



(86) Date de dépôt PCT/PCT Filing Date: 2006/09/26
(87) Date publication PCT/PCT Publication Date: 2007/04/12
(45) Date de délivrance/Issue Date: 2013/07/23
(85) Entrée phase nationale/National Entry: 2008/03/27
(86) N° demande PCT/PCT Application No.: IB 2006/053494
(87) N° publication PCT/PCT Publication No.: 2007/039851
(30) Priorité/Priority: 2005/10/03 (GB0520085.2)

(51) Cl.Int./Int.Cl. *B01J 31/16* (2006.01),
B01J 31/02 (2006.01), *B01J 31/14* (2006.01),
B01J 31/18 (2006.01), *B01J 31/22* (2006.01),
C07C 11/02 (2006.01), *C07C 2/26* (2006.01),
C07C 2/32 (2006.01), *C07C 2/36* (2006.01),
C10G 50/00 (2006.01)

(72) Inventeurs/Inventors:
MCGUINNESS, DAVID SHANE, GB;
RUCKLIDGE, ADAM JOHN, GB

(73) Propriétaire/Owner:
SASOL TECHNOLOGY (PTY) LIMITED, ZA

(74) Agent: SMART & BIGGAR

(54) Titre : OLIGOMERISATION DE COMPOSES OLEFINIQUES EN PRESENCE D'UN CATALYSEUR
D'OLIGOMERISATION, ET ACTIVATEUR CATALYTIQUE COMPRENANT UN GROUPE ORGANIQUE HALOGENE
(54) Title: OLIGOMERISATION OF OLEFINIC COMPOUNDS IN THE PRESENCE OF AN OLIGOMERISATION
CATALYST, AND A CATALYST ACTIVATOR INCLUDING A HALOGENATED ORGANIC GROUP

(57) **Abrégé/Abstract:**

According to the present invention there is provided a process for producing an oligomeric product by the oligomerisation of at least one olefinic compound, by contacting the at least one olefinic compound with the combination of an oligomerisation catalyst and a catalyst activator. The catalyst activator is a compound which includes at least one halogenated organic group which is bound to one or more binding atoms selected from the group consisting of a group 5A atom and a group 6A atom, which one or more binding atoms are in turn bound to a central atom selected from the group consisting of a group 3A atom, and a group 3B to 7B transition metal atom. The oligomerisation catalyst includes the combination of i) a source of a transition metal; and ii) a ligating compound of the formula $(R^1)_m X^1 (Y) X^2 (R^2)_n$. The invention also relates to a combination of an oligomerisation catalyst and a catalyst activator as set out above and to the use of such a combination in an oligomerisation process.

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 April 2007 (12.04.2007)

PCT

(10) International Publication Number
WO 2007/039851 A2

(51) International Patent Classification:

B01J 31/16 (2006.01) *C07C 2/26* (2006.01)
B01J 31/18 (2006.01) *C07C 2/32* (2006.01)
B01J 31/22 (2006.01) *C07C 2/36* (2006.01)
B01J 31/14 (2006.01) *C10G 50/00* (2006.01)
B01J 31/02 (2006.01) *C07C 11/02* (2006.01)

(74) Agent: D M KISCH INC; P O Box 781218, 2146 Sandton (ZA).

(21) International Application Number:

PCT/IB2006/053494

(22) International Filing Date:

26 September 2006 (26.09.2006)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0520085.2 3 October 2005 (03.10.2005) GB

(71) Applicant (for all designated States except US): **SASOL TECHNOLOGY (PTY) LIMITED** [ZA/ZA]; 1 Sturdee Avenue, Rosebank, 2196 Johannesburg (ZA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MCGUINNESS, David, Shane** [AU/GB]; 20 Tarvit Avenue, Cupar Fife KY15 5BW (GB). **RUCKLIDGE, Adam, John** [GB/GB]; 37 St Mary Street, Dundee Tayside DD1 5RA (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: OLIGOMERISATION OF OLEFINIC COMPOUNDS IN THE PRESENCE OF AN OLIGOMERISATION CATALYST, AND A CATALYST ACTIVATOR INCLUDING A HALOGENATED ORGANIC GROUP

(57) Abstract: According to the present invention there is provided a process for producing an oligomeric product by the oligomerisation of at least one olefinic compound, by contacting the at least one olefinic compound with the combination of an oligomerisation catalyst and a catalyst activator. The catalyst activator is a compound which includes at least one halogenated organic group which is bound to one or more binding atoms selected from the group consisting of a group 5A atom and a group 6A atom, which one or more binding atoms are in turn bound to a central atom selected from the group consisting of a group 3A atom, and a group 3B to 7B transition metal atom. The oligomerisation catalyst includes the combination of i) a source of a transition metal; and ii) a ligating compound of the formula $(R^1)_m X^1 (Y) X^2 (R^2)_n$. The invention also relates to a combination of an oligomerisation catalyst and a catalyst activator as set out above and to the use of such a combination in an oligomerisation process.

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**OLIGOMERISATION OF OLEFINIC COMPOUNDS IN THE PRESENCE OF AN
OLIGOMERISATION CATALYST, AND A CATALYST ACTIVATOR INCLUDING A
HALOGENATED ORGANIC GROUP**

5 Technical Field

This invention relates to the oligomerisation of olefinic compounds in the presence of an oligomerisation catalyst, and a catalyst activator including a halogenated organic group.

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 containing heteroaromatic ligands with both phosphorus and nitrogen heteroatoms, selectively catalyse the trimerisation of ethylene to 1-hexene.

20

Processes wherein transition metals and heteroatomic ligands are combined to form catalysts for trimerisation, tetramerisation, oligomerisation and polymerisation of olefinic 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; US Complete Patent Application No. 11/130,106; WO 05/123884 A2 and WO 05/123633 A1.

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

5

Suitable activators include organoaluminium compounds, organoboron compounds, organic 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.

10

A common catalyst activator used in combination with Cr based catalysts for oligomerisation of olefinic compounds is alkylaluminumoxane, particularly methylaluminumoxane (MAO). It is well known that MAO includes significant quantities of alkylaluminium in the form of trimethylaluminium (TMA), and in effect the catalyst
15 activator is a combination of TMA and MAO. The MAO may also be replaced with modified MAO (MMAO).

The use of fluorinated boranes/borates as catalyst activators is also known. In J Organomet. Chem. 683 (2003) 200 triazacyclohexane CrCl_3 complexes were
20 activated with AlR_3 and $[\text{PhN}(\text{Me})_2\text{H}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ to give catalysts active for trimerisation of alpha-olefins. In J. Am. Chem. Soc., 126 (2004) 1304, Cr-based ethylene trimerisation catalysts were activated by treating Cr-aryl complexes with fluorinated aryl-boranes (BARF). IPCOM000031729D discloses the use of fluorinated borate and borane activators in combination with chromium based
25 catalyst in the oligomerisation of olefins.

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In WO 99/64476, catalysts (especially Ziegler-Natta and metallocene polymerisation catalysts) were activated by a combination of halogenated aryl containing Group13 metal or metalloid based Lewis acids and organo-Group13 metal compounds.

- 5 Trityl tetrakis (pentafluorophenoxy) aluminate, $[\text{Ph}_3\text{C}]^+ [\text{Al}(\text{OC}_6\text{F}_5)_4]^-$, has been prepared and employed as a co-catalyst for ethylene and propylene polymerisation with metallocene complexes such as $(\text{C}_5\text{H}_5)_2\text{ZrMe}_2$ in Organometallics, 19 (2000) 1625 and Organometallics, 21 (2002) 3691. Angew. Chem. Int. Ed. 2004, 43, 2066 also discloses compounds such as $[\text{M}(\text{OC}_6\text{F}_5)_n]$ and $[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$ and the use of
- 10 the latter as an activator for ethene and propene polymerisation with a Zr-alkyl complex in the presence of $\text{Al}i\text{Bu}_3$. J. Fluorine Chemistry 2001, 112, 83 discloses the preparation of compounds such as $[\text{Ph}_3\text{C}]^+ [\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$.

- Journal of Organometallic Chemistry, 621 (2001), 184 discloses the use of $[\text{Me}_3\text{NH}]^+$
- 15 $[\text{B}(\text{OC}_6\text{F}_5)_4]^-$ for polymerisation with iron catalysts including tridentate ligands.

It has now been found that compounds of the present invention including at least one halogenated organic group bound to a group 3A or group 3B to 7B central atom by means of one or more binding atoms can be used as activators of oligomerisation

20 catalysts in oligomerisation reactions. In some cases the productivity of the oligomerisation catalysts was found to have been improved compared to when borane or borate activators are used, such as those detailed in IPCOM000031729D. Most surprisingly it also has been found that different activators of this nature can influence the product selectivity of the oligomerisation catalysts. Furthermore, the

25 relative high polymer formation associated with borate activators, was at least reduced in at least some cases.

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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 in the form of an olefin or a compound including a carbon to carbon double bond, by
 5 contacting the at least one olefinic compound with the combination of an oligomerisation catalyst and a catalyst activator, which catalyst activator is a compound which includes

at least one halogenated organic group which is bound to one or more binding
 10 atoms selected from the group consisting of a group 5A atom and a group 6A atom, which one or more binding atoms are in turn bound to a central atom selected from the group consisting of a group 3A atom, and a group 3B to 7B transition metal atom; and

wherein the oligomerisation catalyst includes the combination of

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

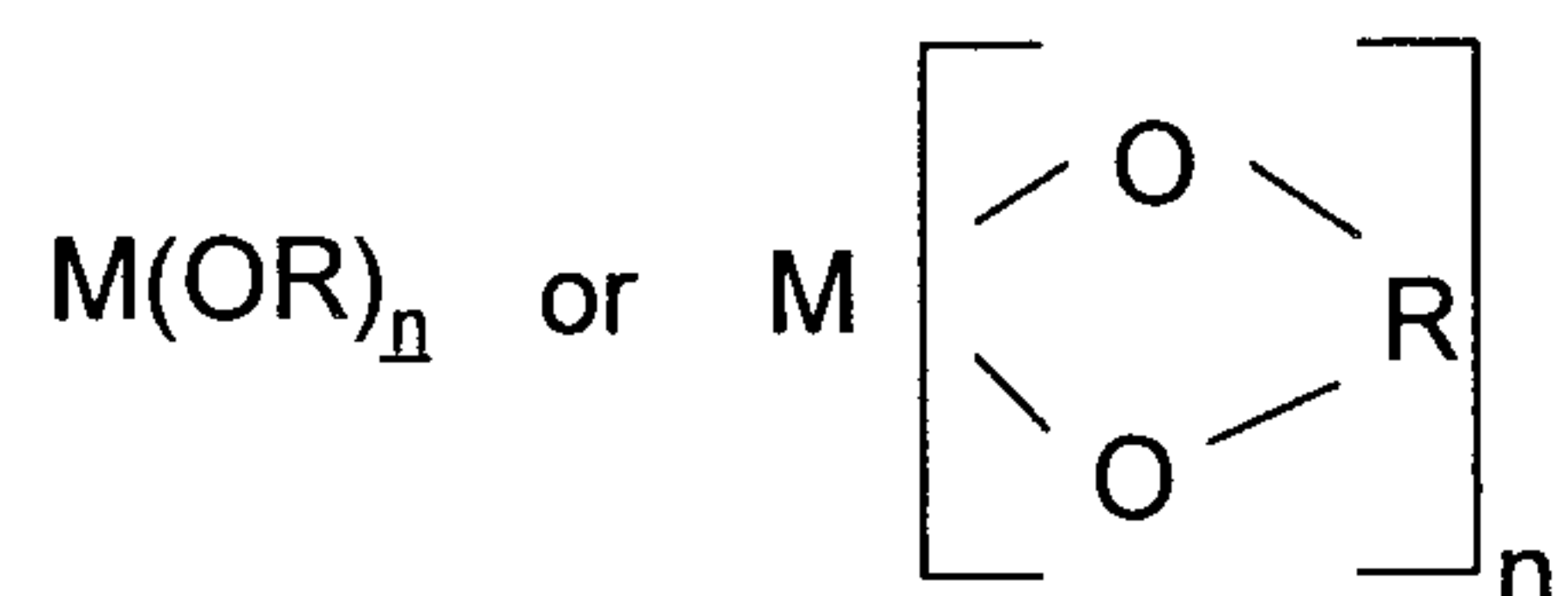


20 wherein: X^1 and X^2 are independently selected from the group consisting of N, P, As, Sb, Bi, O, S and Se;
 Y is a linking group between X^1 and X^2 ;
 m and n are independently 0, 1 or a larger integer; and
 R^1 and R^2 are independently hydrogen, a hydrocarbyl group or
 25 a heterohydrocarbyl group, and R^1 being the same or different when $m > 1$, and R^2 being the same or different when $n > 1$.

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In one process aspect, the invention relates to a process for producing an oligomeric product by the oligomerisation of at least one olefinic compound in the form of an olefin or a compound including a carbon to carbon double bond, by contacting the at least one olefinic compound with the combination of an oligomerisation catalyst and a catalyst activator, which catalyst activator is a salt containing an anion which includes a moiety of the formula:



wherein:

M is selected from the group consisting of a group 3A atom;

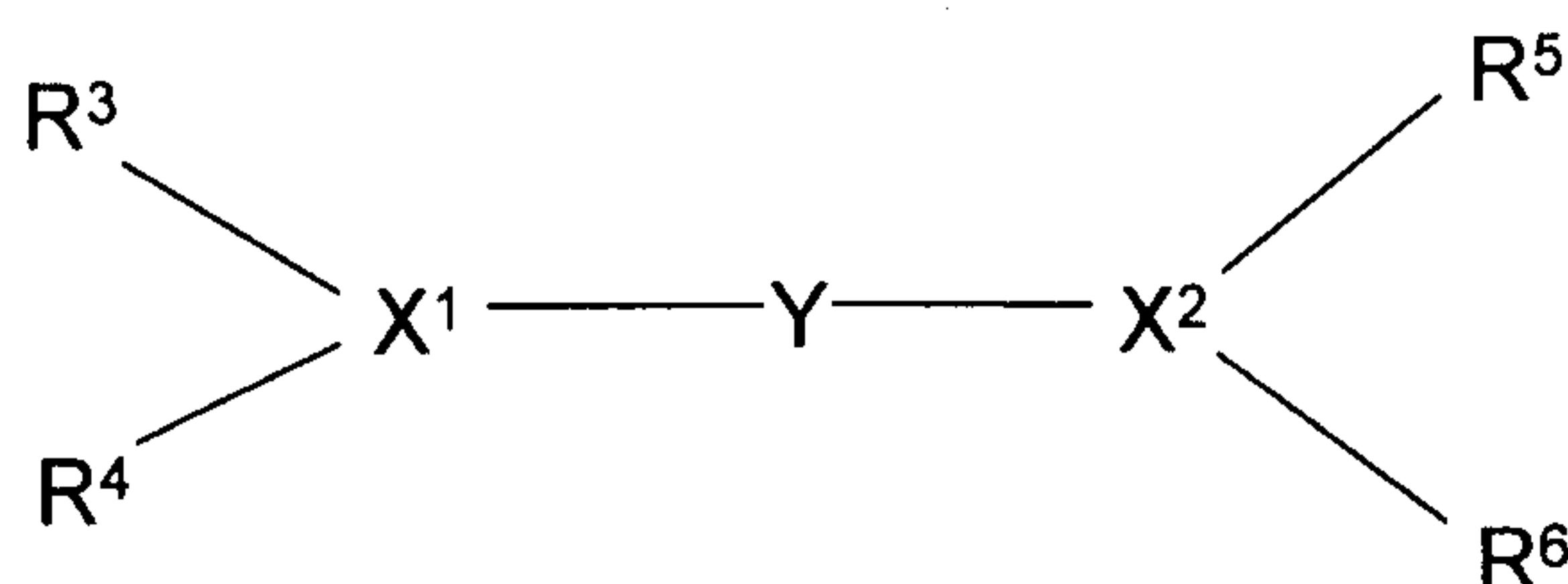
10 n is 1 or a larger integer; and

R is a halogenated organic group, R being the same or different when n is larger than 1; and

wherein the oligomerisation catalyst includes the combination of:

i) a source of Cr; and

15 ii) a ligating compound of the formula:



wherein: X^1 and X^2 are P;

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Y is a linking group between X¹ and X²;

R³ to R⁶ are each independently:

- a hydrocarbyl group

wherein the hydrocarbyl group is a univalent or multivalent group

5 formed by removing one or more hydrogen atoms from a hydrocarbon;

- or a heterohydrocarbyl group

wherein the heterohydrocarbyl group is a univalent or multivalent

organic compound which includes at least one heteroatom, that is not being H or C,

and which organic compound binds with one or more other moieties through one or

10 more carbon atoms of the organic compound and/or one or more heteroatoms of the organic compound;

the process further including a co-activator.

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In this specification a heterohydrocarbyl group is a univalent or multivalent organic compound which includes at least one heteroatom (that is not being H or C), and which organic compound binds with one or more other moieties through one or more carbon atoms of the organic compound and/or one or more heteroatoms of the organic compound. Organoheteryl groups and organyl groups (which include at least one heteroatom) are examples of heterohydrocarbyl groups.

In this specification a hydrocarbyl group is a univalent or multivalent group formed by removing one or more hydrogen atoms from a hydrocarbon.

