

tetramerisation of ethylene provided by WO 07/088329 are all carried out in either chlorobenzene or toluene and no examples of processes conducted in aliphatic solvents are provided.

US 5,919,983 teaches of a catalyst activator for use in the polymerization of α -olefins, using Ziegler-Natta and Metallocene polymerisation catalysts to form high molecular weight polymers. The activators taught are boron salts that respectively comprises a cation which is a Bronsted acid capable of donating a proton, and an inert, non-coordinating anion which includes a boron atom. The skilled person knows that Ziegler-Natta and Metallocene polymerisation technology belongs to a different art field and is fundamentally different to selective oligomerisation technologies.

In IPCOM000031729D, published on 7 October 2004, boron-containing activators were used to activate selective oligomerisation catalyst systems in toluene or an aromatic solvent. When $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $\text{B}(\text{C}_6\text{F}_5)_3$ was used to activate these catalysts, a low productivity catalyst was obtained with the highest productivities observed being around 15000 g/gCr.

It has now been found that the borate activators described herein leads to improved productivity of oligomerisation catalysts, when used in the presence of an aliphatic solvent.

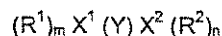
The inventors of the present invention have accordingly found that using borate activators in the oligomerisation process described hereunder results in improved catalyst activation, increased catalyst efficiency and reduced solids formation, which improvements are herein collectively referred to as improved productivity of the activated catalyst.

DISCLOSURE OF THE INVENTION

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

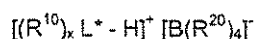
(a) providing an activated oligomerisation catalyst by combining, in any order,

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



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

- iii) a catalyst activator which is an organoboron compound including a cation and a non-coordinating anion of the general formula



wherein:
 L^* is an atom selected from the group consisting of N, S and P;
the cation $[(\text{R}^{10})_x \text{L}^* - \text{H}]^+$ is a Bronsted acid;
x is an integer 1, 2 or 3;
each R^{10} is the same or different when x is 2 or 3 and each is a -H, hydrocarbyl group or a heterohydrocarbyl group;

provided that at least one of R^{10} comprises at least 6 carbon atoms and provided further that the total number of carbon atoms in $(R^{10})_x$ collectively is greater than 12;

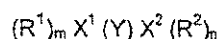
R^{20} independently at each occurrence is selected from the group consisting of hydride, dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, halosubstituted-hydrocarbyl radicals, halosubstituted-alkoxide, halosubstituted-aryloxy and a halosubstituted aromatic ring moiety with at least one halide substituent on the aromatic ring; and

iv) an aliphatic solvent; and

(b) contacting the at least one olefinic compound with the activated oligomerisation catalyst to produce an oligomeric product.

According to the present invention disclosure there is also provided a process for activating an oligomerisation catalyst to produce an oligomeric product, the process comprising the combination, in any order, of

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



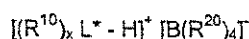
wherein: X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X^1 and/or X^2 allows for such oxidation;

Y is a linking group between X^1 and X^2 which linking group contains at least one nitrogen atom which is directly bonded to X^1 or X^2 ;

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

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

- iii) a catalyst activator which is an organoboron compound including a cation and a non-coordinating anion of the general formula



wherein:

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

the cation $[(R^{10})_x L^* - H]^+$ is a Bronsted acid;

x is an integer 1, 2 or 3;

each R^{10} is the same or different when x is 2 or 3 and each is a -H, hydrocarbyl group or a heterohydrocarbyl group;

provided that at least one of R^{10} comprises at least 6 carbon atoms and provided further that the total number of carbon atoms in $(R^{10})_x$ collectively is greater than 12;

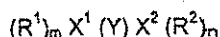
R^{20} independently at each occurrence is selected from the group consisting of hydride, dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, halosubstituted-hydrocarbyl radicals, halosubstituted-alkoxide, halosubstituted-aryloxy and a halosubstituted aromatic ring moiety with at least one halide substituent on the aromatic ring; and

- iv) an aliphatic solvent.

In one aspect, there is provided a process for producing an oligomeric product by the oligomerisation of at least one olefinic compound, the process including

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

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



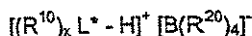
wherein: X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X^1 and/or X^2 allows for such oxidation;

Y is a linking group between X^1 and X^2 which linking group contains at least one nitrogen atom which is directly bonded to X^1 or X^2 ;

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

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

- iii) a catalyst activator which is an organoboron compound including a cation and a non-coordinating anion of the general formula



wherein:

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

the cation $[(R^{10})_x L^* - H]^+$ is a Bronsted acid;

x is an integer 1, 2 or 3;

each R^{10} is the same or different when x is 2 or 3 and each is a -H, hydrocarbyl group or a heterohydrocarbyl group;

provided that at least one of R^{10} comprises at least 6 carbon atoms and provided further that the total number of carbon atoms in $(R^{10})_x$ collectively is greater than 12;

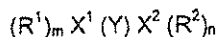
R^{20} independently at each occurrence is selected from the group consisting of hydride, dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, halosubstituted-hydrocarbyl radicals, halosubstituted-alkoxide, halosubstituted-aryloxy and a halosubstituted aromatic ring moiety with at least one halide substituent on the aromatic ring; and

- iv) an aliphatic hydrocarbon fluid solvent; and

(b) contacting the at least one olefinic compound with the activated oligomerisation catalyst to produce an oligomeric product.

In another aspect, there is provided a process for activating an oligomerisation catalyst to produce an oligomeric product, the process comprising the combination, in any order, of

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



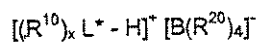
wherein: X^1 and X^2 are independently an atom selected from the group consisting of nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen, sulphur and selenium or said atom oxidized by S, Se, N or O where the valence of X^1 and/or X^2 allows for such oxidation;

Y is a linking group between X^1 and X^2 which linking group contains at least one nitrogen atom which is directly bonded to X^1 or X^2 ;

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

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

iii) a catalyst activator which is an organoboron compound including a cation and a non-coordinating anion of the general formula



wherein:

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

the cation $[(R^{10})_x L^* - H]^+$ is a Bronsted acid;

x is an integer 1, 2 or 3;

each R^{10} is the same or different and each is a $-H$, hydrocarbyl group or a heterohydrocarbyl group;

provided that at least one of R^{10} comprises at least 6 carbon atoms and provided further that the total number of carbon atoms in $(R)_x$ collectively is greater than 12;

R^{20} independently at each occurrence is selected from the group consisting of hydride, dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, halosubstituted-hydrocarbyl radicals, halosubstituted-alkoxide, halosubstituted-aryloxy and a halosubstituted aromatic ring moiety with at least one halide substituent on the aromatic ring; and

iv) an aliphatic hydrocarbon fluid solvent.

In this specification, the following definitions apply:

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

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