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(54) Title: CATALYST SYSTEM FOR OLIGOMERIZATION OF OLEFINS

(57) Abstract: A catalyst system for oligomerization of olefins comprising: a) a metal compound; and b) a ligand of general formula: $(R_1)nX_1$-Z (B-A) -X_2 $(R_2)_n$ wherein: X_1 and X_2 are independently selected from the elements of Group 14, Group 15 and Group 16 of the Periodic Table of Elements; Z is an element selected from Group 15 of the Periodic Table of Elements; B is a linking group; A is a nucleophilic group; R_1 and R_2 are independently optionally substituted hydrocarbyl groups or heterohydrocarbyl groups; and n and m respectively for R_1 and R_2 are independently determined by the respective valence and oxidation state of X_1 and X_2.

CATALYST SYSTEM FOR OLIGOMERIZATION OF OLEFINS

Field of Invention

The present invention relates to a catalyst system and process for the oligomerization of olefins.

Background Art

The oligomerization of olefins, primarily α-olefins, has been extensively studied. However, only a few of such processes have been developed commercially. One known process involves the tetramerization of ethylene to 1-octene. 1-octene is used extensively as a raw material for various chemical products such as in the production of linear low density polyethylene (J. Orgamomet. Chem. 2004, 689, 3641).

Despite the well-known commercial value of 1-octene, there does not exist a commercially successful process for the tetramerisation of ethylene to produce 1-octene selectively. Most conventional metal-catalyzed ethylene oligomerization processes follow a mathematical distribution (Schulz-Flory or Poisson) of α-olefin, which by definition limits the mass percentage of the tetramer formed. It has been advocated that ethylene tetramerization is improbable (Angew. Chem. Int. Ed. 2003, 42, 808; Organometallics 2003, 22, 2564). A primary reason cited is that the proposed nine-membered metallacycle intermediate in the catalytic cycle is the least-favored and hence most difficult to form. This inherent problem limits the efficiency of the process and very often does not meet the high market demand. Accordingly, many attempts have been made to skew the mathematical distribution of olefin to the higher value co-monomer range especially to that of 1-octene.

A significant drawback in most catalyst systems used to oligomerize olefins is that they either do not have very high yields or they have low selectivity in their target products.

US 6,184, 428 discloses the use of a nickel catalyst system comprising 2-diphenyl phosphino benzoic acid (DPPBA) chelating ligand, $NiCl_2 \cdot 6H_2O$ precursor, and sodium tetraphenylborate catalyst activator. The nickel catalyst system is used to oligomerize ethylene to yield a mixture of linear olefins containing 1-octene. The selectivity towards linear C_8 α-olefins is claimed to be only 19%.

The Shell Higher Olefins Process ("SHOP process") is disclosed in US Patent Nos 3,676,523 and 3,635,937. The catalyst system taught in the SHOP process is reported to typically yield only 11 %(wt) 1-octene in its product mixture (Chem Systems PERP reports 90-1,93-6 and 94/95S12).

Ziegler-type technologies based on trialkylaluminium catalysts are known. However, while these catalysts are used commercially, they don't produce very high yields of 1-octene. For example, German Patent No. DE 1,443,927 (Gulf Oil Chemicals Company) and US patent 3,906, 053 (Ethyl Corporation) only achieve yields of about 13-25 %(wt) 1-octene.

In recent years, SASOL (WO 04/056478 & WO 04/056480) filed and reported the first example of ethylene tetramerization to produce 1-octene in high selectivity greater than 30 % in the presence of bidentate ligand, bis(phosphino)amine (PNP) and related diphosphine ligands, in combination with Cr(III) compounds activated by aluminoxanes (MAO) (J. Am. Chem. Soc. 2004, 126, 14712). The WO 04/056478 suggests that bis(phosphino)amine (PNP) is a bidentate ligand, in which

the two P atoms coordinate to the metal centre while the N atom remains uncoordinated.

In view of the above, there is a need to provide a catalytic system that can selectively and efficiently promote ethylene oligomerization to α-olefin co-monomers

There is also a need to provide a catalytic system for ethylene oligomerization that overcomes, or at least ameliorates, one or more of the disadvantages described above.