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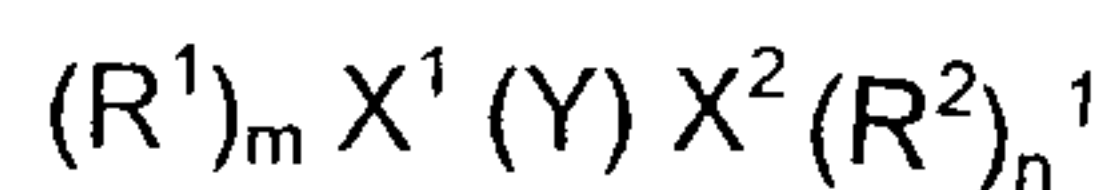
Accordingly to another aspect of the present invention there is provided the use of a combination of a catalyst activator and an oligomerisation catalyst in the oligomerisation of at least one olefinic compound in the form of an olefin or a compound including a carbon to carbon double bond by contacting the at least one olefinic compound with the oligomerisation catalyst, and the catalyst activator, wherein the activator is a compound which includes

at least one halogenated organic group which is bound to one or more binding atoms selected from the group consisting of a group 5A atom and a group 6A atom, which one or more binding atoms are in turn bound to a central atom selected from the group consisting of a group 3A atom, and a group 3B to 7B transition metal atom; and

wherein oligomerisation catalyst includes a combination of

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

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wherein:

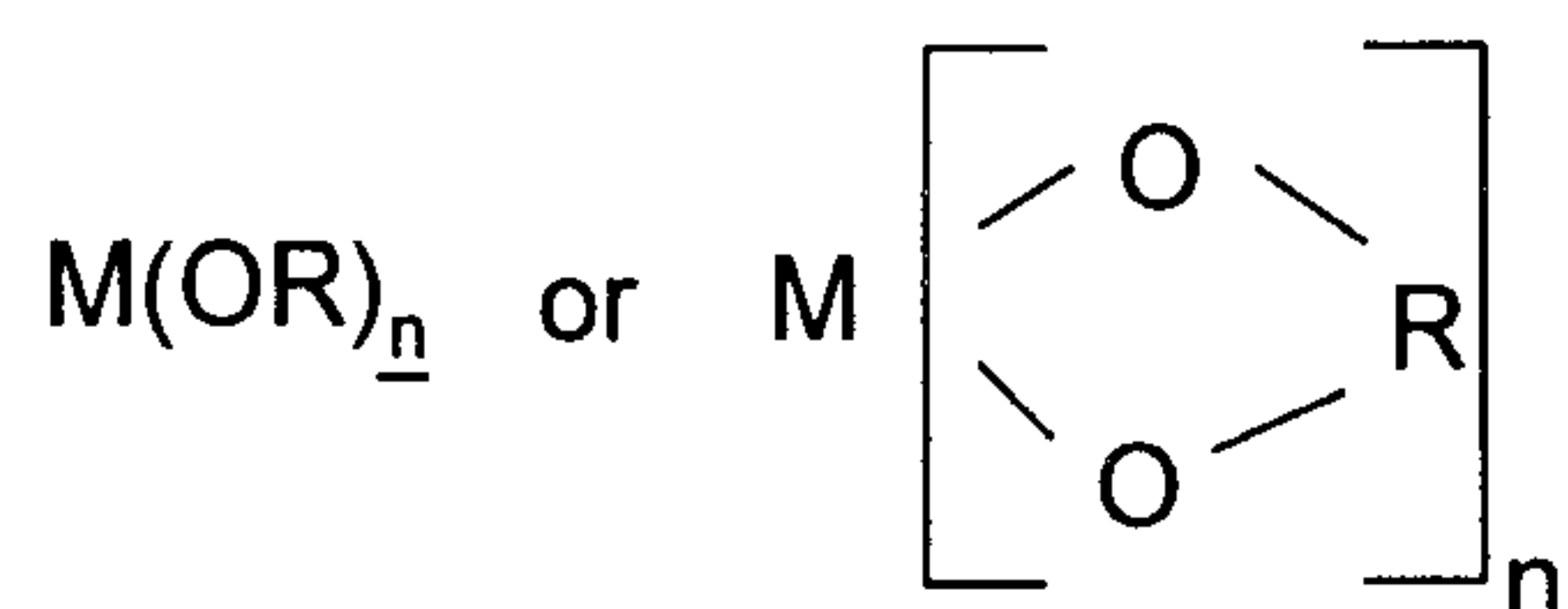
X^1 and X^2 are independently selected from the group consisting of N, P, As, Sb, Bi, O, S and Se;

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

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

R^1 and R^2 are independently hydrogen, a hydrocarbyl 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 $n^1 > 1$.

10 In one use aspect, the invention relates to use of a combination of a catalyst activator and an oligomerisation catalyst in the oligomerisation of at least one olefinic compound in the form of an olefin or a compound including a carbon to carbon double bond by contacting the at least one olefinic compound with the oligomerisation catalyst, and a catalyst activator, wherein the activator is a salt containing an anion which includes a moiety of the formula:



15

wherein:

M is selected from the group consisting of a group 3A atom;

n is 1 or a larger integer; and

20 R is a halogenated organic group, R being the same or different when n is larger than 1; and

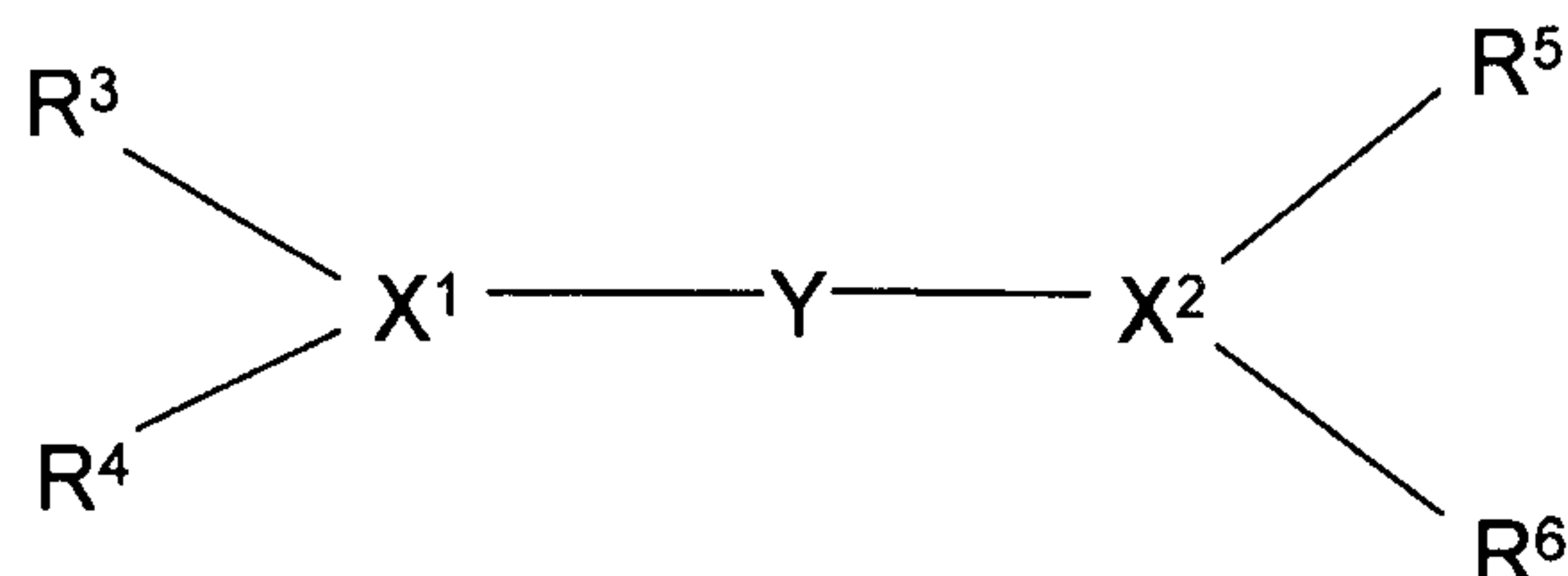
wherein the oligomerisation catalyst includes a combination of:

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i) a source of Cr; and

ii) a ligating compound of the formula:



5

wherein: X^1 and X^2 are P;

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

R^3 to R^6 are each independently:

- a hydrocarbyl group

wherein the hydrocarbyl group is a univalent or multivalent group

10 formed by removing one or more hydrogen atoms from a hydrocarbon;

- or a heterohydrocarbyl group

wherein the heterohydrocarbyl group is a univalent or multivalent

organic compound which includes at least one heteroatom, that is not being H or C,
and which organic compound binds with one or more other moieties through one or

15 more carbon atoms of the organic compound and/or one or more heteroatoms of the
organic compound;

the process further including a co-activator.

It has been found that the activator often provides good activity and even improved
productivity compared to boranes and borates. Polymer formation has also been

20 reduced in at least some cases. In comparison to the use of aluminoxanes as

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activator, the amount of activator required relative to catalyst has been reduced in most cases. This has led to lower waste volumes (such as lower aluminium oxide in the product) and reduced activator cost. It has also been found that the activator influences the product selectivity specifically in respect of the molar ratio of trimer:tetramer formed.

Combination of catalyst and activator

The catalyst and activator may be combined prior to being contacted with the olefinic compound. The catalyst and activator may react with each other to form a reaction product of the catalyst and the activator. The activator and catalyst may form part of the same compound. The said reaction product may be an ionic reaction product.

Activator

Preferably the activator is a Lewis acid.

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As stated above the one or more binding atoms are bound to a central atom selected from the group consisting a group 3A atom, and a group 3B to 7B transition metal atom. The central transition metal atom is preferably selected from the group consisting of Nb, Ta, Y and La. Preferably the transition metal atom is Ta. Preferably
5 the one or more binding atoms are bound to a central group 3A atom. Preferably the central group 3A atom is selected from the group consisting of Al and B, preferably it is Al.

The, or each binding atom is preferably an atom selected from the group consisting
10 of O, N, P and S. Preferably it is O.

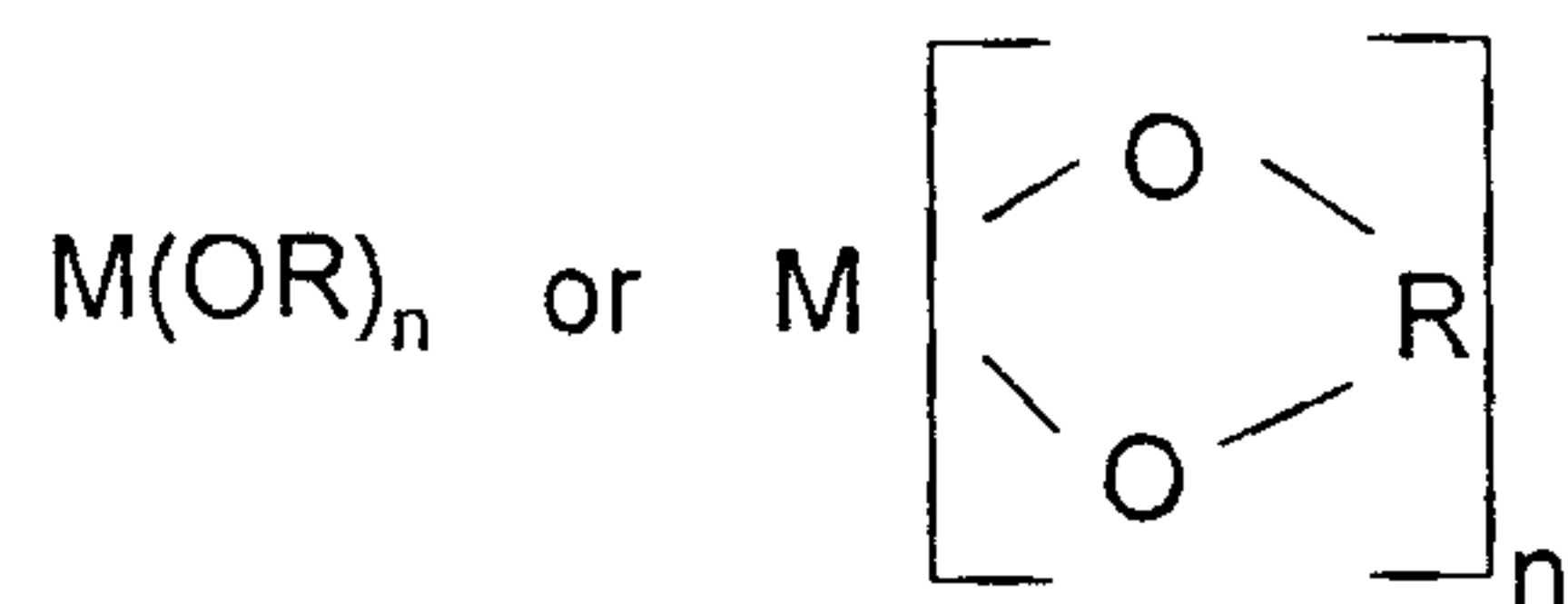
In one embodiment of the invention the activator may include only one or more halogenated organic groups bound to one or more binding atoms as set out above, which one or more binding atoms are groups bound to the central atom as set out
15 above. In an alternative embodiment of the invention the activator may also include one or more atoms or groups of atoms other than said one or more halogenated organic groups bound to said one ore more binding atoms.

The at least one halogenated organic group may be bound to each binding atom by
20 means of a carbon atom and/or a non-carbon atom. The halogenated organic group may be a halogenated hydrocarbyl group or a halogenated heterohydrocarbyl group. The halogenated organic group may be a halogenated organyl group or a halogenated organoheteryl group. Preferably it is a halogenated hydrocarbyl group.

25 In one embodiment of the invention the activator may be a compound of the formula, or the activator may include a moiety of the formula

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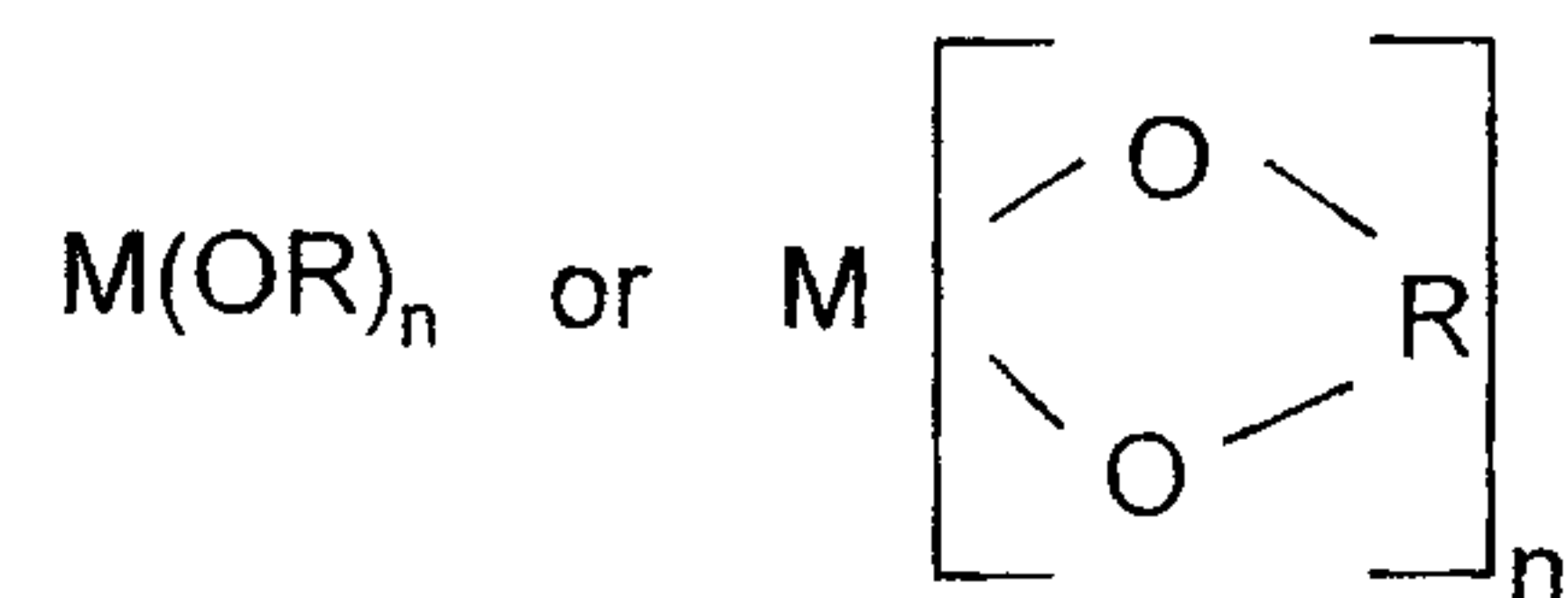
wherein

- 5 M is selected from the group consisting of a group 3A atom, and a group 3B to 7B transition metal atom;
- n is 1 or a larger integer; and
- R is a halogenated organic group, R being the same or different when n is larger than 1.

10 The group 3B to 7B transition metal atom is preferably selected from the group consisting of Nb, Ta, Y and La. Preferably it is Ta. Preferably M is a group 3A atom. Preferably the group 3A atom is selected from the group consisting of Al and B, preferably it is Al.

15 R may be bound to each O by means of a carbon atom and/or a non-carbon atom. R may be a halogenated hydrocarbyl group, or a halogenated heterohydrocarbyl group or a halogenated organyl group, or a halogenated organoheteryl group.

