

25

An additive can be used in the form of a zinc-containing species. The species can be any form of zinc or any zinc containing compound. The zinc compound may undergo reaction *in situ* with the trialkylaluminium to form a new zinc species *in situ*.

30

Specific examples of suitable zinc compounds include zinc, activated zinc, zinc halides, zinc alkyls, zinc oxygenates (including zinc acetate, acetylacetonates and carboxylates) and zinc porphyrin. Preferably, the zinc compound is zinc dialkyl, most preferably dimethyl zinc or diethyl zinc.

35

The zinc compound is present in the reaction of the invention in a sufficient quantity such that the ratio of the molar amount of zinc in the zinc compound to the molar amount of chromium in the source of chromium is between 1 and 10000, preferably between 10 and 1000, and more preferably between 50 and 450.

40

The zinc may be used as any concentration of stock solution and the concentration *in situ* in the reactor should be between 0.0001 mmol/L and 1 mol/L, more preferably between 0.001 mmol/L and 0.1 mol/L, and most preferably between 0.01 mmol/L and 0.01 mol/L.

The zinc compound may be added at any stage during the activation process, most preferably it is added directly to the reactor. The zinc may be used as a mixed stock solution with the trialkylaluminium, or with any other component.

- 5 The Applicant has found that the use of the zinc compound in conjunction with the activator compound significantly reduces the level of solids/polymer formed as by-product during the oligomerisation reaction.

Olefinic compound to be oligomerised

- 10 The olefinic compound may comprise a single olefinic compound or a mixture of olefinic compounds. In one embodiment of the invention it may comprise a single olefin.

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 ethylene, propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, and 1-octene, 1-nonene, 1-decene, 3-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, styrene, *p*-methyl styrene, 1-dodecene or combinations thereof. Preferably, it comprises ethylene or propene, preferably ethylene. The ethylene may be used to produce hexene and/or octene, preferably 1-hexene and/or 1-octene.

Oligomerisation

The oligomerisation process may comprise a trimerisation process, alternatively or additionally it may comprise a tetramerisation process.

25 The process may be oligomerisation of two or more different olefinic compounds to produce an oligomer containing the reaction product of the two or more different olefinic compounds. Preferably however, the oligomerisation (preferably trimerisation and/or tetramerisation) comprises the oligomerisation of a single monomer olefinic compound.

30 In one preferred embodiment of the invention the oligomerisation process is oligomerisation of a single α -olefin to produce an oligomeric α -olefin. Preferably it comprises the trimerisation and/or tetramerisation of ethylene, preferably to 1-hexene and/or 1-octene.

Oligomeric product

35 The oligomeric product may be an olefin, or a compound including an olefinic moiety. Preferably the oligomeric product includes an olefin, more preferably an olefin containing a single carbon-carbon double bond, and preferably it includes an α -olefin. The olefin product may include hexene, preferably 1-hexene, but more preferably it includes octene, preferably

1-octene. In a preferred embodiment of the invention the olefinic product includes a mixture of hexene and octene, preferably a mixture of 1-hexene and 1-octene.

5 In one preferred embodiment of the invention the oligomerisation process is a selective process to produce an oligomeric product containing more than 30% by mass of a single olefin product. The olefin product may be hexene, preferably 1-hexene, but alternatively it may be octene, preferably 1-octene.

10 Preferably the product contains at least 35% of the said olefin, preferably α -olefin, but it may be more than 40%, 50%, or even 60% by mass.

The olefinic product may be branched, but preferably it is non-branched.

Catalyst preparation

15 It is foreseen that i) the source of chromium and ii) the ligating compound (referred to in (a) of the main statement of the invention) may be first reacted together and the resulting product may even be isolated, before combining it with the catalyst activator iii). However, i), ii) and iii) may be combined in any suitable order in the presence or absence of a solvent, but preferably at least some, but preferably all of i), ii) and iii) are first combined and subsequently
20 contacted with the olefinic compound.

The contacting of the olefinic compound with compounds i) to iii) and b) preferably takes place under conditions to allow oligomerisation of the olefinic compound. These conditions are well known to a person skilled in the art and include elevated temperatures and pressure.