Summary

According to a first aspect, there is provided a catalyst system for oligomerization of olefins comprising:

a metal compound; and

a ligand of general formula:

$(R_1)_nX_1\text{-}Z(B\text{-}A)\text{-}X_2(R_2)_m$

wherein:

X_1 and X_2 are independently selected from the elements of Group 14, Group 15 and Group 16 of the Periodic Table of Elements;

Z is an element selected from Group 15 of the Periodic Table of Elements;

B is a linking group;

A is a nucleophilic group;

R_1 and R_2 are independently optionally substituted hydrocarbyl groups or heterohydrocarbyl groups; and

n and m respectively for R_1 and R_2 are independently determined by the respective valence and oxidation state of X_1 and X_2.

Advantageously, use of the catalyst system results in relatively much higher yields and relatively higher selectivity for α-olefins compared to known catalyst systems. More advantageously, the catalyst system is

also thermally stable. In one disclosed embodiment, the activity of the catalyst system was maintained after an oligomerization reaction occurred at relatively high temperatures and pressures. As no significant catalyst composition was observed, the catalyst system is thermally stable.

According to a second aspect, there is provided a process for tetramerization of olefins comprising the step of contacting at least one olefinic monomer with the catalyst system as defined in the first aspect above.

According to a third aspect, there is provided a method of preparing the catalyst system as defined in the first aspect above, comprising the step of mixing solutions of said metal compound and said ligands under conditions to form a metal-ligand coordination complex thereof.

According to a fourth aspect, there is provided a kit for preparing a catalyst system as defined in the first aspect above, the kit comprising said metal compounds, said ligands and instructions for mixing said metal compounds and said ligands.

Definitions

The following are some definitions that may be helpful in understanding the description of the present invention. These are intended as general definitions and should in no way limit the scope of the present invention to those terms alone, but are put forth for a better understanding of the following description.

Unless the context requires otherwise or specifically stated to the contrary, integers, steps, or elements of the invention recited herein as singular integers, steps or elements clearly encompass both

singular and plural forms of the recited integers, steps or elements.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated step or element or integer or group of steps or elements or integers, but not the exclusion of any other step or element or integer or group of elements or integers. Thus, in the context of this specification, the term "comprising" means "including principally, but not necessarily solely".

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations or any two or more of said steps or features.

As used herein, the term "oligomerization" refers a chemical reaction in which olefinic monomers are polymerized to form finite-chain polymers, such as 1-octene. Oligomerization may include dimerization, trimerization and tetramerization of olefinic monomer units.

The term "tetramerization" as used herein, means the catalytic tetramerization of an olefinic monomer to give a product composition enriched in the compound derived from the reaction of four of said olefinic monomers. The term tetramerization includes cases wherein all the olefinic monomers in the feed stream are identical as well as cases wherein the feed stream

contains two or more different olefinic monomers. For example, when the term "tetramerization" is used in relation to the tetramerization of ethylene, the term means the tetramerization of ethylene to form an alkene, such as 1-octene.

The term "olefin" refers to all hydrocarbon compounds comprising at least one carbon-carbon double bond.

The term "α olefin" refers to all hydrocarbon compounds with terminal double bonds. This definition includes, but is not limited to, ethylene, propylene, 1-butente, isobutylene, 1-pentene, 1-hexene, 1-octene and the like.

The term "1-octene selectivity" when used in relation to the tetramerization of ethylene means the amount of 1-octene formed within all C_8 alkenes in the liquid product. The term "C_8 selectivity" or "tetramerization selectivity" when used in relation to the tetramerization of ethylene means the amount of octenes formed within all liquid alkene products, most of which are C_6, C_8, C_{10} and C_{11+} products. The overall yield of 1-octene in the tetramerization of ethylene is the product of the "C_8 selectivity" or "tetramerization selectivity" multiplied by the "1-octene selectivity".

The term "tridentate ligand" refers to a ligand with potentially three donor atoms that are available for coordination with one or more metal centers.