In one embodiment of the invention the activator may be a compound of the formula

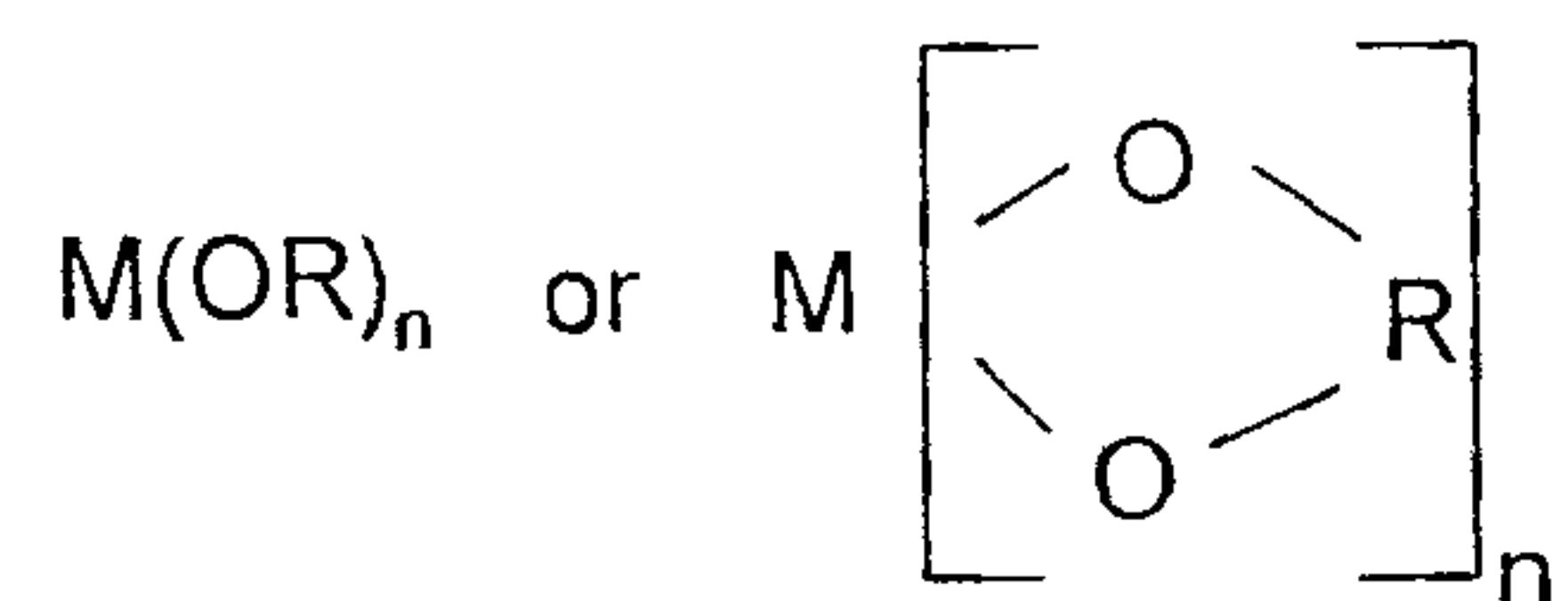


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wherein M, R and n are as defined above. Alternatively the activator may be a compound which includes a moiety of the formula

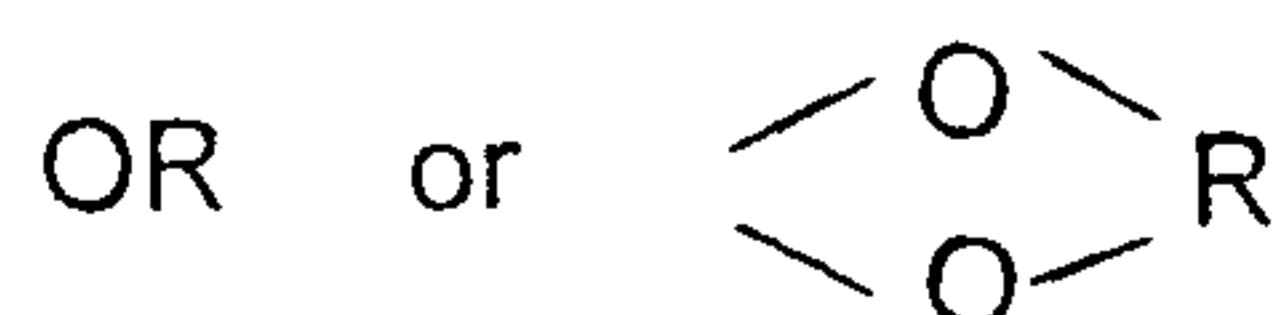
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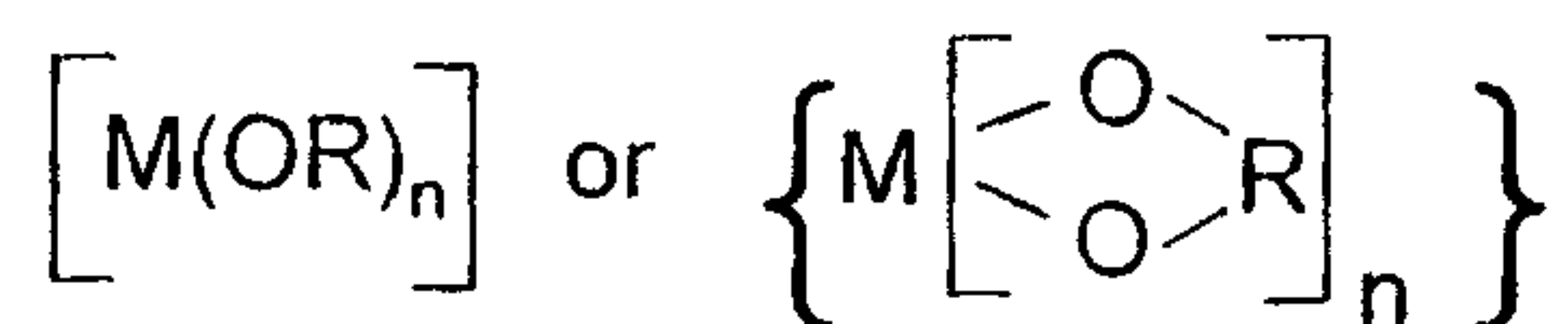
wherein M, R and n are as defined above, and M is bound to at least one moiety Z

5 which is not a



group as defined above. Preferably Z is a halide or a hydrocarbyl group or
 10 heterohydrocarbyl group. Preferably Z is a halide or an organoheteryl group.
 Preferably Z is $-O(R^{10})_2$ wherein R^{10} is a hydrocarbyl group, and R^{10} being the same
 or different. R^{10} may be alkyl and preferably it is ethyl. Alternatively Z may be halide,
 preferably in the form of F. Alternatively, the activator may be a salt containing an
 anion which includes a moiety of the formula

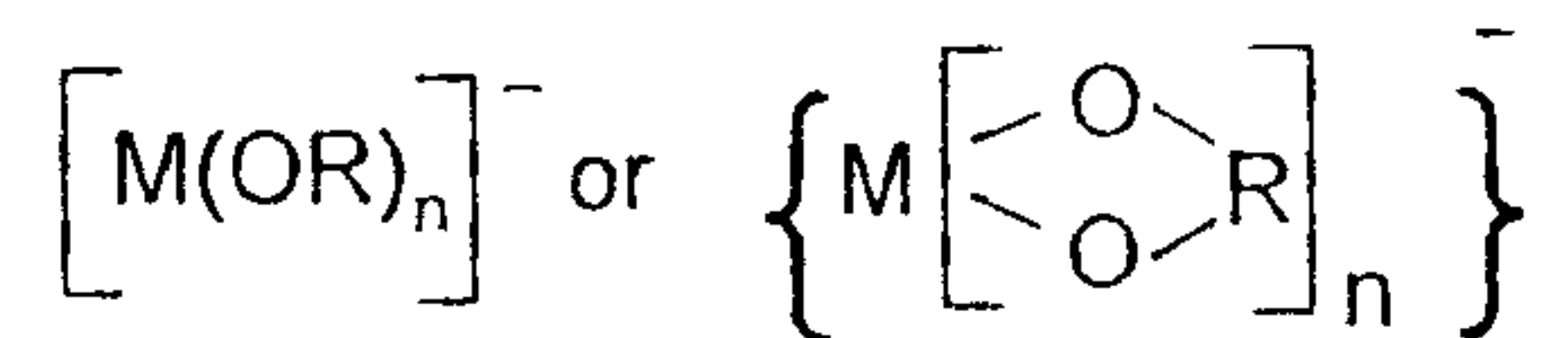
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preferably the anion is

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wherein M, R and n are as defined above.

Preferably R is a halogenated hydrocarbyl group or a halogenated organyl group.

- 5 The halogenated organyl group or halogenated hydrocarbyl group may comprise an organyl group or hydrocarbyl group wherein at least one hydrogen atom has been replaced with a halogen atom. Preferably all the hydrogen atoms of the organyl group or hydrocarbyl group are replaced with halogen atoms. Preferably all the halogen atoms are the same. Preferably the halogen atom is F.

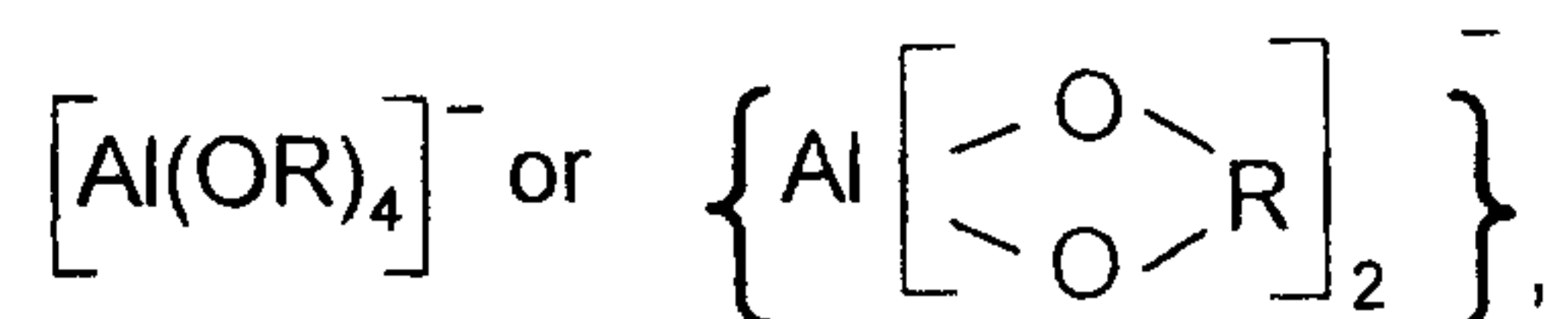
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- The halogenated organic group may be a monovalent or divalent halogenated hydrocarbyl group in the form of a hydrocarbyl group wherein at least one hydrogen atom has been replaced with a halogen atom. Preferably all the hydrogen atoms of the hydrocarbyl group are replaced with halogen atoms. Preferably all the halogen
- 15 atoms are the same. Preferably the halogen atom is F. The halogenated hydrocarbyl group may comprise a halogenated acyclic hydrocarbyl group or a halogenated cyclic hydrocarbyl group. The halogenated acyclic hydrocarbyl group may comprise a halogenated alkyl, preferably a halogenated branched alkyl, preferably halogenated isobutyl or tertiary-butyl. The halogenated cyclic hydrocarbyl
- 20 group may comprise a halogenated aromatic compound, preferably a halogenated phenyl group.

In one embodiment of the invention the activator may be selected from the group consisting of a compound $\text{Al}(\text{OR})_3$, a salt containing the anion

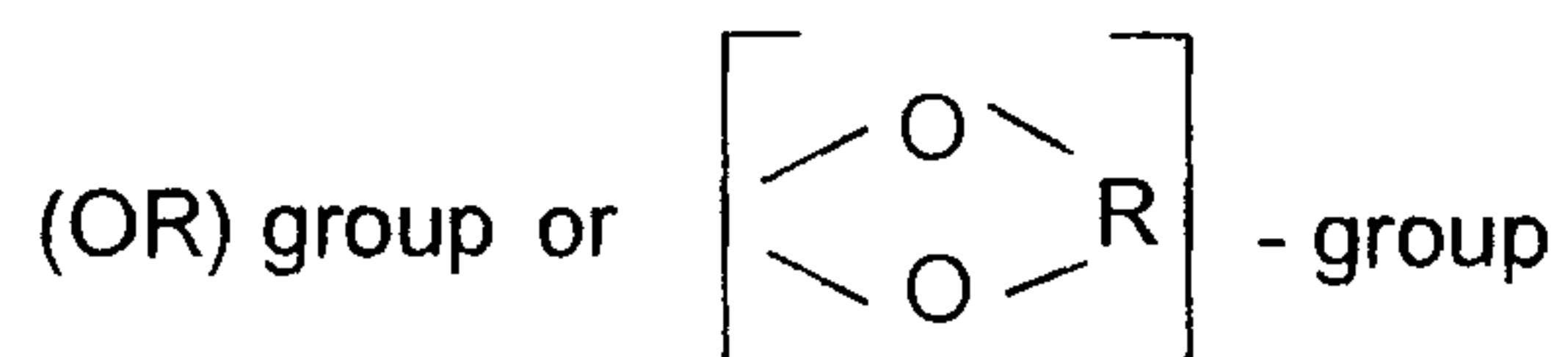
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a compound including a moiety $\text{Al}(\text{OR})_3$ and a salt containing the anion $[\text{Ta}(\text{OR})_6]^-$ wherein R is defined as above.

- 5 In one embodiment of the invention the activator may be selected from the group consisting of $\text{Al}(\text{OC}_6\text{F}_5)_3$; $\text{X}^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$; $\text{X}^+[\text{Al}(\text{OC}_6\text{F}_5)_4]^-$; $\text{X}^+[\text{Al}(\text{C}_6\text{F}_4\text{O}_2)_2]^-$; $\text{X}^+[\text{Al}\{\text{OC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{O}\}_2]^-$; $\text{X}^+[\text{AlF}\{\text{OC}(\text{CF}_3)_3\}_3]^-$; $\text{X}^+[\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]^-$; $(\text{Z})\text{Al}\{\text{OCH}(\text{C}_6\text{F}_5)_2\}_3$; $(\text{Z})\text{Al}\{\text{OC}(\text{CF}_3)_3\}_3$ and $\text{X}^+[\text{Ta}(\text{OC}_6\text{F}_5)_6]^-$ wherein X^+ is a cation including Ph_3C^+ , Me_2PhNH^+ and $(\text{Et}_2\text{O})_2\text{H}^+$; and wherein Z is a moiety bound to Al
- 10 which moiety Z is not an



where R is a halogenated organic group.

15

The amount of activator used may be between 1-100 equivalents relative to the catalyst transition metal. Preferably it is less than 5 equivalents relative to the catalyst transition metal, and most preferably between 1-3 equivalents relative to the catalyst transition metal.

20

The activator may be prepared in situ, alternatively it may be preformed. In one embodiment of the invention the activator may be preformed from the co-activator as described herein below.

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Co-Activator

The process may also include a co-activator which is a compound not falling within the definition of the activator. Preferably the co-activator includes no halogenated organic group which is bound to one or more binding atoms selected from the group consisting of a group 5A atom and a group 6A atom, which one or more binding atoms are in turn bound to a central atom selected from the group consisting of a group 3A atom, and a group 3B to 7B transition metal atom. Preferably the co-activator is a compound which includes at least one moiety selected from the group consisting of an organic group (preferably an organyl group), a halogenated organic group (preferably a halogenated organyl group) and hydrogen; and the moiety being bound to an atom 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.

15

Preferably the co-activator as set out above 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.

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

Suitable organoaluminium compounds include compounds of the formula $\text{Al}(\text{R}^9)_3$ (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), tri-isobutylaluminium (TIBA), tri-*n*-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride,

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diethylaluminium chloride, aluminium isopropoxide, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and aluminoxanes.

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

10 The co-activator may comprise a compound of the formula



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

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

20

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.

25

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.

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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.

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 TMA and MAO) the use of TMA can be avoided as a co-catalyst.

It is foreseen that a co-activator as defined hereinabove will usually be used in combination with an activator as defined above. However, it may be possible, by selecting a suitable source of transition metal (i) and/or a ligating compound (ii), that the use of the co-activator may be avoided. It is believed (without being bound thereto) that a co-activator such as TMA is used to alkylate the catalyst formed by the combination of (i) and (ii) and that the activator then acts on alkyl abstracting agent of the alkylated catalyst to activate the said catalyst.

20

The amount of co-activator employed may be up to 1000 equivalents relative to the transition metal catalyst, but preferable is less than 600 equivalents. Preferably it is in the range between 30-300 equivalents relative to the transition metal catalyst.

25 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.

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Oligomeric product

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

5 containing a single carbon-carbon double bond, and preferably it includes an α -olefin.

The olefin product may include hexene, preferably 1-hexene, alternatively or additionally 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.

10

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 total product of a single olefin product. The olefin product may be hexene, preferably 1-hexene, but alternatively it may be octene, preferably 1-octene.

15

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.

20

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

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and/or tetramerisation) comprises the oligomerisation of a single monomer olefinic compound.

In one preferred embodiment of the invention the oligomerisation process is
5 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.

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.

15 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-
20 butene, 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.

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CatalystSource of transition metal (i)

Preferably the source of transition metal as set out in (i) above is a source of a Group
5 4B to 6B transition metal. Preferably it is a source of Cr, Ti, V, Ta or Zr, more
preferably Cr, Ti, V or Ta. Preferably it is a source of either Cr, Ta or Ti. Most
preferably it is a source of Cr.