25 The solid oligomerisation may be carried out at temperatures from 100°C to 250°C, but temperatures in the range of 15°C to 130°C are preferred, particularly temperatures in the range from 50°C to 120°C. Oligomerisation is preferably carried out at a temperature of at least 0°C, preferably at least 40°C, and preferably at least 50°C. Preferably it is carried out at a pressure of at least 100 kPa, preferably at least 1000 kPa, preferably at least 3000 kPa.

30 The preparation of the activated catalyst may be carried out in a liquid medium, preferably an inert liquid medium. The liquid medium may be the same liquid medium wherein the oligomerisation with the diluted catalyst is carried out.

35 The activated oligomerisation catalyst before dilution may be prepared in the same container as the one in which the diluted activated oligomerisation catalyst is contacted with the olefinic compound to be oligomerised. Preferably the activated oligomerisation catalyst before dilution is prepared in a separate container as the one in which the oligomerisation catalyst is contacted with the olefinic compound to be oligomerised.

40

The source of chromium and ligating compound may be combined to provide any suitable molar ratio, preferably a chromium to ligand compound molar ratio, from about 0.01 : 100 to 10 000 : 1, preferably from about 0.1 : 1 to 10:1.

5 The zinc can be used in any loading compared to the chromium, preferably between 1 and 10000, more preferably between 10 and 1000, most preferably between 50 and 450. The zinc can be used as any concentration of stock solution and the concentration in situ in the reactor can be between 0.0001 mmol/L and 1 mol/L, more preferably between 0.001 mmol/L and 0.1 mol/L, most preferably between 0.01 mmol/L and 0.01 mol/L.

10

The zinc additive can be added at any stage during the activation procedure, most preferably it is added directly to the reactor. The zinc can be used as a mixed stock solution with the trialkylaluminium.

15 The process may also include combining one or more different sources of chromium with one or more different ligating compounds.

The oligomerisation 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, 20 $MgCl_2$, zirconia, artificial hectorite or smectorite clays such as LaponiteTM 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, 25 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.

The invention will now be described, by way of non-limiting examples:

30 **Examples**

In this specification the abbreviation TEA is used for triethylaluminium and PNP is used for bis(diarylphosphanyl)amine ligand

35 A 1 or 1.2L stainless steel reactor was heated to 120°C under vacuum for 30 minutes, cooled to 60 °C and back-filled with Ar. The reactor was charged with solvent and saturated with ethylene.

Separately, TEA then activator salt (as stock solutions) were added sequentially to a stirred 40 solution of $Cr(tBu_2acac)_3$ / PNP. The activation solution was added to the reactor and the

reactor was pressurized to 50 bar with ethylene. The reaction pressure was kept constant through addition of ethylene monitored *via* a flow-meter. After cessation of ethylene uptake, the gas supply was closed and the reactor cooled to 0 °C. Excess ethylene was bled and the reactor contents treated sequentially with 1000 µL of nonane (GC internal standard), MeOH and 10% HCl (aq). A sample of the organic phase was taken for GC-FID analysis. Any solid formed was collected, washed repeatedly with 10% HCl (aq.) and EtOH, dried overnight and weighed.

Example 1: OLIGOMERISATION OF ETHYLENE USING A SYSTEM BASED ON Cr/PNP/[(C₁₈H₃₇)₂N(H)(Me)] [B(C₆F₅)₄]/TEA

In all tests using this reagent the total amount of ZnEt₂ was added to the reactor with the solvent at the pre-scrub stage. All catalysis has been conducted on the 1.2 L rig where typical runs consume > 400 g of ethylene, thus the absolute amount of polymer formed is roughly 1 – 3 g. Given the ability to collect, wash, dry and weigh the polymer to the nearest 10 mg, the accuracy of the polymer quantification is better than 0.0025%.

Table 1 below shows against entry # 316 a standard run using Cr/PNP/TEA/borate in PhCl; the total solid polymer formation is 0.65 % polymer.

In contrast, entry 330 shows a run using the same conditions except with an additional 420 eq. of ZnEt₂. It can be seen that the total solids formation is reduced to 0.38% - representing a 42% reduction in polymer formation.