The term "optionally substituted" as used herein means the group to which this term refers may be unsubstituted, or may be substituted with one or more groups. Exemplary substituent groups include alkyls, alkenyl, alkynyl, thioalkyl, cycloalkyl, cycloalkenyl, heterocycloalkyl, halo, carboxyl, haloalkyl, haloalkynyl,

hydroxyl, alkoxy, thioalkoxy, alkenyloxy, haloalkoxy, haloalkenyloxy, nitro, amino, nitroalkyl, nitroalkenyl, nitroalkynyl, nitroheterocyclyl, alkylamino, dialkylamino, alkenylamine, alkynylamino, acyl, alkenoyl, alkynoyl, acylamino, diacylamino, acyloxy, alkylsulfonyloxy, heterocycloxy, heterocycloamino, haloheterocycloalkyl, alkylsulfenyl, alkylcarbonyloxy, alkylthio, acylthio, phosphorus-containing groups such as phosphono and phosphinyl, aryl, heteroaryl, alkylaryl, alkylheteroaryl, cyano, cyanate, and isocyanate.

The term "hydrocarbyl" means any unit which comprises carbon and hydrogen atoms, whether saturated or unsaturated, linear, branched, cyclic. The hydrocarbyls may be optionally substituted, the meaning of which is within the definition of "optionally substituted" as described above.

The term "heterohydrocarbyl" as used herein refers to a hydrocarbyl group wherein one or more of the carbon atoms is replaced by a heteroatom, such as S, N or O. The carbon atom of the hydrocarbyl group which is replaced by a heteroatom can be either an internal carbon atom of the hydrocarbyl group or the carbon atom through which the heterohydrocarbyl group is attached.

The term "alkyl group" includes within its meaning monovalent ("alkyl") and divalent ("alkylene") straight chain or branched chain saturated aliphatic groups having from 1 to 10 carbon atoms, eg, 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms. For example, the term alkyl includes, but is not limited to, methyl, ethyl, 1-propyl, isopropyl, 1-butyl, 2-butyl, isobutyl, tert-butyl, amyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, pentyl, isopentyl, hexyl, 4-methylpentyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl,

1,2,2-trimethylpropyl, 1,1,2-trimethylpropyl, 2-ethylpentyl, 3-ethylpentyl, heptyl, 1-methylhexyl, 2,2-dimethylpentyl, 3,3-dimethylpentyl, 4,4-dimethylpentyl, 1,2-dimethylpentyl, 1,3-dimethylpentyl, 1,4-dimethylpentyl, 1,2,3-trimethylbutyl, 1,1,2-trimethylbutyl, 1,1,3-trimethylbutyl, 5-methylheptyl, 1-methylheptyl, octyl, nonyl, decyl, and the like.

The term "alkenyl group" includes within its meaning monovalent ("alkenyl") and divalent ("alkenylene") straight or branched chain unsaturated aliphatic hydrocarbon groups having from 2 to 10 carbon atoms, eg, 2, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms and having at least one double bond, of either E, Z, cis or trans stereochemistry where applicable, anywhere in the alkyl chain. Examples of alkenyl groups include but are not limited to ethenyl, vinyl, allyl, 1-methylvinyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, 3-butentyl, 1,3-butadienyl, 1-pentenyl, 2-pententyl, 3-pentenyl, 4-pentenyl, 1,3-pentadienyl, 2,4-pentadienyl, 1,4-pentadienyl, 3-methyl-2-butenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 1,3-hexadienyl, 1,4-hexadienyl, 2-methylpentenyl, 1-heptenyl, 2-heptentyl, 3-heptenyl, 1-octenyl, 1-nonenyl, 1-decenyl, and the like.

The term "alkynyl group" as used herein includes within its meaning monovalent ("alkynyl") and divalent ("alkynylene") straight or branched chain unsaturated aliphatic hydrocarbon groups having from 2 to 10 carbon atoms and having at least one triple bond anywhere in the carbon chain. Examples of alkynyl groups include but are not limited to ethynyl, 1-propynyl, 1-butynyl, 2-butynyl, 1-methyl-2-butynyl, 3-methyl-1-butynyl, 1-pentynyl, 1-hexynyl, methylpentynyl, 1-

heptynyl, 2-heptynyl, 1-octynyl, 2-octynyl, 1-nonyl, 1-decynyl, and the like.

The term "cycloalkyl" as used herein refers to cyclic saturated aliphatic groups and includes within its meaning monovalent ("cycloalkyl"), and divalent ("cycloalkylene"), saturated, monocyclic, bicyclic, polycyclic or fused polycyclic hydrocarbon radicals having from 3 to 10 carbon atoms, eg, 3, 4, 5, 6, 7, 8, 9, or 10 carbon atoms. Examples of cycloalkyl groups include but are not limited to cyclopropyl, 2-methylcyclopropyl, cyclobutyl, cyclopentyl, 2-methylcyclopentyl, 3-methylcyclopentyl, cyclohexyl, and the like.