The source of the Group 4B to 6B transition metal may be an inorganic salt, an
10 organic salt, a coordination compound or an organometallic complex.

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

20 Ligating compound

X^1 and/or X^2 may be a potential electron donor for coordination with the transition
metal referred to in (i).

25 An electron donor is defined as an entity that donates electrons used in chemical,
including dative covalent, bond formation.

X^1 and/or X^2 , may be independently oxidised by S, Se, N or O.

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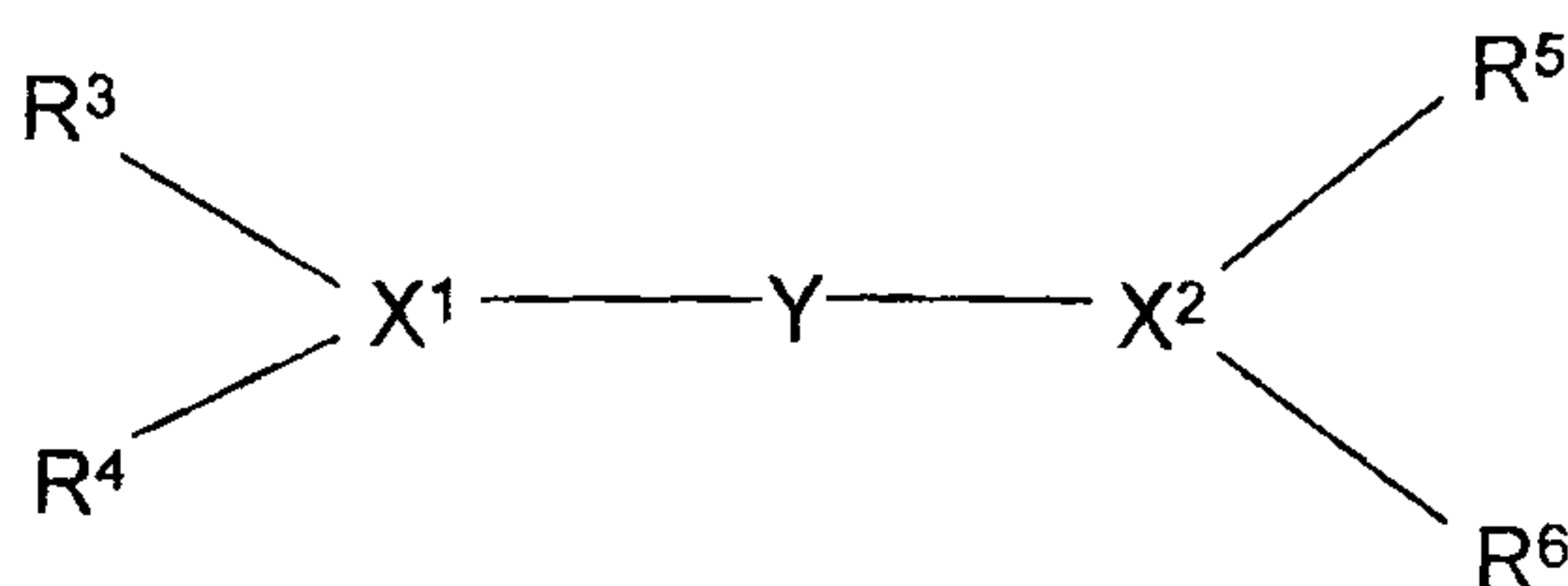
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X^1 and/or X^2 may be independently phosphorus or phosphorus oxidised by S, Se, N or O. Preferably X^1 and X^2 are the same, and preferably both are P.

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 or tridentate ligand, preferably a bidentate ligand.

Preferably the ligating compound is of the formula



15

wherein Y is as defined above; X^1 and X^2 are independently selected from the group consisting of N, P, As, Sb and Bi; and R^3 to R^6 are each independently a hydrocarbyl group or a heterohydrocarbyl group.

Preferably X^1 and X^2 are independently selected from the group consisting of P, S and N. Preferably X^1 and X^2 are the same. Preferably both X^1 and X^2 are P.

One or more of R^3 to R^6 may be a substituted hydrocarbyl group or a substituted heterohydrocarbyl group, that is at least one substituent is bound to the hydrocarbyl group or the heterohydrocarbyl group. In this specification a substituent with

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reference to compounds bound to X^1 and/or X^2 is a moiety (excluding H) which is bound to a linear structure or a cyclic structure bound to X^1 and/or X^2 , but the substituent does not form part of the linear or cyclic structure. The linear or cyclic structure may be selected from the group consisting of a linear hydrocarbyl, a cyclic hydrocarbyl and a cyclic heterohydrocarbyl group. Linear hydrocarbyl may include ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, ethynyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl and decynyl. Cyclic hydrocarbyl may include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cyclopentenyl, cyclohexenyl, cyclo-octenyl, phenyl, cyclopentadienyl, naphthalenyl, norbornyl, adamantyl, phenanthrenyl, anthracenyl, phenalenyl, tetrahydronaphthalenyl, decalyl, indenyl and tetrahydroindenyl. Cyclic heterohydrocarbyl may include tetrahydrofuranyl, tetrahydrothiophenyl, pyrrolidenyl, piperidineyl, pyrrolineyl, oxazolyl, thiazolyl, furanyl, thiophenyl, pyrazolinyl, pyrazolyl, imidazolyl, benzofuranyl, coumaranyl and indolyl.

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

Preferably none of R^3 to R^6 are aromatic with a ring atom of the aromatic ring structure bound to either X^1 or X^2 and with a polar substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X^1 or X^2 .

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

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

5

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 have any polar substituent. In one embodiment of the invention at least two of (but preferably
10 all of) R^3 to R^6 are aromatic 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 R^3 to R^6 have a non-polar substituent other than H as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X^1 or X^2 .

15 Preferably none of the aromatic R^3 to R^6 have a non-polar substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X^1 or X^2 . Preferably all of aromatic R^3 to R^6 are non-substituted aromatic compounds. R^3 to R^6 may be independently selected from the group consisting of a non-aromatic compound; an aromatic compound; and a heteroaromatic compound.
20 Preferably each of R^3 to R^6 is an aromatic or heteroaromatic compound, more preferably an aromatic compound (including a substituted aromatic compound). The aromatic compound (or substituted aromatic compound) may comprise phenyl or a substituted phenyl.

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

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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, 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.

Any one of R^3 to R^6 may be independently linked to one or more of each other, or to Y to form a cyclic structure.

R^3 and R^4 may be the same and R^5 and R^6 may be the same. R^3 to R^6 may all be the same.

15

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

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R^6 have a substituent as a non-ring atom bound to a ring atom of the aromatic ring structure adjacent to the ring atom bound to X^1 or X^2 .

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

- 5 Suitable polar substituents may be a methoxy, ethoxy, isopropoxy, C_3 - C_{20} alkoxy, phenoxy, methoxymethyl, methylthiomethyl, 1,3-oxazolyl, methoxymethoxy, hydroxyl, amino, pentafluorophenoxy, tosyl, methylsulfanyl, trimethylsiloxy, dimethylamino, sulphate, nitro, halides or the like.
- 10 Y may be selected from the group consisting of an organic linking group such as a hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl and a substituted heterohydrocarbyl; an inorganic linking group such as a single atom link (that is X^1 and X^2 are bound to the same atom); methylene; dimethylmethylene; 1,2-ethane; 1,2-ethene; 1,1-cyclopropane; 1,1-cyclobutane; 1,1-cyclohexane; 1,1-cyclopentane; 1,2-15 cyclopentane; 1,2-cyclohexane; 1,2-phenylene; 1,8-naphthyl; 9,10-phenanthrene; 4,5-phenanthrene; 1,3-propane; 1,2-catechol, 1,2-diarylhydrazine and 1,2-dialkylhydrazine; $-B(R^7)-$, $-Si(R^7)_2-$, $-P(R^7)-$ and $-N(R^7)-$ where R^7 is hydrogen, a hydrocarbyl or heterohydrocarbyl 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, 20 substituted aryl, aryloxy, substituted aryloxy, halogen, alkoxycarbonyl, carbonyloxy, alkoxy, aminocarbonyl, carbonylamino, dialkylamino, silyl groups or derivatives thereof, and aryl substituted with any of these substituents. Preferably R^7 may be a hydrocarbyl or a heterohydrocarbyl group. R^7 may be methyl, ethyl, propyl, isopropyl, cyclopropyl, allyl, butyl, tertiary-butyl, sec-butyl, cyclobutyl, pentyl, isopentyl, 25 neopentyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclo-octyl, decyl, cyclodecyl, 1,5-dimethylheptyl, 2-naphthylethyl, 1-naphthylmethyl, adamantylmethyl, adamantyl, 2-isopropylcyclohexyl, 2,6-dimethylcyclohexyl, cyclododecyl, 2-methylcyclohexyl, 3-methylcyclohexyl, 4-methylcyclohexyl, 2-ethylcyclohexyl, 2-isopropylcyclohexyl, 2,6-

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dimethyl-cyclohexyl, *exo*-2-norbornanyl, isopinocampheyl, dimethylamino, phthalimido, pyrrolyl, trimethylsilyl, dimethyl-tertiary-butylsilyl, 3-trimethoxysilane-propyl, indanyl, cyclohexanemethyl, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 4-tertiary-butylphenyl, 4-nitrophenyl, (1,1'-bis(cyclohexyl)-4,4'-methylene), 1,6-hexylene, 1-naphthyl, 2-naphthyl, N-morpholine, diphenylmethyl, 1,2-diphenyl-ethyl, phenylethyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2,6-dimethyl-phenyl, 1,2,3,4-tetrahydronaphthyl, or a 2-octyl group.

In one embodiment of the invention Y may exclude $(CH_2)_xZ(CH_2)_y$, where Z is $-P(R^8)-$, $-N(R^8)-$, $-As(R^8)-$, $-Sb(R^8)-$ or $-S-$ and x and y are individually 1-15 and wherein R^8 is hydrogen or a halogen or a nitro group or a hydrocarbyl or a substituted hydrocarbyl group.

In another embodiment of the invention Y includes no heteroatom (that is an atom other than H or C) as a ring member of a heteroaromatic ring structure in the shortest link of Y between X^1 and X^2 . Y may include at least one heteroatom (that is neither H or C) in the shortest link of Y between X^1 and X^2 and preferably said heteroatom is different to X^1 and X^2 . Preferably X^1 and X^2 are the same and said heteroatom is different to X^1 and X^2 , preferably said heteroatom is N.

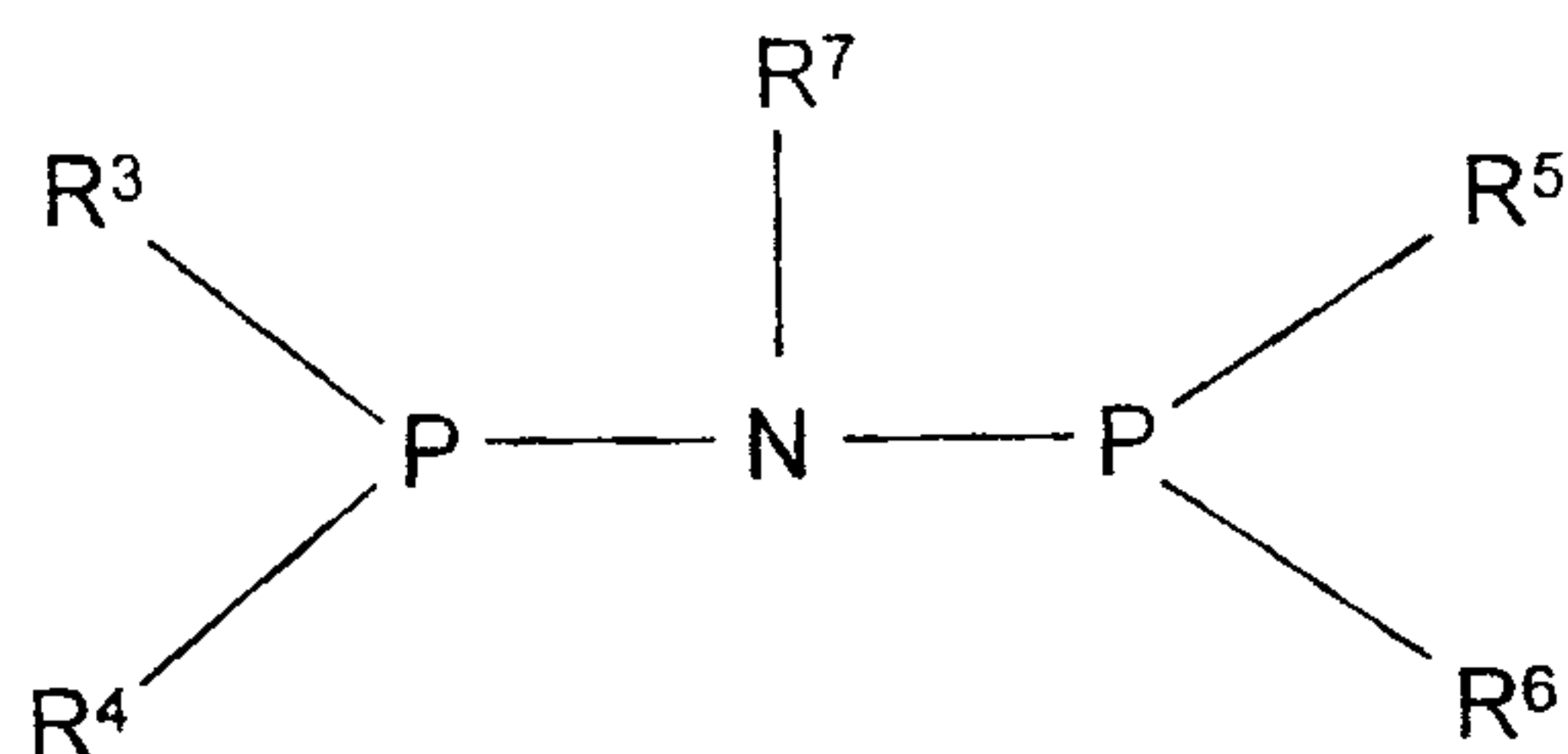
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Y may include a first atom bound to X^1 and a different atom bound to X^2 , such as the case where Y is 1,2 ethane. Preferably Y includes or is a single atom bound to both X^1 and X^2 .

25 Preferably the ligating compound is of the formula

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

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

Non limiting examples of the ligating compound are $(\text{phenyl})_2\text{PN}(\text{propyl})\text{P}(\text{phenyl})_2$;

$(\text{phenyl})_2\text{PN}(\text{cyclopentyl})\text{P}(\text{phenyl})_2$; $(\text{phenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$;

- 10 $(\text{phenyl})_2\text{PN}((4\text{-}t\text{-butyl})\text{-phenyl})\text{P}(\text{phenyl})_2$;

$(2\text{-naphthyl})_2\text{PN}(\text{methyl})\text{P}(\text{phenyl})_2$;

$(2\text{-methylphenyl})(\text{phenyl})\text{PN}(\text{isopropyl})\text{P}(2\text{-methylphenyl})(\text{phenyl})$;

$(\text{ethyl})(\text{phenyl})\text{P-}1,2\text{-benzene-P}(\text{ethyl})(\text{phenyl})$;

$(4\text{-methoxyphenyl})_2\text{PN}(\text{isopropyl})\text{P}(\text{phenyl})_2$;

- 15 $(2\text{-methoxyphenyl})_2\text{P-}1,2\text{-benzene-P}(2\text{-methoxyphenyl})_2$;

The ligating compound may include a polymeric moiety to render the reaction product of the source of transition metal and the said ligating compound to be soluble at higher temperatures and insoluble at lower temperatures e.g. 25°C. This approach

- 20 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 transition metal catalysts can also be immobilised by binding the ligating compound to silica, silica gel, polysiloxane or

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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.

5 Non-limiting 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-
10 (N(P(*p*-methoxyphenyl)₂)₂)-benzene, 1,4-di-(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
15 the art and procedures forming part of the state of the art.

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-
20 formed.

The source of transition metal and ligating compound may be combined (*in situ* or *ex situ*) to provide any suitable molar ratio, preferably a transition metal to ligand compound molar ratio, from about 0.01 : 100 to 10 000 : 1, preferably from about 0.1
25 : 1 to 10:1.

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

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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, MgCl_2 , zirconia, artificial hectorite or smectite 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, 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.

Process

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

The olefinic compound or mixture of olefinic compounds may be contacted with the catalysts at a pressure of 1 barg or higher, preferably greater than 10 barg (1000 kPa), more preferably greater than 30 barg (3000 kPa). Preferred pressure ranges are from 10 to 300 barg (1000 to 3000 kPa), more preferably from 30 to 100 barg (3000 to 10000 kPa).

The process may be carried out at temperatures from -100 °C to 250 °C. Temperatures in the range of 15-150 °C are preferred. Particularly preferred temperatures range from 35-120°C.

The reaction products derived from the reaction as described herein, may be prepared using the disclosed catalysts by a homogeneous liquid phase reaction in

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the presence or absence of an inert solvent, and/or by slurry reaction where the catalysts and the oligomeric product is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase
5 reaction, using conventional equipment and contacting techniques.

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

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

25 According to another aspect of the present invention there is provided an oligomerisation product prepared by a process substantially as described hereinabove.