Entry 312 is a borate run in the aliphatic solvent cyclohexane, included for comparison; the polymer formation is 0.57 %. As can be seen from entries 354 (25 eq.), 346 (50 eq.), 345 (100 eq.), 73 (150 eq.), 348 (420 eq.), addition of ZnEt₂ at 50 equivalents or above successfully reduces the level of polymer formation to an average of 0.35 % - an average reduction of 35%. Entries 234 (1000 eq), 237 (5000 eq) and 238 (10000 eq) all show that even at high zinc loadings the level of polymer is reduced, whilst maintaining good activity.

Entry 239 is a borate run in the aliphatic solvent cyclohexane with a different ligand and chromium source, included for comparison; the polymer formation is 0.78%. As can be seen from entries 236 (1 eq.) and 235 (10 eq.), addition of ZnEt₂ even at these very low loadings, successfully reduces the level of polymer formation to an average of 0.45%.

Entry 324 is a run performed in 2,2,4-trimethylpentane (TMP) which shows a polymer formation level of 0.92%. Runs 347 and 332 show that addition of 50 and 420 eq of ZnEt₂ can reduce this polymer level to an average of 0.46%.

Looking at all examples in Table 1 it can be seen that the addition of ZnEt₂ has little or no effect upon the amount of 1-hexene and 1-octene formed.

Table 1. Results of catalyst testing with varying amounts of diethyl zinc.

Entry #	Solvent	ZnEt ₂ Eq.	Cat. Time (min)	Activity g/gCr/h	Hexene and octene wt % ^b	Polymer wt % ^c (g)
316	PhCl	0	75.3	5,214,575	83.2	0.65 (2.63)
330	PhCl	420	43.3	9,081,307	82.0	0.38 (1.49)
312	CyH	0	86.0	4,549,445	81.9	0.57 (2.41)
239 ^e	CyH	0	154	1,786,201	87.5	0.78 (2.34)
236 ^e	CyH	1	111.6	2,935,441	85.6	0.43 (1.53)
235 ^e	CyH	10	87.1	3,670,522	86.5	0.46 (1.59)
354	CyH	25	85.3	4,133,342	82.3	0.37 (1.41)
346	CyH	50	97.0	3,733,376	82.5	0.31 (1.22)
345	CyH	100	94.5	4,046,426	81.6	0.47 (1.96)
73	CyH	150	112.6	3,469,238	83.4	0.25 (1.08)
348	CyH	420	94.6	3,774,950	83.3	0.37 (1.45)
234 ^e	CyH	1000	99.6	3,161,004	86.8	0.45 (1.54)
237 ^e	CyH	5000	120.0	2,291,502	87.0	0.32 (0.95)
238 ^e	CyH	10000	224.0	1,014,743	87.4	0.21 (0.52)
324	TMP	0	114.2	3,531,036	82.2	0.92 (4.01)
347	TMP	50	154.7	2,407,089	81.2	0.47 (1.89)
332	TMP	420	232.0	1,660,724	82.1	0.44 (1.77)

General conditions: ^a 1.25 μmol $\text{Cr}(\text{Bu}_2\text{acac})_3$; 1.2 eq. $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})\{(\text{CH}_2)_5\text{CH}_3\}\}-\text{PPh}_2$; 1.2eq. $[(\text{C}_{18}\text{H}_{37})_2\text{N}(\text{H})(\text{Me})][\text{B}(\text{C}_6\text{F}_5)_4]^-_2$; 420 eq. TEA (50 eq. activation, 370 eq. reactor); p(=) 50 bar 60°C; 200 mL solvent; 1.2 L rig. ^b = % of liquid fraction ^c = % of total product formed (liquid and solid). ^e 1.25 μmol $\text{Cr}(2\text{-EH})_3$; 1.2 eq. $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})\{\text{C}(\text{H})(\text{Me})\{(\text{CH}_2)_4\text{CH}_3\}\}\}-\text{PPh}_2$

5

Example 2: OLIGOMERISATION OF ETHYLENE USING A SYSTEM BASED ON MAO

For this study, catalysis was either performed in cyclohexane or in 2,2,4-trimethylpentane. Catalyst activity and product selectivity data is summarised in Table 2. The polymeric product made in catalysis was carefully isolated, repeatedly washed and dried.

10 Entry 056 represents the optimum MAO activated catalysis that can be achieved in CH for the two sets of precatalysts and entry 181 for catalysis in 2,2,4-trimethylpentane. Diethyl or dimethyl zinc is added to the reactor in the normal "pre-scrub phase", which immediately follows solvent addition to the reactor.