The term "cycloalkenyl" as used herein, refers to cyclic unsaturated aliphatic groups and includes within its meaning monovalent ("cycloalkenyl") and divalent ("cycloalkenylene"), monocyclic, bicyclic, polycyclic or fused polycyclic hydrocarbon radicals having from 3 to 10 carbon atoms and having at least one double bond, of either E, Z, cis or trans stereochemistry where applicable, anywhere in the alkyl chain. Examples of cycloalkenyl groups include but are not limited to cyclopropenyl, cyclopentenyl, cyclohexenyl, and the like.

The term "aryl" refers to a carbocyclic (consisting entirely of carbon and hydrogen) aromatic group or a heterocyclic aromatic group. Exemplary aryls include, but are not limited to, phenyl, naphthyl, indenyl, indanyl, azulenyl, fluorenyl, anthracenyl, furyl, thienyl, pyridyl, pyrrolyl, oxazolyly, thiazolyl, imidazolyl, pyrazolyl, 2-pyrazolinyl, pyrazolidinyl, isoxazolyl, isothiazolyl, 1,2,3-oxadiazolyl, 1,2,3-triazolyl, 1,3,4-thiadiazolyl, pyridazinyl, pyrimidinyl. pyrazinyl, 1,3,5-triazinyl, 1,3,5-trithianyl, indolizinyl, indolyl, isoindolyl, 3H-indolyl, indolinyl, benzo[b]furanyl, 2,3-

dihydrobenzofuranyl, benzo[b]thiophenyl, 1H-indazolyl, benzimidazolyl, benzthiazolyl, purinyl, 4H-quinolizinyl, quinolinyl, isoquinolinyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, 1,8-naphthyridinyl, pteridinyl, carbazolyl, acridinyl, phenazinyl, phenothiazinyl, and phenoxazinyl.

The term "aryloxy," alone or in combination, refers to a radical of formula aryl-O--, wherein aryl is as defined above. Examples of aryloxy radicals include, but are not limited to, phenoxy, naphthoxy, pyridyloxy and the like.

The term "amino" as used herein refers to groups of the form $-NR_aR_b$ wherein R_a and R_b are individually selected from the group including but not limited to hydrogen, optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, and optionally substituted aryl groups.

The term "aromatic heterocyclic group" means a cyclic group containing one or more of hetero atoms optionally selected from O, S and N in the ring, and said cyclic group may condense with a carbocycle or another heterocycle. Exemplary 5- to 6-membered aromatic heterocyclic groups include pyrrolyl, imidazolyl, pyrazolyl, pyridyl, pyridazinyl, pyrimidinyl, pyrazinyl, triazinyl, isoxazolyl, oxazolyl, oxadiazolyl, isothiazolyl, thiazolyl, thiadiazolyl, furyl, thienyl and the like, and condensed aromatic heterocyclic groups such as indolyl, benzimidazolyl, indazolyl, indolizinyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, naphthyridinyl, quinoxalinyl, pteridinyl, benzisoxazolyl, benzoxazolyl, oxadiazolyl, benzoxadiazolyl, benzisothiazolyl, benzothiazolyl, benzothiadiazolyl, benzofuryl, benzothienyl, carbazolyl,

phenazinyl and the like. The aromatic heterocyclic group may be optionally substituted as defined above.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Disclosure of embodiments

The present invention is further described in the following embodiments, which are included for purpose of illustration and not for limitation of the scope of that which the applicants claim to be the invention.

In one embodiment, at least one of X_1 and X_2 are selected from the group consisting of nitrogen, phosphorous, arsenic, antimony, bismuth, oxygen, sulfur, and selenium. In one embodiment, at least one of X_1 and X_2 are phosphorous. X_1 and X_2 may both be phosphorous.

In one embodiment, Z is nitrogen.