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According to another aspect of the present invention there is provided the combination of an oligomerisation catalyst and a catalyst activator, which catalyst activator is a compound which includes

at least one halogenated organic group which is bound to one or more
 5 binding atoms selected from the group consisting of a group 5A atom and a group 6A atom, which one or more binding atoms are in turn bound to a central atom selected from the group consisting of a group 3A atom, and a group 3B to 7B transition metal atom; and

wherein the oligomerisation catalyst includes the combination of

- 10 iii) a source of a transition metal; and
 iv) a ligating compound of the formula



15 wherein: X^1 and X^2 are independently selected from the group consisting of N, P, As, Sb, Bi, O, S and Se;
 Y is a linking group between X^1 and X^2 ;
 m and n^1 are independently 0, 1 or a larger integer; and
 R^1 and R^2 are independently hydrogen, a hydrocarbyl group or
 20 a heterohydrocarbyl group, and R^1 being the same or different when $m > 1$, and R^2 being the same or different when $n^1 > 1$.

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

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Brief Description of the Drawings

Figure 1 shows the molecular structure of $\{\text{Al}(\text{OC}_6\text{F}_5)_3\}_2$ prepared in Example 1.

Figure 2 shows the molecular structure of $(\text{Et}_2\text{O})\text{Al}[\text{OCH}(\text{C}_6\text{H}_5)_2]_3$ prepared in Example 3.

- 5 Figure 3 shows the molecular structure of $(\text{Et}_2\text{O})\text{Al}[\text{OC}(\text{CF}_3)_3]_3$ prepared in Example 4.

Figure 4 is a plot of the mass ratio of C_8/C_6 as a function of amount of activator, corresponding to Examples 34-37.

Examples

- 10 In the examples that follow, all manipulations were carried out under inert conditions, using standard Schlenk techniques. All solvents were dried and degassed via normal procedures. $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ was prepared following the method described by Krossing et. al., Journal of Fluorine Chemistry, 112 (2001), 83-90. The ethylene used in the catalyst testing was supplied by BOC and was grade 3.0 unless otherwise stated.

15 **Example 1. Preparation of $\{\text{Al}(\text{OC}_6\text{F}_5)_3\}_2$**

A solution of 2M perfluorophenol (7.0 ml, 14 mmol) in toluene was added to a flask and a 1.9M solution of triethylaluminium (2.0 ml, 3.8 mmol) was added dropwise. The solution was then heated to 60°C for 4 hours and then allowed to cool. The solvent toluene was reduced under vacuum and 10 ml of petroleum spirits added.

- 20 The resulting powder that formed was washed four times with petroleum spirits (5 ml) and dried under vacuum to afford a white powder. Yield: 1.694g (77%) Anal. Calcd. for (found) $\text{C}_{18}\text{F}_{15}\text{O}_3\text{Al}$: C 37.52 (37.34). ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$): -161.2, -162.1, -162.8 (*ortho*-F); -169.9 (*meta*-F); 179.0 (*para*-F). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): 143.0, 142.4, 139.2, 136.0, 132.8, 129.7 (CF). The molecular structure of
25 the compound is shown in Figure 1.

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Example 2. Preparation of $[(Et_2O)_2H][Al(OC_6F_5)_4]$

- 5 At 0°C a solution of perfluorophenol (7.5 ml, 15 mmol) in 20 ml of diethylether was treated dropwise with 1.9M triethylaluminium solution (1.7 ml, 3.2 mmol). After 2 hours at room temperature the solvent was removed under vacuum and the product washed twice with petroleum spirits to give a white powder. Yield: 1.641g (56%).
- Anal. Calc. for (found) $C_{32}H_{21}O_6F_{20}Al$: C 42.31 (42.28), H 2.33 (2.47). ^1H NMR (300
10 MHz, $CDCl_3$): 5.60 (br, 1H, $H(OEt_2)$); 4.39 (q, $J=7Hz$, 8H, OCH_2CH_3); 1.55 (t, $J=7Hz$, 12H, OCH_2CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): -163.7 (d, $J=22Hz$, *ortho*-F); -165.8 (t, $J=22Hz$, *meta*-F); -171.1 (t, $J=22Hz$, *para*-F). ^{13}C NMR (75 MHz, $CDCl_3$): 142.0, 140.0, 138.8, 136.6 (CF); 71.9 (OCH_2); 13.9 (OCH_2C_3).

15 **Example 3. Preparation of $(Et_2O)Al\{OCH(C_6F_5)_2\}_3$.**

At 0°C a solution of $(C_6F_5)_2C(H)OH$ (5.79 g, 15.9 mmol) in 15 ml of diethylether was treated dropwise with 1.9M $AlEt_3$. The addition of $AlEt_3$ was continued portionwise until the starting alcohol was completely consumed by NMR analysis. The solvent

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was then removed under vacuum, the residue taken up in diethylether, and the solvent removed again to yield a white powder. Yield: 5.743 g (91%). Anal. Calcd. for $C_{43}H_{13}O_4F_{30}$ (found): C 43.38 (44.14), H 1.10 (1.50). ^1H NMR (300 MHz, $CDCl_3$): 6.65 (s, 3H, OCH); 4.18 (q, $J=7$ Hz, 4H, OCH_2CH_3); 1.32 (t, $J=7$ Hz, 6H, OCH_2CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): -144.5 (*ortho*-F); -155.2 (*meta*-F); -162.6 (*para*-F). ^{13}C NMR (75 MHz, $CDCl_3$): 146.5, 143.2, 139.6, 136.2 (CF); 116.8 (*ipso*-C); 69.6 (OCH_2CH_3); 61.7 (OCH); 13.3 (OCH_2CH_3). The molecular structure of the compound is shown in Figure 2.

Example 4. Preparation of $(Et_2O)Al\{OC(CF_3)_3\}_3$.

10 A solution of 4 ml (29 mmol) of perfluoro-tert-butanol in 10 ml of diethylether was cooled to 0°C and treated with a 1.9M solution of triethylaluminium (3 ml, 5.7 mmol). After stirring overnight the solution was heated to 65°C for a further day. After cooling the solvent was removed under vacuum to give fine needles of colorless product. Yield: 4.383g (95%). ^1H NMR (300 MHz, $CDCl_3$): 4.34 (q, $J=7$ Hz, 4H, OCH_2CH_3);
15 1.43 (t, $J=7$ Hz, 6H, OCH_2CH_3). ^{19}F NMR (282 MHz, $CDCl_3$): -75.9 (CF_3). The molecular structure of this compound is shown in Figure 3.

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5 **Example 5. Ethylene oligomerisation with $\text{Al}(\text{OC}_6\text{F}_5)_3$ activator.**

A 300ml stainless steel reactor equipped with mechanical stirring was heated to 120°C and purged with ethylene. Toluene (80 ml) was added, saturated with ethylene, and the reactor brought to 45°C. $\text{CrCl}_3(\text{thf})_3$ (30µmol) and $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ (30µmol) were added to a Schlenk flask under nitrogen and dissolved in 20 ml of
10 toluene. To this solution was added 3 mmol of AlEt_3 (100 equivalents relative to Cr), and the resulting mixture was added to the reactor followed by 40µmol $\text{Al}(\text{OC}_6\text{F}_5)_3$. The reactor was immediately charged with 40 bar of ethylene and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 30 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath.
15 Excess ethylene was bled and the reactor contents treated sequentially with 1000µL of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was

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collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 4.124g. The product distribution is shown in Table 1.

Example 6. Ethylene oligomerisation with Al(OC₆F₅)₃ activator.

- 5 The same procedure as for example 5 was followed with the exception that 9mmol of AlEt₃ was employed (300 equivalents relative to Cr). The total product mass was 3.655g. The product distribution is shown in Table 1.

Example 7. Ethylene oligomerisation with Al(OC₆F₅)₃ activator.

- 10 The same procedure as for example 5 was followed with the exception that 3mmol of triisobutylaluminium (TIBAL, 100 equivalents relative to Cr) was employed in place of AlEt₃. The total product mass was 1.556g. The product distribution is shown in Table 1.

15 **Example 8. Ethylene oligomerisation with Al(OC₆F₅)₃ activator.**

The same procedure as for example 5 was followed with the exception that 0.9mmol of AlEt₃ was employed (30 equivalents relative to Cr). The total product mass was 9.067g. The product distribution is shown in Table 1.

20 **Example 9. Ethylene oligomerisation with perfluorophenol (*in-situ* activator).**

- CrCl₃(thf)₃ (30μmol) and Ph₂PN(ⁱPr)PPh₂ (30μmol) were added to a Schlenk flask under nitrogen and dissolved in 20 ml of toluene. This was treated with 90μmol of C₆F₅OH followed by 0.9 mmol (30 equivalents) of AlEt₃. The resulting solution was immediately added to the reactor (reactor conditions as detailed in example 5), and
- 25 charged with 40 bar ethylene. After 30 minutes the contents were worked up as detailed in example 5. The total product mass was 5.319g. The product distribution is shown in Table 1.

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Example 10. Comparative example of ethylene oligomerisation without phosphine ligand.

The same procedure as in example 9 was followed with the exception that
 5 $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ was omitted. The total product mass was 5.788g. The product distribution is shown in Table 1.

Example 11. Ethylene oligomerisation with $[(\text{Et}_2\text{O})_2\text{H}][\text{Al}(\text{OC}_6\text{F}_5)_4]$ activator.

The procedure of example 5 was followed with $10\mu\text{mol}$ $\text{CrCl}_3(\text{thf})_3$, $12\mu\text{mol}$
 10 $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 1 mmol AlEt_3 (100 equivalents), and $15\mu\text{mol}$ of $[(\text{Et}_2\text{O})_2\text{H}][\text{Al}(\text{OC}_6\text{F}_5)_4]$. The total product mass was 0.873g. The product distribution is shown in Table 1.

Example 12. Ethylene oligomerisation with $(\text{Et}_2\text{O})\text{Al}\{\text{OC}(\text{CF}_3)_3\}_3$ activator.

15 The procedure of example 5 was followed with $20\mu\text{mol}$ $\text{CrCl}_3(\text{thf})_3$, $20\mu\text{mol}$ $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 2 mmol AlEt_3 (100 equivalents), and $35\mu\text{mol}$ of $(\text{Et}_2\text{O})\text{Al}\{\text{OC}(\text{CF}_3)_3\}_3$. The total product mass was 4.26g. The product distribution is shown in Table 1.

Example 13. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.

20 A 300ml stainless steel reactor equipped with mechanical stirring was heated to 120°C and purged with ethylene. Methylcyclohexane (80 ml) was added, saturated with ethylene, and the reactor brought to 65°C . Methylcyclohexane solutions of $\text{Cr}(\text{acac})_3$ (10ml of 1.0mM, $10\mu\text{mol}$) and $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ (5ml of 2.5mM, $12.5\mu\text{mol}$) were added to a Schlenk flask under nitrogen and treated with 1.0 mmol of AlEt_3 (100
 25 equivalents relative to Cr) . The resulting solution was added to the reactor followed by $15\mu\text{mol}$ of $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$. The reactor was immediately charged with 40 bar of ethylene and the pressure kept constant throughout the reaction by the

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continuous addition of ethylene. After 60 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000 μ L of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while

5 the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 25.36g. The product distribution is shown in Table 1.

Example 14. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.

10 The procedure of example 5 was followed with 30 μ mol $\text{CrCl}_3(\text{thf})_3$, 30 μ mol $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 0.9 mmol AlEt_3 (30 equivalents), and 40 μ mol of $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$. The reaction was continued for 1 hour. The total mass of product was 41.98g. The product distribution is shown in Table 1.

15 **Example 15. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.**

The same procedure as in example 14 was followed with the exception that 3mmol of AlEt_3 (100 equivalents) was employed. The total mass of product was 52.62g. The product distribution is shown in Table 1.

20 **Example 16. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.**

The procedure of example 5 was followed with 10 μ mol $\text{CrCl}_3(\text{thf})_3$, 12 μ mol $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 6 mmol AlEt_3 (600 equivalents), and 12 μ mol of $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$. The total mass of product was 0.748g. The product distribution is shown in Table 1.

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Example 17. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.

The procedure of example 5 was followed with $10\mu\text{mol}$ $\text{CrCl}_3(\text{thf})_3$, $12\mu\text{mol}$ $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 3 mmol AlEt_3 (300 equivalents), and $15\mu\text{mol}$ of $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$. The reaction was continued for 1 hour. The total mass of product was 29.77g. The product distribution is shown in Table 1.

Example 18. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.

The same procedure as in example 17 was followed with the exception that 1mmol of AlEt_3 (100 equivalents) was employed. The total mass of product was 39.06g. The product distribution is shown in Table 1.

Example 19. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.

$[\text{CrCl}_3\{\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2\}]_2$ ($10\mu\text{mol}$ of Cr) was added to a Schlenk flask under nitrogen and suspended in 20 ml of toluene. This was treated with 1mmol of AlEt_3 (100 equivalents) to give a homogeneous solution. $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ ($10\mu\text{mol}$) was added to the reactor (reactor conditions as detailed in example 5), followed by the Cr/PNP/ AlEt_3 solution, and the reactor was charged with 40 bar ethylene. After 30 minutes the contents were worked up as detailed in example 5. The total product mass was 8.65g. The product distribution is shown in Table 1.

Example 20. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.

A 300ml stainless steel reactor equipped with mechanical stirring was heated to 120°C and purged with ethylene. Methylcyclohexane (80 ml) was added, saturated with ethylene, and the reactor brought to 65°C . $\text{CrCl}_3(\text{thf})_3$ ($10\mu\text{mol}$) and $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ ($12\mu\text{mol}$) were added to a Schlenk flask under nitrogen and dissolved in 5 ml of toluene. To this solution was added 1 mmol of AlEt_3 (100 equivalents relative to Cr). The resulting solution was added to the reactor followed

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by 15 μ mol of $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$. The reactor was immediately charged with 40 bar of ethylene and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 60 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000 μ L of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 30.97g. The product distribution is shown in Table 1.

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Example 21. Comparative example of ethylene oligomerisation with $\text{B}(\text{C}_6\text{F}_5)_3$ activator.

A 300ml stainless steel reactor equipped with mechanical stirring was heated to 120°C and purged with ethylene. Toluene (80 ml) was added, saturated with ethylene, and the reactor brought to 45°C. $\text{CrCl}_3(\text{thf})_3$ (20 μ mol) and $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$ (20 μ mol) were added to a Schlenk flask under nitrogen and dissolved in 20 ml of toluene. To this solution was added 3 mmol of AlEt_3 (100 equivalents relative to Cr), and the resulting mixture was added to the reactor followed by 30 μ mol $\text{B}(\text{C}_6\text{F}_5)_3$. The reactor was immediately charged with 50 bar of ethylene and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 30 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000 μ L of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 0.611g. The product distribution is shown in Table 1.

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Example 22. Comparative ethylene oligomerisation with MMAO-3A activator

The same procedure as in example 20 was followed with the exception that 1mmol of MMAO-3A was employed as an activator in the place of AlEt₃ and

[Ph₃C][Al{OC(CF₃)₃}]₄, and 40 bar of ethylene was fed. The total mass of product was

5 13.49g. The product distribution is shown in Table 1.

Example 23. Comparative ethylene oligomerisation with MMAO-3A activator.

The same procedure as in example 20 was followed with the exception that 4.0mmol of MMAO-3A was employed as an activator in the place of AlEt₃ and

10 [Ph₃C][Al{OC(CF₃)₃}]₄, and 30 bar of ethylene was fed. The total mass of product was 37.39g. The product distribution is shown in Table 1.

Example 24. Preparation of Cr(CO)₄ Ph₂PN(ⁱPr)PPh₂

Cr(CO)₆ (1.54 g, 7.0 mmol) and Ph₂PN(ⁱPr)PPh₂ (2.99 g, 7.0 mmol) were dissolved in

15 diglyme (60 ml) and heated to 170 °C for 2 hours during which time the solution turned yellow. The solution was cooled and methanol (40 ml) was added which precipitated a yellow solid. The solution was filtered and the solid was washed with MeOH and dried *in vacuo*. Yield = 2.65 g (64 %). Anal. Calcd. for C₃₁H₂₇CrNO₄P₂ (found): C 62.95 (62.94), H 4.60 (4.55), N 2.37 (2.31).

20

Example 25. Preparation of [Cr(CO)₄Ph₂PN(ⁱPr)PPh₂][Al{OC(CF₃)₃}]₄

A dichloromethane (5 ml) solution of Ag[Al{OC(CF₃)₃}]₄ (147 mg, 0.13 mmol) was added to a dichloromethane (5 ml) solution of Cr(CO)₄Ph₂PN(ⁱPr)PPh₂ (75 mg, 0.13mmol). The solution immediately darkened and after stirring for 1 hour the

25 solution was filtered and the solid washed with dichloromethane (2 x 5 ml). The solvent was removed *in vacuo* from the combined organic fractions to leave a blue solid. Yield = 150 mg (74 %). Anal. Calcd. for C₄₇H₂₇AlCrF₃₆NO₈P₂ (found): C 36.22 (36.19), H 1.75 (1.73), N 0.90 (0.87).