15 Catalyst performance is shown for the standard run that contains 50 eq. of diethyl zinc (entry 059), and is further accompanied by a noteworthy reduction in solids (from 0.8 % to 0.6 %). Diethyl zinc again appears to have little effect on the total selectivity of the catalyst; entry 056 (83.5 %) versus 059 (83.9 %).

20 Although a clear activity enhancement is seen when 50 eq of ZnMe_2 is used (entry 185), there is no reduction in solids. However, increasing the equivalents from 50 to 100 shows a reduction from 0.49 to 0.41% as well as a significant increase in activity.

Table 2. The effect of ZnR_2 R = Me or Et on MMAO catalysis.

Entry (eq. ZnEt_2)	Productivity g/gCr	Activity g/gCr/H	Hexene and octene wt % ^b	Pol wt % (g) ^c
056 ^a (0 eq. ZnEt_2)	3 446895	1 969654	80.7	0.80 (2.83)
058 ^a (100 eq. ZnEt_2)	2 476986	1 170230	82.4	0.60 (1.49)
059 ^a (50 eq. ZnEt_2)	3 298861	1 691724	83.9	0.60 (1.49)
181 ^d (0 eq. ZnMe_2)	1 805992	2 642916	87.1	0.49 (0.92)
190 ^d (100 eq. ZnMe_2)	1 899827	3 864054	86.8	0.41 (0.81)

General conditions: ^a2.0 μmol $\text{Cr}(\text{acac})_3$ and 1.2 eq. $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})\{\text{CH}_2\}_2\text{CH}_3\}\text{-PPh}_2$; MAO (480 eq.); 50 bar ethylene; 60°C; 200 mL cyclohexane. ^b = % of liquid fraction ^c = % of total product formed (liquid and solid) ^d2.0 μmol $\text{Cr}(\text{acac})_3$ and 1.1 eq. $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})(\text{iPr})\}\text{-PPh}_2$ in 2,2,4-trimethylpentane; MAO (480 eq.); 45 bar ethylene; 60°C; 300 mL.

5 Example 3 Change in Conditions

The results reflected in Table 3 below show that the effect of adding ZnEt_2 is not affected by the choice of chromium source and co-catalysts used. This effect is also not unique to the PNP ligand system as not only does it work with $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})(\text{iPr})\}\text{-PPh}_2$, $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})\{\text{CH}_2\}_5\text{CH}_3\}\text{-PPh}_2$, and the bulky (*o*-Me- C_6H_4)₂ $\text{P-N}(\text{iPr})\text{-PPh}_2$ ligands but also with other ligands such as $\text{Ph}_2\text{P-N}(\text{Me})\text{-N}(\text{CH}_2\text{CH}_2\text{Pr}^i)\text{-P}$, *bis*(diphenylphosphanyl)ethane (DPPE) and *bis*(diphenylphosphanyl)methane (DPPM). This indicates that the effect of ZnEt_2 is not exclusive to tetramerisation systems PNP, PNNP, and DPPE but also, as expected, applies to unselective oligomerisation systems, DPPM. The most significant change in the use of ZnEt_2 comes upon running in alternative solvents.

15

Table 3. Results of catalyst testing with varying conditions.

Entry #	Cr / L / A ^f	ZnEt ₂ Eq.	Cat. Time (min)	Activity g/gCr/h	Hexene and octene wt % ^d	Polymer wt % ^c (g) ^e
424	$\text{Cr}(\text{tBu}_2\text{acac})_3$ / $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})\{\text{CH}_2\}_5\text{CH}_3\}\text{-PPh}_2$ / OAB	0	207.0	1,744,506	83.0	0.85 (3.34)
423	$\text{Cr}(\text{tBu}_2\text{acac})_3$ / $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})\{\text{CH}_2\}_5\text{CH}_3\}\text{-PPh}_2$ / OAB	420	151.5	2,469,579	82.4	0.77 (3.12)
427	$\text{Cr}(\text{acac})_3$ / $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})\{\text{CH}_2\}_2\text{CH}_3\}\text{-PPh}_2$ / TA	0	39.9	9,962,823	84.1	1.76 (7.55)
426	$\text{Cr}(\text{acac})_3$ / $\text{Ph}_2\text{P-N}\{\text{C}(\text{H})(\text{Me})\{\text{CH}_2\}_2\text{CH}_3\}\text{-PPh}_2$ / TA	420	49.6	8,718,296	83.2	0.38 (1.79)