In one embodiment, linking group B is an optionally substituted hydrocarbyl or optionally substituted heterohydrocarbyl. B may be an optionally substituted, straight, branched and cyclic alkyl, alkenyl, alkynyl,

aryl, aryloxy, diaryl and heteroaryl. The linking group B may have up to 8 carbon atoms. In one embodiment, said linking group B is one of methyl, ethyl, propyl, butyl, pentyl , hexyl, heptyl and octyl. In one embodiment, said linking group B is selected to be a single atom spacer.

In one embodiment, A is selected from the group consisting of optionally substituted hydroxyl, ethers, cycloethers, thioethers, imino, imine, amine, amino, carbene, aromatic heterocyclic and phosphines.

The ether may be a primary ether. The primary ether may be a diethylether group or a dipropylether group. Exemplary ethers and cycloethers include dialkyl ethers, diaryl ethers, dialkaryl ethers, diaralkyl ethers, alkyl aryl ethers, alkyl alkaryl ethers, alkyl aralkyl ethers, aryl alkaryl ethers, aryl aralkyl ethers and alkaryl aralkyl ethers. Included within the ethers are compounds such as dimethyl ether; diethyl ether; dipropyl ether; diisopropyl ether; dibutyl ether; diisoamyl ether; di-tert-butyl ether; diphenyl ether; dibenzyl ether; divinyl ether; butyl methyl ether; butyl ethyl ether; sec-butyl methyl ether; tert-butyl methyl ether; cyclopentyl methyl ether; cyclohexyl ethyl ether; tert-amyl methyl ether; sec-butyl ethyl ether; chloromethyl methyl ether; trimethylsilylmethyl methyl ether; bis(trimethylsilylmethyl) ether; bis(2,2,2-trifluoroethyl) ether; methyl phenyl ether; ethylene oxide; propylene oxide; 1,2-epoxybutane; cyclopentene oxide; epichlorohydrin; furan; 2,3-dihydrofuran; 2,5-dihydrofuran; tetrahydrofuran; 2-methyltetrahydrofuran; 2,5-dimethyltetrahydrofuran; 2-methylfuran; 2,5-dimethylfuran; tetrahydropyran; 1,2-epoxybut-3-ene; styrene oxide; 2-ethylfuran; oxazole; 1,3,4-oxadiazole; 3,4-dichloro-1,2-epoxybutane; 3,4-dibromo-1,2-epoxybutane; dimethoxymethane; 1,1-dimethoxyethane;

1,1,1-trimethoxymethane; 1,1,1-trimethoxyethane; 1,1,2-trimethoxyethane; 1,1-dimethoxypropane; 1,2-dimethoxypropane; 2,2-dimethoxypropane; 1,3-dimethoxypropane; 1,1,3-trimethoxypropane; 1,4-dimethoxybutane; 1,2-dimethoxybenzene; 1,3-dimethoxybenzene; 1,4-dimethoxybenzene; ethylene glycol dimethyl ether; di(ethylene glycol)dimethyl ether; di(ethylene glycol)diethyl ether; di(ethylene glycol)dibutyl ether; di(ethylene glycol)tert-butyl methyl ether; tri(ethylene glycol)dimethyl ether; tri(ethylene glycol)diethyl ether; tetra(ethylene glycol)dimethyl ether; 2,2-diethyl-1,3-dimethoxypropane; 2-methyl-2-ethyl-1,3-dimethoxypropane; 2-methoxyfuran; 3-methoxyfuran; 1,3-dioxolane; 2-methyl-1,3-dioxolane; 2,2-dimethyl-1,3-dioxolane; 2-ethyl-2-methyl-1,3-dioxolane; 2,2-tetramethylene-1,3-dioxolane; 2,2-pentamethylene-1,3-dioxolane; 1,3-dioxane; 1,4-dioxane; 4-methyl-1,3-dioxane; 1,3,5-trioxane and 3,4-epoxytetrahydrofuran, any one of its structurally analogs and mixtures thereof.