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Example 26. Ethylene oligomerisation with $[\text{Cr}(\text{CO})_4\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$

A 300 ml glass Buchi reactor was heated to 120 °C and evacuated and back filled with nitrogen 3 times. Methylcyclohexane (40 ml) was added followed by a toluene (10 ml) solution of $[\text{Cr}(\text{CO})_4\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (31 mg, 20 μmol). To the

5 reactor AlEt_3 (2 mmol, 100 equivalents relative to Cr) was added and the reactor was immediately charged with ethylene to a pressure of 8 bar. The solution was then irradiated with UV light from a High Pressure 100 Watt Mercury Vapor Short Arc lamp with a total intensity of 13 Wcm^{-1} for 10 minutes. The ethylene was slowly vented to a pressure of approximately 0.5 bar and the solution was then transferred to a 300ml

10 stainless steel reactor equipped with mechanical stirring which had been heated to 120 °C, purged with ethylene, methylcyclohexane (50 ml) added and the reactor temperature brought to 60 °C. The reactor was immediately charged with 40 bar of ethylene and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 45 minutes the ethylene supply was closed and the reactor

15 cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000 μL of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 38.97 g. The product distribution is shown in

20 Table 1.

Example 27. Ethylene oligomerisation with $[\text{Cr}(\text{CO})_4\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$

A 300ml stainless steel reactor equipped with mechanical stirring was heated to 120°C and purged with ethylene. Methylcyclohexane (90 ml) was added and the

25 reactor brought to 60 °C. $[\text{Cr}(\text{CO})_4\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (8 mg, 5 μmol) was dissolved in toluene (10 cm^3) and Et_3Al (2 mmol, 400 equivalents relative to Cr) was added. The resultant solution was added to the reactor and the reactor was immediately charged with 40 bar of ethylene and the pressure kept constant

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throughout the reaction by the continuous addition of ethylene. After 60 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000 μ L of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase
 5 was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 10.74 g. The product distribution is shown in Table 1.

Example 28. Ethylene oligomerisation with $[\text{Cr}(\text{CO})_4\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$

10 A 300ml stainless steel reactor equipped with mechanical stirring was heated to 120°C and purged with ethylene. Methylcyclohexane (90 ml) was added and the reactor brought to 60 °C. Et_3Al (0.5 mmol, 100 equivalents relative to Cr) followed by tri-iso-butylaluminium (1.5 mmol, 300 equivalents relative to Cr) was added. $[\text{Cr}(\text{CO})_4\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ (8 mg, 5 μ mol) was dissolved in toluene (10
 15 cm^3) and the resultant solution was added to the reactor. The reactor was immediately charged with 40 bar of ethylene and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 60 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000 μ L of
 20 nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 17.47g. The product distribution is shown in Table 1.

25 **Example 29. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ activator.**

The same procedure as in example 17 was followed with the exception that 1mmol of AlEt_3 (100 equivalents) was employed and the ethylene source was Linde 4.5. The total mass of product was 65.31g. The product distribution is shown in Table 1.

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Example 30. Ethylene oligomerisation with $[\text{Cr}(\text{CO})_4\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$

The same procedure as in example 27 was followed with the exception that 1mmol of AlEt_3 (100 equivalents) was employed and the ethylene source was Linde 4.5. The total mass of product was 32.8g. The product distribution is shown in Table 1.

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Example 31. Ethylene oligomerisation with $[\text{Cr}(\text{CO})_4\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$

The same procedure as in example 27 was followed with the exception that 1mmol of AlEt_3 (200 equivalents) was employed and the ethylene source was Linde 4.5. The total mass of product was 36.4 g. The product distribution is shown in Table 1.

10

Example 32. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Ta}(\text{OC}_6\text{F}_5)_6]$ activator.

The procedure of example 5 was followed with 10 μmol $\text{CrCl}_3(\text{thf})_3$, 12 μmol $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 1 mmol AlEt_3 (100 equivalents), and 20 μmol of $[\text{Ph}_3\text{C}][\text{Ta}(\text{OC}_6\text{F}_5)_6]$. The total product mass was 0.691g. The product distribution is shown in Table 1.

15

Example 33. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{AlF}\{\text{OC}(\text{CF}_3)_3\}_3]$ activator.

The procedure of example 5 was followed with 10 μmol $\text{CrCl}_3(\text{thf})_3$, 12 μmol $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 1 mmol AlEt_3 (100 equivalents), and 15 μmol of $[\text{Ph}_3\text{C}][\text{AlF}\{\text{OC}(\text{CF}_3)_3\}_3]$. The total product mass was 1.187g. The product distribution is shown in Table 1.

20

Example 34. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]$ activator.

The procedure of example 5 was followed with 10 μmol $\text{CrCl}_3(\text{thf})_3$, 12 μmol $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 1 mmol AlEt_3 (100 equivalents), and 10 μmol of $[\text{Ph}_3\text{C}][\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]$. The total product mass was 3.60g. The product distribution is shown in Table 1, while the ratio of C_8/C_6 is shown in Figure 4.

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Example 35. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]$ activator.

The procedure of example 5 was followed with 10 μmol $\text{CrCl}_3(\text{thf})_3$, 12 μmol $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 1 mmol AlEt_3 (100 equivalents), and 15 μmol of $[\text{Ph}_3\text{C}][\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]$. The total product mass was 6.66g. The product distribution is shown in Table 1, while the ratio of C_8/C_6 is shown in Figure 4.

Example 36. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]$ activator.

The procedure of example 5 was followed with 10 μmol $\text{CrCl}_3(\text{thf})_3$, 12 μmol $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 1 mmol AlEt_3 (100 equivalents), and 20 μmol of $[\text{Ph}_3\text{C}][\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]$. The total product mass was 7.14g. The product distribution is shown in Table 1, while the ratio of C_8/C_6 is shown in Figure 4.

Example 37. Ethylene oligomerisation with $[\text{Ph}_3\text{C}][\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]$ activator.

The procedure of example 5 was followed with 10 μmol $\text{CrCl}_3(\text{thf})_3$, 12 μmol $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, 1 mmol AlEt_3 (100 equivalents), and 30 μmol of $[\text{Ph}_3\text{C}][\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]$. The total product mass was 27.62g. The product distribution is shown in Table 1, while the ratio of C_8/C_6 is shown in Figure 4.

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Table 1. Product distributions obtained in examples 5-19.

Example	Productivity g/gCr	% PE	% C ₆	1-C ₆	%C ₈	1-C ₈
5	2640	3.1	85.1	96.9	6.1	85.2
6	2340	2.3	89.9	95.6	4.7	74.4
7	997	6.4	86.0	97.8	4.0	96.8
8	5810	8.2	85.2	98.5	3.9	94.6
9	3410	16.0	78.3	97.9	1.8	84.4
10	3710	95.0	1.5	60.7	0.9	100
11	1680	12.6	63.9	95.0	23.5	97.6
12	4100	1.0	87.0	97.0	6.0	88.5
13	48770	3.6	24.7	82.4	64.9	99.1
14	26910	7.0	15.3	66.7	69.9	98.8
15	33730	0.7	16.2	66.9	72.9	98.6
16	1440	3.3	28.2	66.3	60.1	96.7
17	57250	1.3	16.9	66.3	72.7	98.0
18	75120	4.6	16.0	69.6	68.8	98.9
19	16630	8.5	13.6	66.1	64.8	98.9
20	59560	0.6	25.0	82.5	66.6	99.2
21	587	25.2	21.4	73.3	47.6	96.9
22	25940	33.9	18.2	86.6	45.8	99.2
23	71 860	0.20	27.7	88.9	64.2	99.4
26	37492	0.8	22.5	78.9	68.9	98.9
27	41305	0.3	23.2	75.8	74.2	99.4
28	67240	0.8	21.7	76.5	72.7	99.0
29	125600	0.41	16.3	68.9	72.2	99.0
30	126320	0.23	21.4	78.1	70.7	99.0
31	139832	1.1	21.4	78.8	72.4	99.0
32	1330	13.7	46.6	89.7	39.6	98.5
33	2280	33.3	34.6	80.8	32.1	87.7
34	6925	10.0	57.8	94.7	30.3	95.4
35	12810	21.6	44.0	95.9	25.5	98.2
36	13730	7.9	27.9	85.9	56.0	99.2
37	53120	6.5	18.6	76.3	68.2	99.4

Percentages are all mass%. 1-C₆ and 1-C₈ refer to mass% selectivity within the total

C₆ and C₈ fractions respectively.

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Example 38. Ethylene oligomerisation with [(EtHex₃TAC)CrCl₃], Et₃Al co-activator and [Ph₃C][Al{OC(CF₃)₃]₄] activator.

A 300mL stainless steel reactor equipped with mechanical stirring was heated to 130°C under vacuum for 1 hour. After cooling under vacuum and back-filling with Ar, 10 [Ph₃C][Al{OC(CF₃)₃]₄] (30 μmol) and [(EtHex₃TAC)CrCl₃] [that is {tris-N,N,N,-ethylhexyl}1,3,5-tiazocyclohexane] (20 μmol) were added to the reactor as a solution in toluene (100 mL) and the reactor brought to 40°C. Et₃Al (2.0 mmol, 100 equivalents relative to Cr) was then added to the reactor and the vessel immediately charged with 2 bar of ethylene (Linde 4.5 grade) and the pressure kept constant throughout 15 the reaction by the continuous addition of ethylene. After 37 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000μL of nonane (GC

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internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 13.870g. The product distribution is shown in Table 2.

5

Example 39. Ethylene oligomerisation with [(EtHex₃TAC)CrCl₃], Et₃Al co-activator and [Ph₃C][Al{OC(CF₃)₃]₄] activator.

A 300mL stainless steel reactor equipped with mechanical stirring was heated to 130°C under vacuum for 1 hour. After cooling under vacuum and back-filling with Ar, [Ph₃C][Al{OC(CF₃)₃]₄] (30 µmol) and [(EtHex₃TAC)CrCl₃] (20 µmol) were added to the reactor as a solution in toluene (100 mL) and the reactor brought to 50°C. Et₃Al (2.0 mmol, 100 equivalents relative to Cr) was then added to the reactor and the vessel immediately charged with 5 bar of ethylene (Linde 4.5 grade) and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 17 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000µL of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 12.203g. The product distribution is shown in Table 2.

Example 40. Comparative ethylene oligomerisation with [(EtHex₃TAC)CrCl₃] and MAO activator.

A 300mL stainless steel reactor equipped with mechanical stirring was heated to 130°C under vacuum for 1 hour. After cooling under vacuum and back-filling with Ar, toluene (90 mL) and MAO (4.0 mmol, 200 equivalents relative to Cr) was added to the reactor and the temperature maintained at 40°C. In a schlenk [(EtHex₃TAC)CrCl₃] (20 µmol) was dissolved in toluene (10 mL) and MAO (2.0 mmol, 100 equivalents

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relative to Cr) added. The resultant solution was added to the reactor and the vessel immediately charged with 2 bar of ethylene (Linde 4.5 grade) and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 36 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath.

5 Excess ethylene was bled and the reactor contents treated sequentially with 1000 μ L of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 9.941g. The product distribution is shown in Table 2.

10

Example 41. Comparative ethylene oligomerisation with [(EtHex₃TAC)CrCl₃] and MMAO activator.

A 300mL stainless steel reactor equipped with mechanical stirring was heated to 130°C under vacuum for 1 hour. After cooling under vacuum and back-filling with Ar, 15 toluene (90 mL) and MMAO (4.0 mmol, 200 equivalents relative to Cr) was added to the reactor and the temperature maintained at 40°C. In a schlenk [(EtHex₃TAC)CrCl₃] (20 μ mol) was dissolved in toluene (10 mL) and MMAO (2.0 mmol, 100 equivalents relative to Cr) added. The resultant solution was added to the reactor and the vessel immediately charged with 5 bar of ethylene (Linde 4.5 grade) and the pressure kept 20 constant throughout the reaction by the continuous addition of ethylene. After 36 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000 μ L of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was 25 collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 38.286g. The product distribution is shown in Table 2.

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Table 2. Product distributions obtained in examples 38-41.

Example	Productivity g/gCr	Activity g/gCr/hr/bar	% PE	% C ₆	1-C ₆	%C ₈	1-C ₈
38	13345	10820	46.1	36.6	99.2	3.7	86.0
39	11742	8288	62.3	28.4	99.3	4.7	90.6
40	9565	7971	25.1	43.8	99.0	3.0	71.0
41	36838	3400	29.8	34.1	99.4	4.3	91.2

Percentages are all mass%. 1-C₆ and 1-C₈ refer to mass% selectivity within the total C₆ and C₈ fractions respectively.

- 5 **Example 42. Ethylene oligomerisation with [((Decyl-S-CH₂CH₂)₂NH)CrCl₃], Et₃Al co-activator and [Ph₃C][Al{OC(CF₃)₃]₄] activator.**

A 300mL stainless steel reactor equipped with mechanical stirring was heated to 130°C under vacuum for 1 hour. After cooling under vacuum and back-filling with Ar, [Ph₃C][Al{OC(CF₃)₃]₄] (30 μmol) and [((Decyl-S-CH₂CH₂)₂NH)CrCl₃] (20 μmol) were
10 added to the reactor as a solution in toluene (100 mL) and the reactor brought to 85°C. Et₃Al (2.0 mmol, 100 equivalents relative to Cr) was then added to the reactor and the vessel immediately charged with 40 bar of ethylene (Linde 3.5 grade) and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 21 minutes the ethylene supply was closed and the reactor cooled in
15 an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000μL of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The total product mass was 4.317g. The product distribution is shown in
20 Table 3.

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Example 43. Comparative ethylene oligomerisation with $[\{(Decyl-S-CH_2CH_2)_2NH\}CrCl_3]$ and MAO activator.

A 300mL stainless steel reactor equipped with mechanical stirring was heated to 130°C under vacuum for 1 hour. After cooling under vacuum and back-filling with Ar, $[\{(Decyl-S-CH_2CH_2)_2NH\}CrCl_3]$ (44 μ mol) was added to the reactor as a solution in toluene (100 mL) and the reactor brought to 100°C. MAO (29.9 mmol, 680 equivalents relative to Cr) was then added to the reactor and the vessel immediately charged with 40 bar of ethylene (Linde 3.5 grade) and the pressure kept constant throughout the reaction by the continuous addition of ethylene. After 30 minutes the ethylene supply was closed and the reactor cooled in an ice/water bath. Excess ethylene was bled and the reactor contents treated sequentially with 1000 μ L of nonane (GC internal standard), MeOH and 10% HCl. A sample of the organic phase was taken for GC-FID analysis while the solid polyethylene produced was collected by filtration, washed with MeOH and dried at 100°C. The product distribution is shown in Table 3.

Table 3. Product distributions obtained in examples 42-43.

Example	Productivity g/gCr	Activity g/gCr/hr	% PE	% C ₆	1-C ₆	%C ₈	1-C ₈
42	3865	11044	0.7	84.2	99.3	3.3	93.7
43	13950	27900	2.3	96.1	99.5	-	-

Percentages are all mass%. 1-C₆ and 1-C₈ refer to mass% selectivity within the total C₆ and C₈ fractions respectively.

Example 44. 1-hexene trimerisation with $[(EtHex_3TAC)CrCl_3]$, Et₃Al co-activator and $[Ph_3C][Al\{OC(CF_3)_3\}_4]$ activator.

A 250 mL round bottom flask was dried *in vacuo*, back-filled with dry N₂ and charged with $[Ph_3C][Al\{OC(CF_3)_3\}_4]$ (0.0363g, 30 μ mol), $[(EtHex_3TAC)CrCl_3]$ (0.0116g, 20 μ mol), 1-hexene (20 mL), nonane (1 mL, as GC standard) and toluene (20 mL). This

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solution was heated in an oil bath to 40 °C. Once a steady temperature had been achieved a solution of AlEt₃ 1.9M in toluene (1.1ml, 2mmol, 100 equivalents relative to Cr) was added. Upon activation the brown/yellow solution became yellow over a few seconds. The solution was stirred at constant temperature for 2 hours. The reaction was quenched with methanol (2ml) and water (2ml). Samples (0.2ml) were taken from the reaction solution just prior to activation and after quenching. These were added to DCM (1.5ml) and analysed by GC-FID. The product distribution is shown in Table 4.

Example 45. Comparative 1-hexene trimerisation with [(EtHex₃TAC)CrCl₃] and MMAO activator.

A 250 mL round bottom flask was dried *in vacuo*, back-filled with dry N₂ and charged with [(EtHex₃TAC)CrCl₃] (0.0116g, 20 µmol), 1-hexene (20 mL), nonane (1 mL, as GC standard) and toluene (20 mL). This solution was heated in an oil bath to 40 °C.

Once a steady temperature had been achieved a solution of MMAO 1.9M in heptanes (3.2ml, 6.0mmol, 300 equivalents relative to Cr) was added. Upon activation the purple solution instantly became green. The solution was stirred at constant temperature for 2 hours. The reaction was quenched with methanol (2ml) and water (2ml). Samples (0.2ml) were taken from the reaction solution just prior to activation and after quenching. These were added to DCM (1.5ml) and analysed by GC-FID. The product distribution is shown in Table 4.

Table 4. Product distributions obtained in examples 44-45.

Example	TON Mol 1-C ₆ / mol Cr	Activity Mol 1-C ₆ / mol Cr / hr	Selectivity to C18 fraction
44	29.9	14.9	>99%
45	1199.2	599.6	>99%

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The above detailed examples reveal several advantages that can be achieved through the use of the activators and co-activators disclosed herein. Firstly, it is found that ethylene oligomerisation with a combination of a Cr source, $\text{Ph}_2\text{PN}(\text{iPr})\text{PPh}_2$, and an alkylaluminumoxane such a MAO or MMAO normally furnishes an oligomeric mixture composed predominately of 1-hexene and 1-octene, in which the amount of 1-octene is greater than the amount of 1-hexene. This is illustrated in comparative example 23, and further examples can be found in WO 04/056479 as well as Bollmann et. al., J. Am. Chem. Soc., 126 (2004) 14712. Surprisingly however, examples 5-9 and 11-12 show that it is possible to produce an oligomer composed predominately of 1-hexene by replacing aluminumoxane activators with the activators and co-activators disclosed herein. Furthermore, it can be concluded by considering all examples, and as shown in Figure 4, that control over the ratio of 1-hexene to 1-octene can be achieved through the choice of activator employed, the amount of activator employed, or the relative ratio of activator to co-activator.