434 ^c	Cr(^t Bu ₂ acac) ₃ / Ph ₂ P-N{C(H)(Me)({CH ₂ }) ₅ CH ₃ }- PPh ₂ / RB	0	135.0	2,874,486	83.1	2.36 (9.93)
435 ^c	Cr(^t Bu ₂ acac) ₃ / Ph ₂ P-N{C(H)(Me)({CH ₂ }) ₅ CH ₃ }- PPh ₂ / RB	100	89.6	3,530,896	83.8	1.85 (6.35)
445 ^b	Cr(2-EH) ₃ / DPPE/ RB	0	74.0	115,961	70.5	24.7 (4.59)
446 ^b	Cr(2-EH) ₃ / DPPE/ RB	100	107.0	147,931	71.1	13.0 (4.44)
447 ^b	Cr(2-EH) ₃ / DPPM/ RB	0	95.7	17,092	28.8	77.9 (2.76)
448 ^b	Cr(2-EH) ₃ / DPPM/ RB	100	107.2	16,159	27.9	66.2 (2.48)
452 ^b	Cr(2-EH) ₃ / (<i>o</i> -Me-C ₆ H ₄) ₂ P-N(ⁱ Pr)-PPh ₂ / RB	100	49.5	632,715	91.0	4.94 (1.67)
453 ^b	Cr(2-EH) ₃ / (<i>o</i> -Me-C ₆ H ₄) ₂ P-N(ⁱ Pr)-PPh ₂ / RB	0	18.0	443,168	91.0	23.02 (1.99)
454 ^b	Cr(2-EH) ₃ / Ph ₂ P-N(Me)-N-(CH ₂ CH ₂ Pr ⁱ)- PPh ₂ / RB	100	51.5	441,991	90.2	11.47 (2.83)
455 ^b	Cr(2-EH) ₃ / Ph ₂ P-N(Me)-N-(CH ₂ CH ₂ Pr ⁱ)- PPh ₂ / RB	0	65.8	80,240	86.9	61.88 (3.54)
428	Cr(^t Bu ₂ acac) ₃ / Ph ₂ P-N{C(H)(Me)({CH ₂ }) ₅ CH ₃ }- PPh ₂ / RB	420 ZnMe ₂	80.3	4,044,548	83.9	0.43 (1.50)

General conditions: ^a 1.25 μmol Cr; 1.2eq. Ligand; 1.2eq. Anion; 420 eq. TEA (50 eq. activation, 370 eq.; 200 mL solvent 1.2 L reactor p(=) 50 bar ; 60°C; 200 mL solvent; 1.2 L rig. ^b

150 eq. TEA (activation) 65 mL solvent 300 mL reactor. ^c Al^tBu₃ in place of TEA. ^d = % of liquid fraction ^e = % of total product formed (liquid and solid). ^f OAB = [Oct₃NH][B(C₆F₅)₄]; RB = [(C₁₈H₃₇)₂N(H)Me][B(C₆F₅)₄]; TA = [Ph₃C][Al(O^tBu^F)₄]; Cr(2-EH)₃ = Cr(2-ethylhexanoate)₃; DPPE = *bis*(diphenylphosphanyl)ethane; DPPM = *bis*(diphenylphosphanyl)methane.

5

The use of zinc alkyl, in particular diethyl zinc in conjunction with the Cr/PNP/TEA/borate catalyst system and dimethyl zinc in conjunction with the Cr/PNP/MMAO system clearly has benefits in reducing the level of polymer formation by a significant amount, whilst increasing the rate of catalysis.

10 It is further noted that only a low level of ZnEt₂ is required to achieve this effect, circa 50-100 equivalents, with higher loadings of Zn offering little further advantage.

The use of this reagent also fulfils the requirement on having little or no effect upon the selective oligomerisation mechanism with little perturbation in the total target oligomer value being observed.