The thioether may be selected from the group consisting of dialkyl thioethers, methyl-ethyl-thioether, diethyl-thioether, diaryl thioethers, dialkaryl thioethers, diaralkyl thioethers, alkyl aryl thioethers, alkyl alkaryl thioethers, alkyl aralkyl thioethers, aryl alkaryl thioethers, aryl aralkyl thioethers and alkaryl aralkyl thioethers. Exemplary thioethers include 2,3-dihydrothiophene; 2,5-dihydrothiophene; tetrahydrothiophene; 2-methyltetrahydrothiophene; 2,5-dimethyltetrahydrothiophene; 4,5-dihydro-2-methylthiophene; 2-methylthiophene; 2,5-dimethylthiophene; 3-bromothiophene; 2,3-benzothiophene; 2-methylbenzothiophene; dibenzothiophene; isobenzothiophene; 1,1-bis(methylthio)ethane; 1,1,1-tris(methylthio)ethane; 1,1,2-tris(methylthio)ethane;

1,1-bis(methylthio)propane; 1,2-bis(methylthio)propane; 2,2-bis(methylthio)propane; 1,3-bis(methylthio)propane; 1,1,3-tris(methylthio)propane; 1,4-bis(methylthio)butane; 1,2-bis(methylthio)benzene; 1,3-bis(methylthio)benzene; 1,4-bis(methylthio)benzene; 2-methylthiothiophene; 3-methylthiothiophene; 2-methylthiotetrahydropyran; 3-methylthiotetrahydropyran; 1,3-dithiolane; 2-methyl-1,3-dithiolane; 2,2-dimethyl-1,3-dithiolane; 2-ethyl-2-methyl-1,3-dithiolane; 2,2-tetramethylene-1,3-dithiolane; 2,2-pentamethylene-1,3-dithiolane; 2-vinyl-1,3-dithiolane; 2-chloromethyl-1,3-dithiolane; 2-methylthio-1,3-dithiolane.

The amino may be selected from the group consisting of a primary amine, secondary amine and a tertiary amine.

The aromatic heterocyclic may be selected from the group consisting of thiophene, pyrrole, imidazole, pyrazole, thiazole, isothiazole, oxazole, triazole, pyridine, pyrazine, pyrimidine, pyridazine, benzothiazole, benzothiophene, indole, isoindole and benzoxazole.

Exemplary phosphines include dicyclohexylphosphine, tricyclohexylphosphine, triethylphosphine, tributylphosphine, diethylphenylphosphine, dicyclohexylphenylphosphine, tribenzylphosphine, ortho-tolyldiphenylphosphine, di(ortho-tolyl)phenylphosphine, triisopropylphosphine, triisobutylphosphine, tritertbutylphosphine, phenylphosphine, diphenylphosphine, triphenylphosphine, tri-toluylphosphine, trialkylphosphoine, tri-(isopropyl)phosphine, tri-(n-butyl)phosphine, tri-(n-naphthyl)phosphine, di-(n-butyl)chlorophosphine, di-(n-butyl)phosphine, di-(n-isobutyl)phosphine, (3-sulfo-4-methylphenyl)di(4-methylphenyl)phosphine, (3-sulfo-4-methoxyphenyl)di(4-methoxyphenyl)phosphine, (3-sulfo-4-

chlorophenyl)di(4-chlorophenyl)phosphine, di(3-sulfophenyl)phenylphosphine, di(4-sulfophenyl)phenylphosphine, di(3-sulfo-4-methylphenyl)(4-methylphenyl)phosphine, di(3-sulfo-4-methoxyphenyl)(4-methoxyphenyl)phosphine, di(3-sulfo-4-chlorophenyl)(4-chlorophenyl)phosphine, tri(3-sulfophenyl)phosphine, tri(4-sulfophenyl)phosphine, tri(3-sulfo-4-methylphenyl)phosphine, tri(3-sulfo-4-methoxyphenyl)phosphine, tri(3-sulfo-4-chlorophenyl)phosphine, (2-sulfo-4-methylphenyl)(3-sulfo-4-methylphenyl)(3,5-disulfo-4-methylpheny l)phosphine or (3-sulfophenyl)(3-sulfo-4-chlorophenyl)(3,5-disulfo-4-chlorophenyl)phosphine.

R_1 and R_2 may be independently optionally substituted, straight, branched and cyclic alkyl, alkenyl, alkynyl, aryl, aryloxy, diaryl and heteroaryl. In one embodiment, R_1 and R_2 may be independently straight chain or branched chain alkyls. In one embodiment, R_1 and R_2 may be independently selected from the group consisting of methyl, ethyl, propyl and butyl. In another embodiment, R_1 and R_2 may be independently selected from the group consisting of benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylKydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranyl group.