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A second advantage that can be achieved is a reduction in the total amount of aluminium that can be used while still maintaining acceptable productivity and selectivity. Comparative example 22 shows that when the amount of MMAO-3A is reduced down to 100 equivalents relative to chromium, a lower productivity results and a large amount of polymer is formed. Comparison of example 22 with examples 15 and 18 shows that a higher productivity and lower polymer content can be achieved with similar total amounts of aluminium. As such, there is provided a means by which waste volumes can be reduced. Furthermore, the co-activators that can be used in the present invention, such as triethylaluminium, are generally substantially less expensive than aluminumoxanes, and as such a lower activator cost is achievable for a given amount of oligomeric product.

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Compared to the use of borane or borate activators, which also allow inexpensive co-activators such as triethylaluminum to be employed, the activators disclosed herein are capable of much improved productivity. This is illustrated in comparative example 21, and further examples can be found in IPCOM000031729D, which show that
5 borane and borate activators lead to lower productivity for oligomer formation. Examples 14, 15, 17 and 18 show that greatly improved productivities can be achieved through the use of the activators disclosed herein.

Examples 26-28 illustrate that it is possible to use a system in which the source of
10 transition metal, ligating compound, and activator are all constituents of a single chemical compound. Example 26 shows that such a system is also capable of producing acceptable productivity and low solids formation with reduced total amounts of aluminum.

15 Examples 29-30 compared to examples 18 and 27 respectively show that the productivity obtained from a particular catalyst system is dependent on the source of ethylene used.

Examples 38-39 further demonstrate the application of the activator to other catalyst
20 systems, specifically those employing tridentate ligands. More specifically a facially capping tridentate ligand. It can be seen by reference to the comparative examples 40 and 41 that compared to MAO or MMAO activators a significant reduction in the amount of aluminum utilized is achieved. Simultaneously a catalyst is generated with a higher activity per bar ethene per gram Cr per hour. It should be noted that in
25 comparative example 40 an ethene pressure of 5 bar (as opposed to 2 bar in examples 38 and 39) is required for the catalyst to function.

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Examples 42 further demonstrates the application of the activator to other catalyst systems, specifically those employing tridentate ligands. More specifically a meridional-binding mode tridentate ligand. Example 43 shows a comparison with MMAO.

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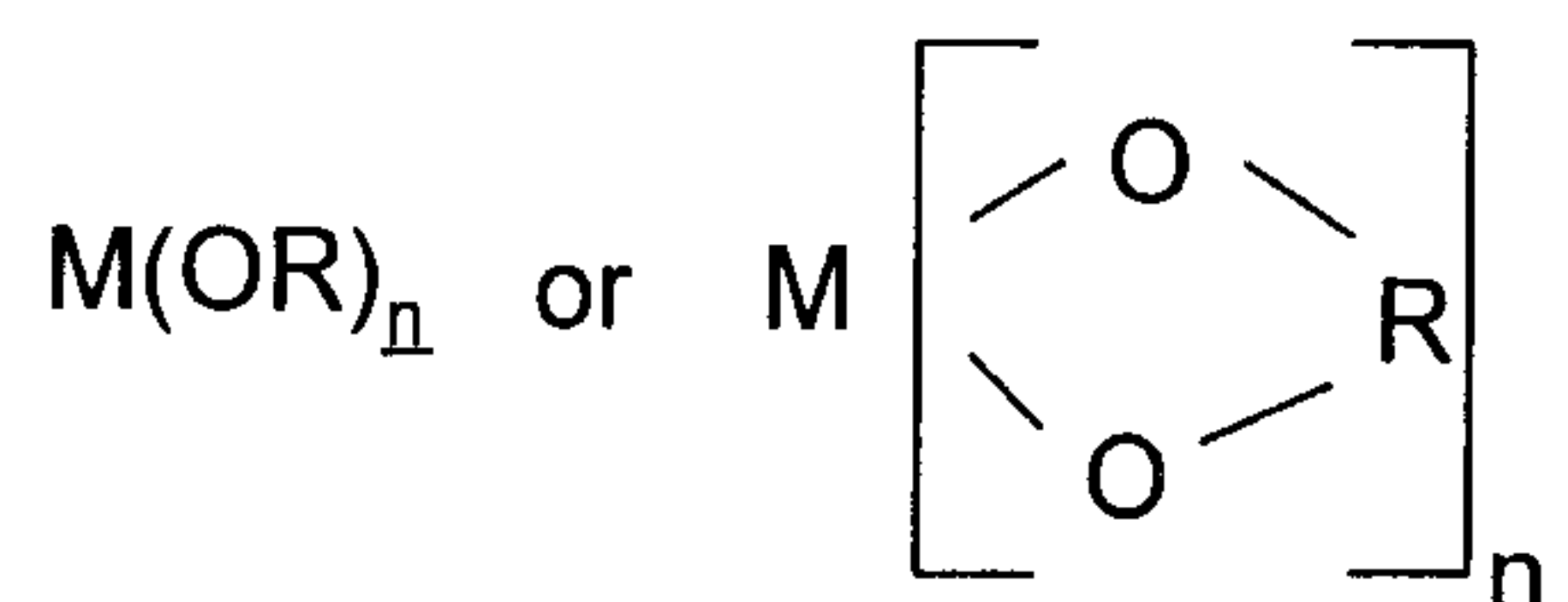
Examples 44 demonstrates the application of the activator in conjunction with catalyst systems for the oligomerisation of α -olefins. Specifically the trimerisation of 1-hexene. Example 45 is a comparative example with MMAO as activator.

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CLAIMS:

1. A process for producing an oligomeric product by the oligomerisation of at least one olefinic compound in the form of an olefin or a compound including a carbon to carbon double bond, by contacting the at least one olefinic compound with the combination of an oligomerisation catalyst and a catalyst activator, which catalyst activator is a salt containing an anion which includes a moiety of the formula:



wherein:

M is selected from the group consisting of a group 3A atom;

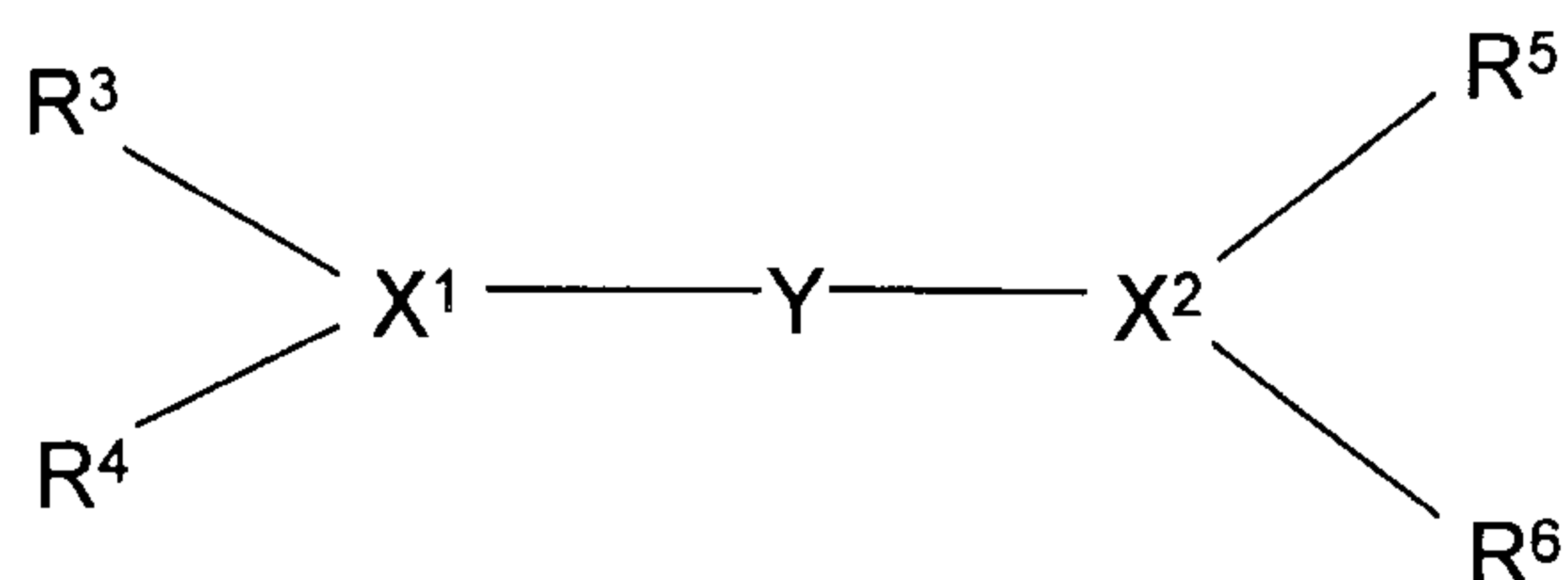
10 n is 1 or a larger integer; and

R is a halogenated organic group, R being the same or different when n is larger than 1; and

wherein the oligomerisation catalyst includes the combination of:

i) a source of Cr; and

15 ii) a ligating compound of the formula:



wherein: X^1 and X^2 are P;

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

R^3 to R^6 are each independently:

- a hydrocarbyl group

5 wherein the hydrocarbyl group is a univalent or multivalent group
formed by removing one or more hydrogen atoms from a hydrocarbon;

- or a heterohydrocarbyl group

10 wherein the heterohydrocarbyl group is a univalent or multivalent
organic compound which includes at least one heteroatom, that is not being H or C,
and which organic compound binds with one or more other moieties through one or
more carbon atoms of the organic compound and/or one or more heteroatoms of the
organic compound;

the process further including a co-activator.

2. The process of claim 1, wherein the group 3A atom is selected from the
group consisting to Al and B.

15 3. The process of claim 2, wherein the group 3A atom is Al.

4. The process of any one of claims 1 to 3, wherein R is: (α) a halogenated
hydrocarbyl group, wherein the hydrocarbyl group is a univalent or multivalent group
formed by removing one or more hydrogen atoms from a hydrocarbon; β a
halogenated heterohydrocarbyl group, wherein the heterohydrocarbyl group is a
20 univalent or multivalent organic compound which includes at least one heteroatom,
that is not being H or C, and which organic compound binds with one or more other
moieties through one or more carbon atoms of the organic compound and/or one or
more heteroatoms of the organic compound; (γ) a halogenated organyl group, or (δ)
a halogenated organoheteryl group.

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5. The process of claim 4, wherein R is a halogenated hydrocarbyl group or a halogenated organyl group.

6. The process of claim 5, wherein all the hydrogen atoms of the organyl group or hydrocarbyl group are replaced with halogen atoms and all the halogen
5 atoms are the same.

7. The process of claim 6, wherein all the halogen atoms are F.

8. The process of claim 1, wherein the activator is selected from the group consisting of a salt containing the anion:



10 wherein R is as defined in claim 1.

9. The process of claim 1, wherein the activator is selected from the group consisting of $\text{X}^+[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]^-$; $\text{X}^+[\text{Al}(\text{OC}_6\text{F}_5)_4]^-$; $\text{X}^+[\text{Al}(\text{C}_6\text{F}_4\text{O}_2)_2]^-$; $\text{X}^+[\text{Al}\{\text{OC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{O}\}_2]^-$; $\text{X}^+[\text{AlF}\{\text{OC}(\text{CF}_3)_3\}_3]^-$; and $\text{X}^+[\text{Al}_2\text{F}\{\text{OC}(\text{CF}_3)_3\}_6]^-$; wherein X^+ is a cation.

15 10. The process of claim 9, wherein X^+ is Ph_3C^+ , Me_2PhNH^+ or $(\text{Et}_2\text{O})_2\text{H}^+$.

11. The process of any one of claims 1 to 10, wherein the co-activator is an organoaluminium compound and/or an organoboron compound.

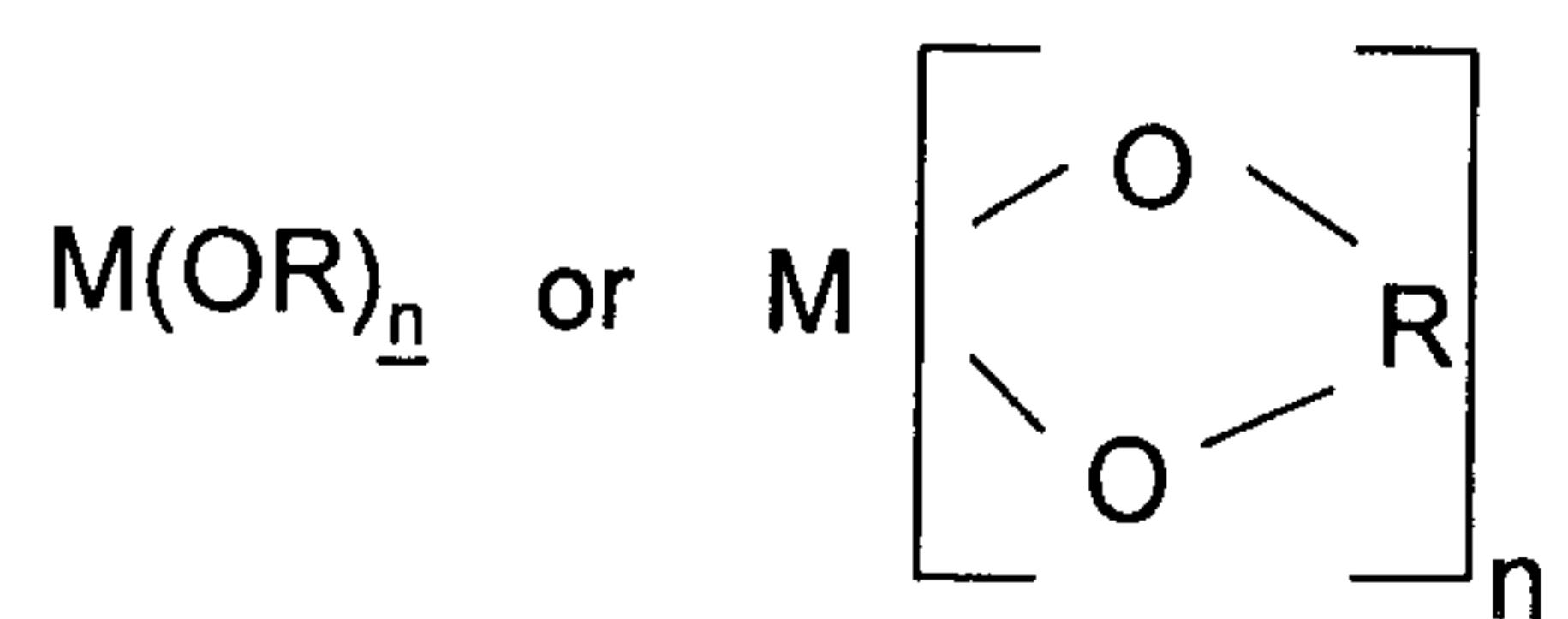
12. The process of claim 11, wherein the co-activator is an organoaluminium compound of the formula $\text{Al}(\text{R}^9)_3$ wherein each R^9 is independently
20 an organyl group, a halogenated organyl group or a halide, with at least one of R^9 being an organyl group or a halogenated organyl group.

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13. The process of claim 12, wherein the co-activator is selected from the group consisting of trimethylaluminium (TMA); triethylaluminium (TEA), tributylaluminium, tri-isobutylaluminium (TIBA) and tri-n-octylaluminium.