15

CLAIMS

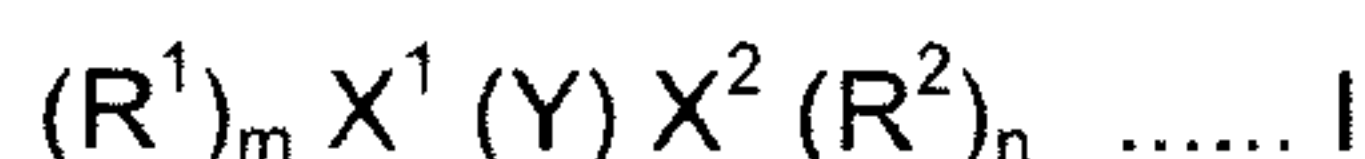
1. A process for producing an oligomeric product by oligomerisation of at least one olefinic compound, the process including:

5

a) providing an activated oligomerisation catalyst by combining, in any order,

- i) a source of chromium;
- ii) a ligating compound of the formula I

10



wherein: X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X^1 and/or X^2 allows for such oxidation;

15

Y is a linking group between X^1 and X^2 ;

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

R^1 and R^2 are independently hydrogen, a hydrocarbyl group, an organoheteryl group or a heterohydrocarbyl group, and R^1 being the same or different when $m > 1$, and R^2 being the same or different when $n > 1$;

20

iii) a catalyst activator or combination of catalyst activators;

b) providing a zinc compound; and

c) contacting the at least one olefinic compound with a composition containing the activated oligomerisation catalyst and the zinc compound, the zinc compound being present in a sufficient quantity such that the ratio of the molar amount of zinc in the zinc compound to the molar amount of chromium in the source of chromium is between 1 and 10000.

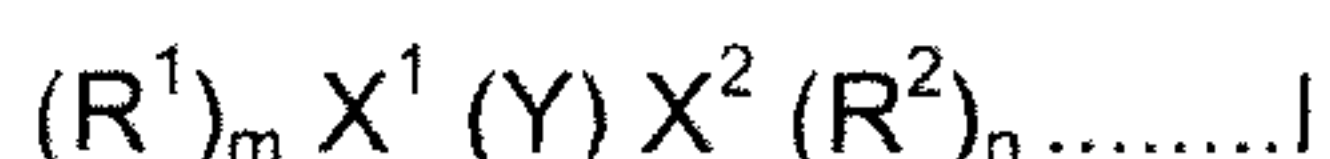
25

2. A process for activating an oligomerisation catalyst to be used to produce an oligomeric product from at least one olefinic compound, the process comprising the combination, in any order, of

30

- i) a source of chromium;
- ii) a ligating compound of the formula I

35



wherein: X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth,

oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X^1 and/or X^2 allows for such oxidation;

Y is a linking group between X^1 and X^2 ;

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

5 R^1 and R^2 are independently hydrogen, a hydrocarbyl group an organoheteryl group or a heterohydrocarbyl group, and R^1 being the same or different when $m > 1$, and R^2 being the same or different when $n > 1$;

10 iii) a catalyst activator or combination of catalyst activators;
iv) a zinc compound, the zinc compound being present in a sufficient quantity such that the ratio of the molar amount of zinc in the zinc compound to the molar amount of chromium in the source of chromium is between 1 and 10000 .

15 3. The process of claim 1 or claim 2 wherein the zinc compound is present in the reaction of the invention in a sufficient quantity such that the ratio of the molar amount of zinc in the zinc compound to the molar amount of chromium in the source of chromium is between 10 and 1000.