The metal of said metal compound may be a transition metal. The transition metal may have a valence of (+3). The metal of said metal compound may be selected from the group consisting of Group 6 metals, and Group 10 metals of the Periodic Table of Elements. The metal of said

metal compound may be one of chromium and nickel. In one embodiment, the metal is chromium with a valence of (+3).

The metal compound is selected from a group consisting of a metal inorganic salt and a metal organic salt. The metal compound may be a chromium containing salt. Exemplary chromium containing salts include chromium bichloride tris-tetrahydrofuran complex, chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium (III) octanoate, chromium (III) acetylacetonoate, chromium hexacarbonyl and chromium (III) 2-ethylhexanoate. In one embodiment, the transition metal compound is chromium (III) acetylacetonoate.

The ligand may be selected from the group consisting of $(C_2H_5)_2PN(CH_2CH_2SCH_3)P(C_2H_5)_2$, $(C_2H_5)_2PN(CH_2CH_2SCH_2CH_3)P(C_2H_5)_2$, $(C_2H_5)_2PN(CH_2CH_2CH_2SCH_3)P(C_2H_5)_2$, $Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$, $(C_2H_5)_2PN(CH_2CH_2CH_2OCH_2CH_3)P(C_2H_5)_2$, $(C_2H_5)_2PN(CH_2CH_2CH_2OCH_2CH_2CH_2CH_3)P(C_2H_5)_2$, $(C_2H_5)_2PN(CH_2CH_2C_5H_4N)P(C_2H_5)_2$.

The catalyst system may further comprise an activator. The activator may be selected from the group consisting of organo-aluminium compounds, organo-boron compounds, organic salts and inorganic acids and salts. The activator may be selected from the group consisting of silver and alkali metal salts. Exemplary activators are organoaluminium such as trimethylaluminium (TMA), triethylaluminium (TEA), tri-n-butyl aluminium, tri-isobutylaluminium (TIBA), tri-n-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride and aluminoxanes (also called alumoxanes).

In one embodiment, the activator is an alumoxane. Exemplary aluminoxanes include methyl aluminoxane (MAO),

modified methyl aluminoxane (MMAO) , tetraisobutyl dialuminoxane (TIBAO) , tetra-n-butyl dialuminoxane and tetra-n-octyl dialuminoxane. Most preferably, the activator is methyl aluminoxane (MAO).

In a preferred embodiment, the disclosed catalyst system is thermally stable. The activity of the catalyst system can be maintained without any loss, for more than 5 hours at a temperature of more than 60 °C. The activity of the catalyst system can be maintained without any substantial loss for at least 8 hours, at a temperature of approximately 80°C to 110°C.

In another preferred embodiment, the disclosed catalyst system catalyses the tetramerization of olefins. The disclosed catalyst system may catalyse the tetramerization of α-olefins. More particularly, the disclosed catalyst system may catalyse the tetramerization of ethylene to 1-octene.

The ligand of the catalyst system may be a tridentate ligand.

It has been found by the present inventors that the catalytic system disclosed herein can be used to produce a high yield of 1-octene with high selectivity. Without being bound by any particular theory, it is thought that the donor-Z-functionalized nucleophilic group(A), in one embodiment being donor-N-functionalized bis(phosphino)amines, contain both strong and weak donor groups (hemilabile ligands) show improved catalyst stability and selectivity and result in catalytic site isolation. It is postulated that the hemilabile arm in the disclosed ligands is capable of reversible dissociation from the metal center. For example, where X_1 and X_2 are both phosphorous and Z is nitrogen (ie a "PNP" arm in the ligand) it is thought that such dynamic behavior produces vacant coordination sites that allow

complexation of substrates during the catalytic cycle, while the P^{III} centre is firmly anchored to the metal.

Also disclosed herein is a process for tetramerization of olefins comprising the step of contacting at least one olefinic monomer with the catalyst system.

The process may comprise the step of forming a co-ordination complex of said catalyst system from said metal compound and said ligand before said contacting step.

The process may comprise the step of maintaining the pressure during said contacting step in the range of about 10 Bar (1Mpa) to about 50 Bar (5MPa) or about 15 Bar (1.5MPa) to about 40 Bar (4MPa) or about 25 Bar (1.5MPa) to about 40 Bar (4MPa).

