Non-limiting examples of selective ethylene tetramerisation catalyst systems include the ubiquitous Cr / bis(phosphino)amine (i.e. 'PNP') systems, particularly of the type $(Ar^1)(Ar^2)PN(R)P(Ar^3)(Ar^4)$, where $Ar^1$ to $Ar^4$ are aryl groups such as phenyl and R is a hydrocarbyl or a heterohydrocarbyl group, beginning with PNP ligands containing no substituents on the phenyl rings bonded to the P-atoms (e.g. as described in WO 2004/056479) and those with m- or *p*-methoxy groups on the phenyl rings (e.g. as described in WO 2004/056480). In addition to this, PNP systems containing *o*-fluoro groups on the phenyl rings are described in US 2008/0242811 and US 2010/0081777, and PNP systems bearing pendant donor atoms on the nitrogen linker are described in WO 2007/088329. Multi-site PNP ligands are discussed in US 2008/0027188. In addition to the Cr/PNP systems, chromium systems bearing N,N-bidentate ligands (e.g. as described in US 2006/0247399) can be used. PNP ligands with alkylamine or phosphinoamine groups bonded to one of the PNP phosphines (i.e. 'PNPNH' and 'PNPNP' ligands) are described in WO 2009/006979. Finally, carbon bridged diphosphine (i.e. 'PCCP' ligands) are described in WO 2008/088178 and WO 2009/022770.

Related ethylene trimerisation catalysts with high selectivity for 1-hexene can be obtained by using PNP ligands with ortho-methoxy or ortho-alkyl substituents on the phenyl rings bonded to the P-atoms (e.g. as described in WO2002/04119, WO2004/056477 and ~~WO2012~~WO2010/034101).

The above catalyst systems suffer from a number of shortcomings. These include low catalyst activity and high polymer co-product formation, particularly when operated at elevated temperatures, especially above 80°C. Many of these catalysts also suffer from high selectivity towards heavy oligomers (C10 to C30+ olefins). These problems are especially evident for tetramerisation catalysts, where the challenge of obtaining good catalyst performance together with good selectivity towards 1-octene at high reaction temperatures is severe.

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In some embodiments of the invention, $R^{EWG}$ is more electron withdrawing than a hydrogen atom substituent.

In some embodiments of the invention, $R^{EWG}$ has a positive $\sigma_p$ value, where $\sigma_p$ is the Hammett constant for a substituent's effect when located at the para-position of a phenyl ring. In some preferred embodiments, $R^{EWG}$ has a $\sigma_p$ value of greater than +0.15.

$R^{EWG}$ may be a divalent group that is bonded to ~~Y~~A and also bonded to another ring atom of the aromatic ring of which ~~Y~~A is a substituent, to form a cyclic structure.

In some embodiments, $R^{EWG}$ is selected from a group comprising halogen-substituted alkyl, halogen-substituted cycloalkyl, halogen-substituted aryl, heteroaryl, $-SO_2R^6$, $-(C=O)R^6$, -CN; where $R^6$ is a hydrogen, a hydrocarbyl group, or a heterohydrocarbyl group.

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In some embodiments, $R^{EWG}$ is selected from a group comprising halogen-substituted alkyl, halogen-substituted cycloalkyl, halogen-substituted aryl and heteroaryl.

**CLAIMS**

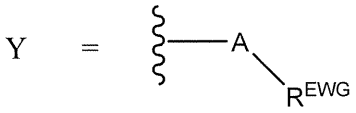
1. A process for the oligomerisation of ethylene to predominantly 1-hexene or 1-octene or mixtures of 1-hexene and 1-octene, the process including contacting ethylene with a catalyst under ethylene oligomerisation conditions, said catalyst comprising:

   i) a source of chromium;

   ii) a ligating compound of the formula

   $$R^1R^2P^1XP^2R^3R^4$$

   wherein $P^1$ and $P^2$ are phosphorus atoms;
   X is a linking group between $P^1$ and $P^2$; and
   $R^1$ to $R^4$ are independently a hydrocarbyl group, an organoheteryl group or a heterohydrocarbyl group, wherein at least one of $R^1$, $R^2$, $R^3$, and $R^4$ includes a substituted aromatic ring directly bonded to $P^1$ or $P^2$ and which is substituted at a ring atom adjacent to the ring atom bonded to $P^1$ or $P^2$ with a substituent Y, where Y ~~can be represented as~~comprises:

   such that A is selected from the group consisting of O, S and $NR^5$, where $R^5$ is a hydrocarbyl, heterohydrocarbyl or organoheteryl group; and
   $R^{EWG}$ is an electron withdrawing group; and

   iii) optionally a catalyst activator or combination of catalyst activators.

2. The process as claimed in claim 1, wherein $R^1$ to $R^4$ all include aromatic or heteroaromatic moieties directly bonded to $P^1$ or $P^2$.

3. The process as claimed in claim 1 or claim 2, wherein at least one of the $R^1$ to $R^4$ groups is a substituted phenyl group and all of the remaining $R^1$ to $R^4$ groups are optionally substituted phenyl groups.

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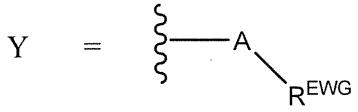
   $R^1$ to $R^4$ are independently a hydrocarbyl group, an organoheteryl group or a heterohydrocarbyl group, wherein at least one of $R^1$, $R^2$, $R^3$, and $R^4$ includes a substituted aromatic ring directly bonded to $P^1$ or $P^2$ and which is substituted at a ring atom adjacent to the ring atom bonded to $P^1$ or $P^2$ with a substituent Y, where Y comprises:

   such that A is selected from the group consisting of O, S and $NR^5$, where $R^5$ is a hydrocarbyl, heterohydrocarbyl or organoheteryl group; and
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