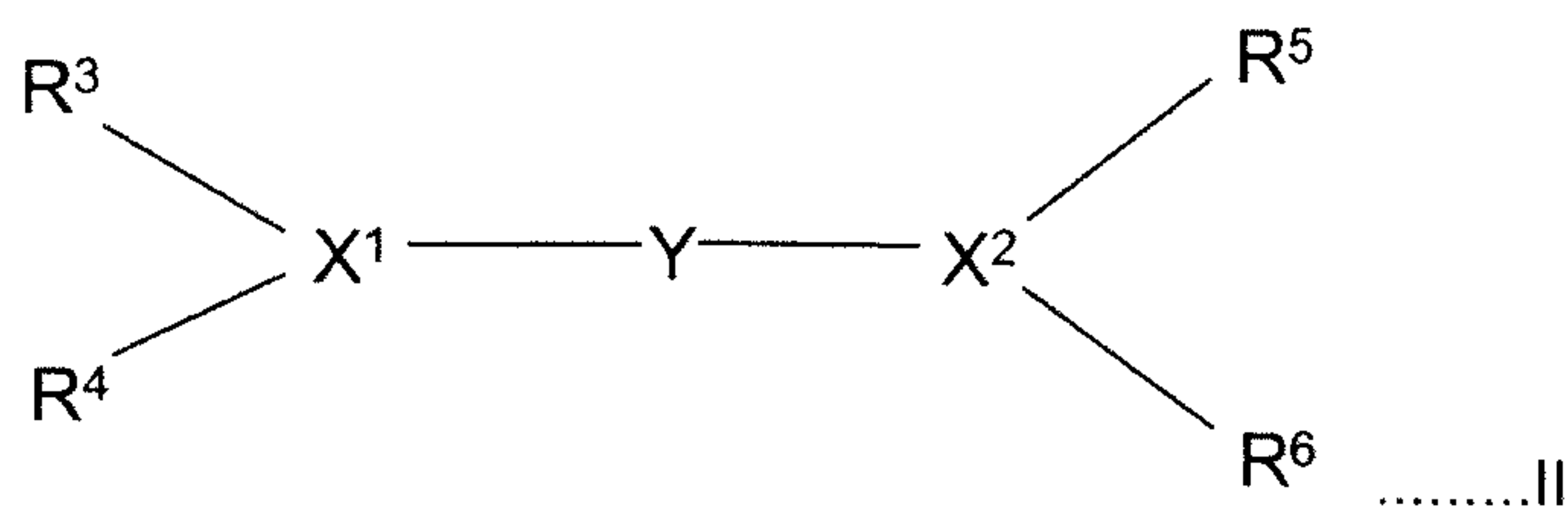
20 4. The process of claim 1 or claim 2 wherein the zinc compound is present in the reaction of the invention in a sufficient quantity such that the ratio of the molar amount of zinc in the zinc compound to the molar amount of chromium in the source of chromium is between 50 and 450.

25 5. The process of any one of the preceding claims wherein the process includes the use of a solvent.

6. The process of any one of the preceding claims wherein the oligomerisation catalyst is a trimerisation catalyst or a tetramerisation catalyst.

30 7. The process of any one of the preceding claims wherein X^1 and X^2 are independently phosphorus or phosphorus oxidised by S or Se or N or O.

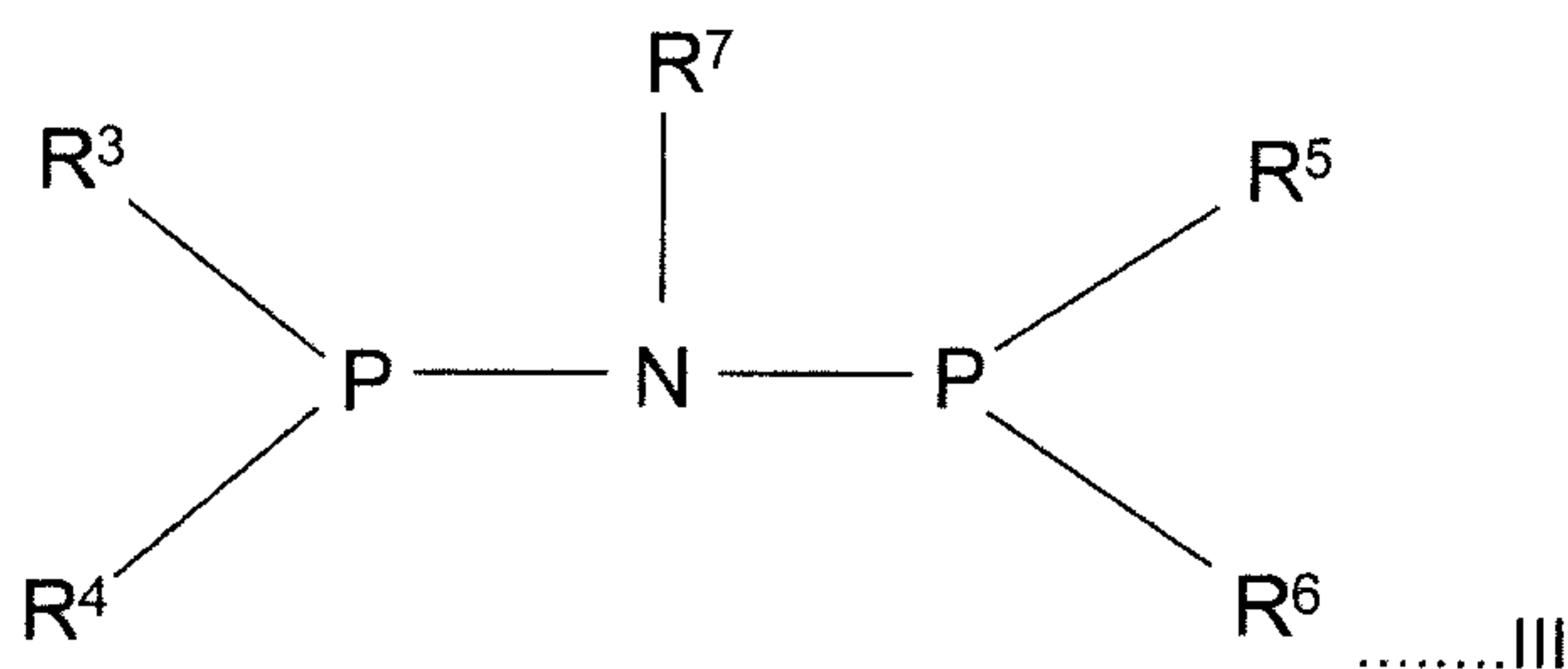
35 8. The process of any one of the preceding claims wherein the ligating compound is of the formula II