14. Use of a combination of a catalyst activator and an oligomerisation catalyst in the oligomerisation of at least one olefinic compound in the form of an olefin or a compound including a carbon to carbon double bond by contacting the at least one olefinic compound with the oligomerisation catalyst, and a catalyst activator, wherein the activator is a salt containing an anion which includes a moiety of the formula:



wherein:

M is selected from the group consisting of a group 3A atom;

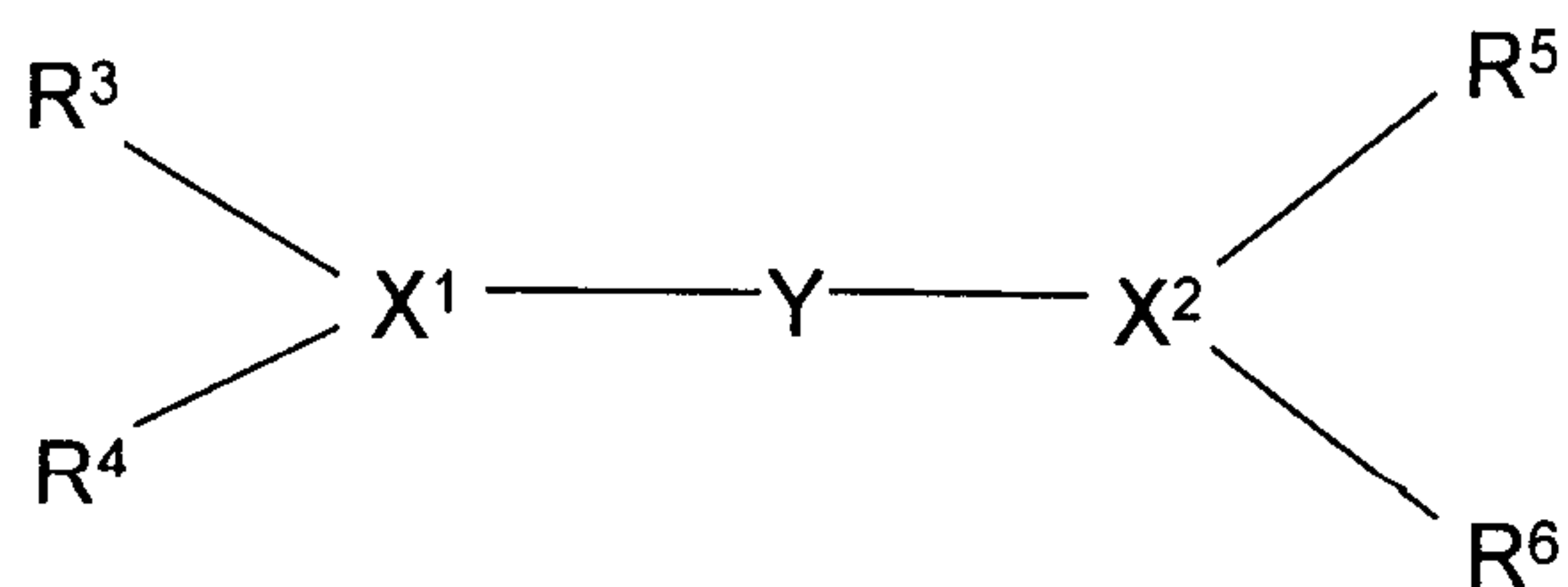
n is 1 or a larger integer; and

R is a halogenated organic group, R being the same or different when n is larger than 1; and

wherein the oligomerisation catalyst includes a combination of:

i) a source of Cr; and

ii) a ligating compound of the formula:



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wherein: X^1 and X^2 are P;

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

R^3 to R^6 are each independently:

- a hydrocarbyl group

5 wherein the hydrocarbyl group is a univalent or multivalent group
formed by removing one or more hydrogen atoms from a hydrocarbon;

- or a heterohydrocarbyl group

 wherein the heterohydrocarbyl group is a univalent or multivalent
organic compound which includes at least one heteroatom, that is not being H or C,
10 and which organic compound binds with one or more other moieties through one or
more carbon atoms of the organic compound and/or one or more heteroatoms of the
organic compound;

the process further including a co-activator.

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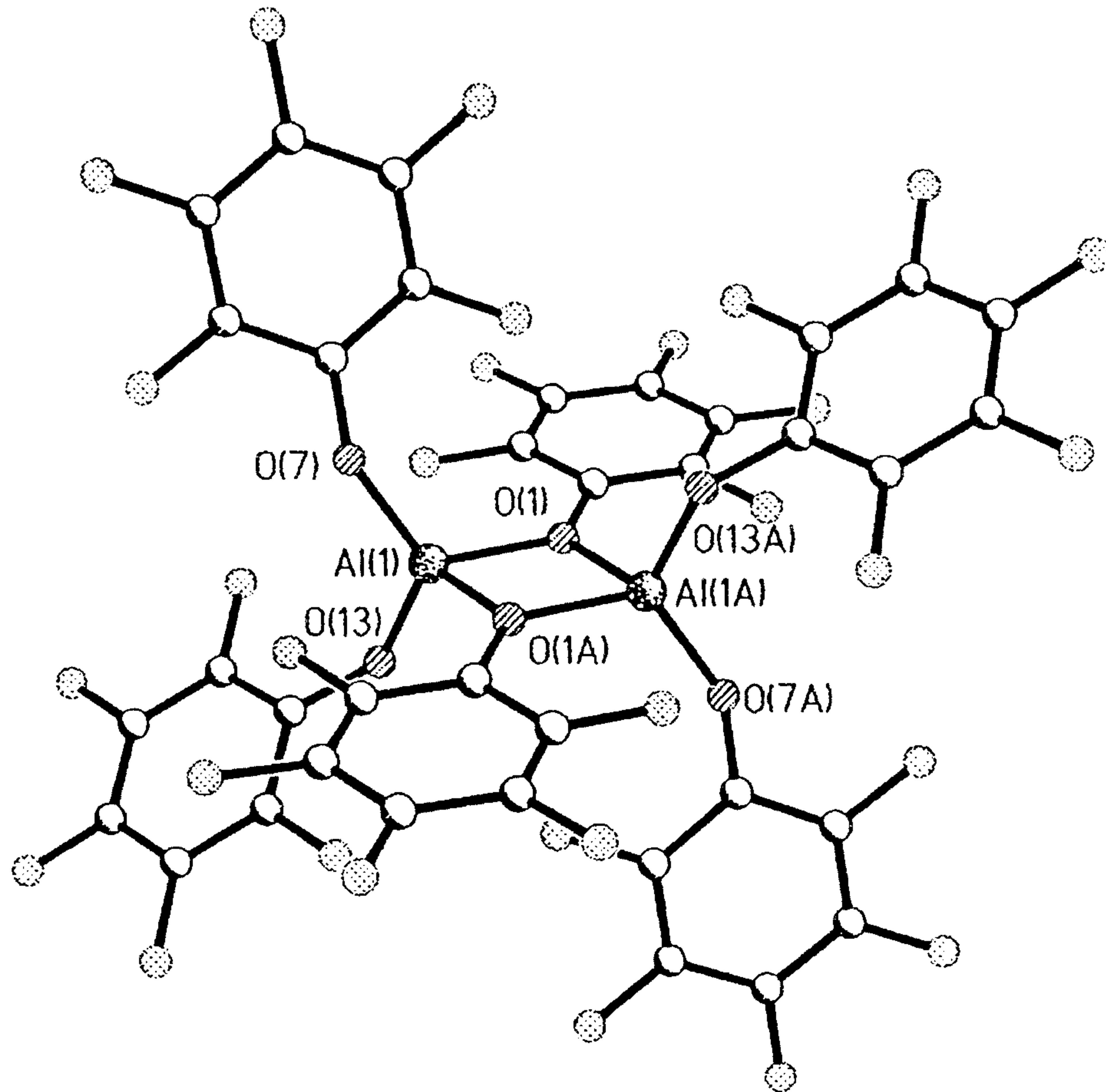


Figure 1.

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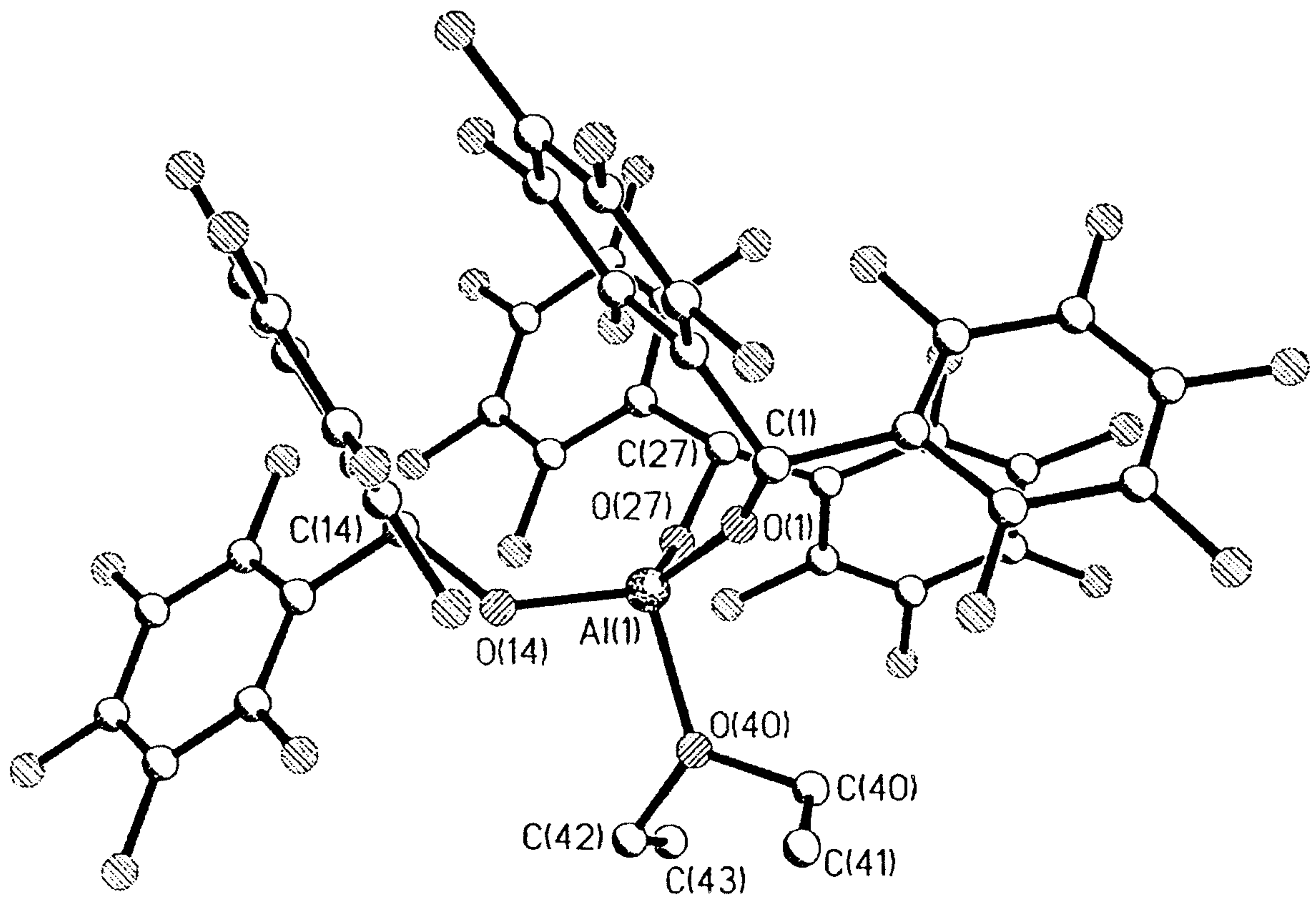


Figure 2.

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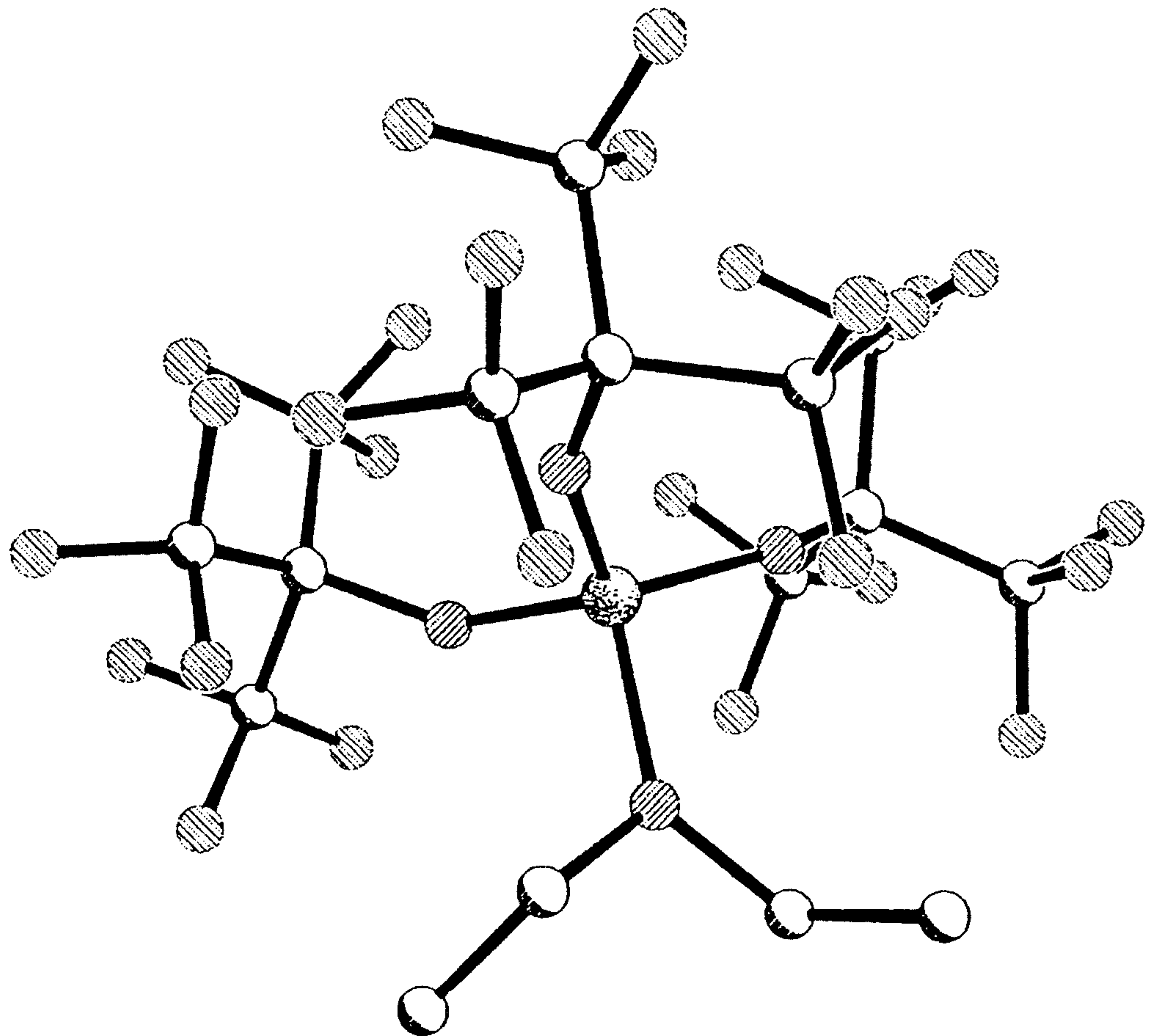


Figure 3.

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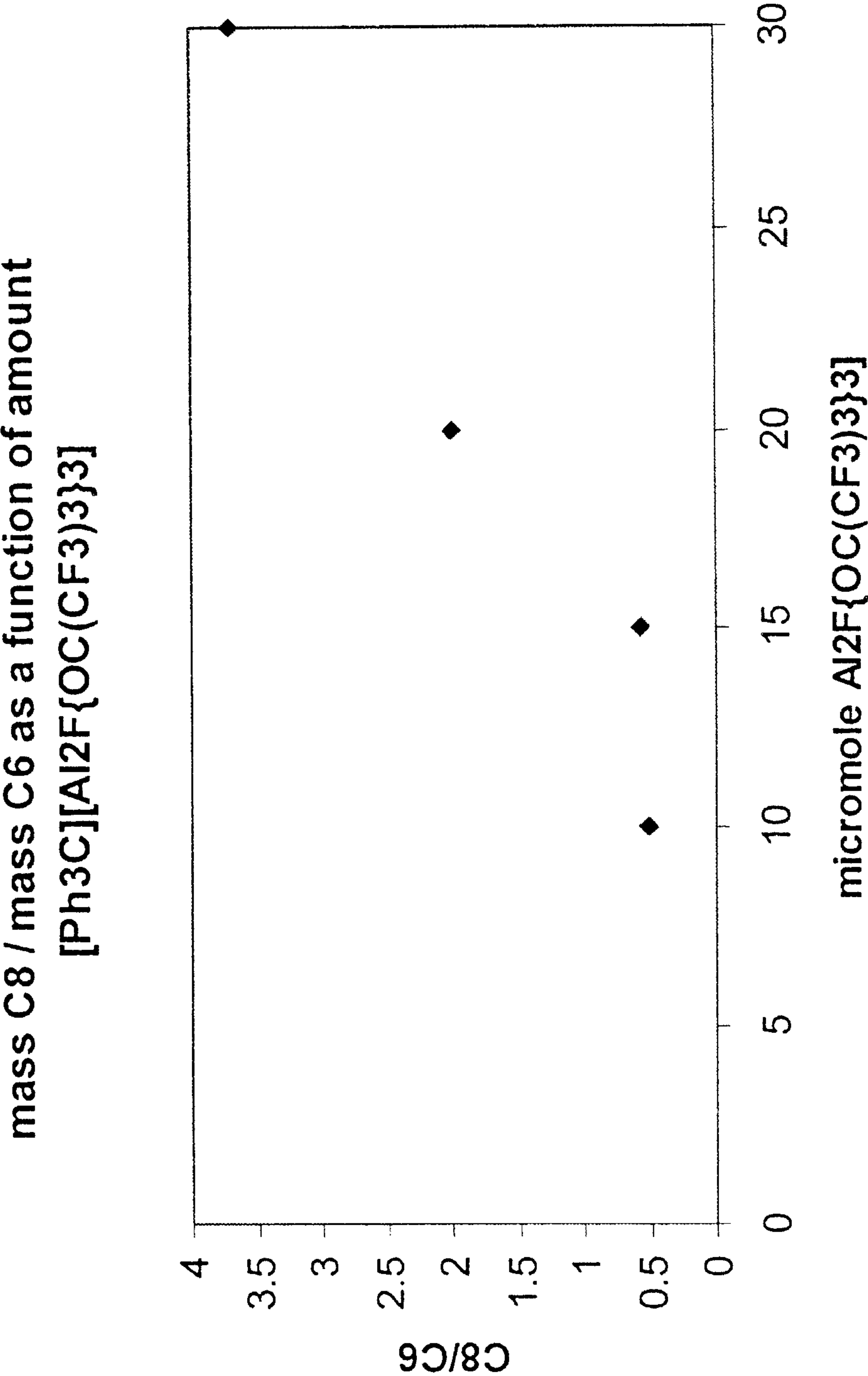


Figure 4.