wherein Y is a linking group between X¹ and X², X¹ and X² are independently selected from the group consisting of nitrogen, phosphorus, arsenic, antimony and bismuth and R³ to R⁶ are each independently a hydrocarbyl group or a heterohydrocarbyl group.

9. The process of any one of the preceding claims wherein Y is selected from the group consisting of an organic linking group comprising a hydrocarbylene, substituted hydrocarbylene, heterohydrocarbylene and a substituted heterohydrocarbylene; an inorganic linking group comprising either a single- or two-atom linker spacer; and a group comprising methylene; dimethylmethylene; ethylene; ethene-1,2-diyl; propane-1,2-diyl, propane-1,3-diyl; cyclopropane-1,1-diyl; cyclopropane-1,2-diyl; cyclobutane-1,2-diyl, cyclopentane-1,2-diyl; cyclohexane-1,2-diyl, cyclohexane-1,1-diyl; 1,2-phenylene; naphthalene-1,8-diyl; phenanthrene-9,10-diyl, phenanthrene-4,5-diyl, 1,2-catecholate, 1,2-diarylhydrazine-1,2-diyl (-N(Ar)-N(Ar)-) where Ar is an aryl group; 1,2-dialkylhydrazine-1,2-diyl (-N(Alk)-N(Alk)-) where Alk is an alkyl group; -B(R⁷)-, -Si(R⁷)₂-, -P(R⁷)- and -N(R⁷)- where R⁷ is hydrogen, a hydrocarbyl or heterocarbyl or halogen.

10. The process of claim 8 wherein the ligating compound is of the formula III



wherein R³ to R⁷ are each independently a hydrocarbyl group or a heterohydrocarbyl group.

11. The process of claim 10 wherein each of R³ to R⁶ is an alkyl selected from the group consisting of methyl, ethyl and isopropyl or an aromatic selected from the group consisting of phenyl and substituted phenyl.

12. The process of claim 1 or claim 2 wherein the activator is selected from the group of organoboron compound, alumoxanes including modified aluminoxanes, aluminum alkyls,

other metal or main group alkyl or aryl compounds, ionizing activators which are neutral or ionic, Lewis acids, reducing acids oxidising agents and combinations thereof.

13. The process of claim 1 or claim 2 wherein the process includes a reagent selected from a
5 Group 13 reagent, a divalent metal reagent or an alkali metal reagent.

14. The process of claim 1 or claim 2 wherein the zinc compound is selected from zinc,
activated zinc, and zinc-containing compounds selected from the group comprising zinc
halides, zinc alkyls, zinc oxygenates including zinc acetate, zinc acetylacetonates and zinc
10 carboxylates, and zinc porphyrin.

15. The process of claim 15 wherein the zinc-containing compound is a zinc dialkyl, including
dimethyl zinc and diethyl zinc.