The process may comprise the step of maintaining the temperature during said contacting step in the range of about 0°C to about 110°C or about 50°C to about 110°C or about 80°C to about 110°C.

The process may further comprise the step of providing an amount of said metal compound to said ligand in the molar ratio in the range of from about 1:1 to about 1:2.5 or about 1:1 to about 1:2.

The tetramerization process may be performed in any one of a number of suitable reactors, which are well known to one skilled in the art. Typically the tetramerization process of the present invention may be carried out in a batch, semi-batch or continuous mode.

Also disclosed herein is a method of preparing the catalyst system, comprising the step mixing liquids of said metal compound and said ligands under conditions to form a metal-ligand coordination complex thereof.

The method of preparing said catalyst may comprise first preparing said ligand. Preparation of the ligand

may comprise the step of adding a mixture of optionally substituted phosphine and halide substituted hydrocarbon to a mixture of nitrogen containing precursor and halide substituted hydrocarbon. The process may then comprise the step of mixing the resulting solution for about 10 hours to 24 hours or about 15 to about 24 hours.

After said mixing step, the process may comprise the step of evaporating said halide substituted hydrocarbon to dryness before adding an organic solvent and subsequently filtering the resultant suspension.

Also disclosed herein is a kit for preparing a catalyst system, the kit comprising said metal compounds, said ligands and instructions for mixing said metal compounds and said ligands. In one embodiment, materials to make the ligands may be supplied together with instructions on how to make said ligands.

Modes for Carrying Out the Disclosed Embodiments

Non-limiting examples of disclosed catalyst system embodiments will be further described.

Experimental conditions

All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or argon with an M. Braun Labmaster 130 Inert Gas System.

NMR spectra were measured on a Bruker ACF300 300 MHz FT NMR spectrometers (1H at 300.14 MHz, 13C at 75.43 MHz and 31P at 121.49 MHz).

All reagent chemicals were obtained from Sigma-Aldrich of St Louis, Missouri, United States of America or Stem Chemicals of Stem Chemicals, Newburyport, Massachusetts, United States of America unless stated otherwise. In all the examples, the molar mass of the

activator methylaluminoxane (MAO) was taken to be 58.016 g/mol, corresponding to the (CH_3-Al-O) unit, in order to calculate the molar quantities of MAO used in the preparation of the catalysts described below. Ethylene oligomerization products were analysed by Gas chromatography-mass spectrometry (GC-MS) and GC-FID (Gas Chromatography - Flame Ionization Detector)

Preparation of ligands

Example 1a) :Preparation of $Et_2PN(CH_2CH_2SCH_3)PEt_2$ (1a)

To a mixture of 2-(methylthio)ethylamine (101 mg, 1.11 mmol) and triethylamine (0.6 ml) in dichloromethane (5 ml) at room temperature (r.t.) was added a solution of chlorodiethylphosphine (277 mg, 2.22 mmol) in dichloromethane (4 ml). The resulting solution was stirred for 20 h, the dichloromethane evaporated to dryness and 5 ml of toluene added. The suspension was filtered through a layer of celite to remove the triethylammonium salt formed. The product $Et_2PN(CH_2CH_2SCH_3)PEt_2$ (1a) (192 mg, 0.72 mmol, 65 % yield) was isolated as an colorless oil after removed the solvent. 31P NMR ($CDCl_3$): δ 58.52.

Example 1b): Preparation of $Et_2PN(CH_2CH_2SCH_2CH_3)PEt_2$ (1b)

To a mixture of 2-(ethylthio)ethylamine (42 mg, 0.4 mmol) and triethylamine (0.2 ml) in dichloromethane (4 ml) at room temperature (r.t.) was added a solution of chlorodiethylphosphine (99 mg, 0.8 mmol) in dichloromethane (2 ml). The resulting solution was stirred for 20 h, the dichloromethane evaporated to dryness and 5ml of toluene added. The suspension was filtered through a layer of celite to remove the triethylammonium salt formed. The product $Et_2PN(CH_2CH_2SCH_2CH_3)PEt_2$ (1b) (84 mg, 0.299 mmol, 75 %

yield) was isolated as an colorless oil after removed the solvent.

Example 1c): Preparation of $Et_2PN(CH_2CH_2CH_2SCH_3)PEt_2$ (1c)

To a mixture of 3-(methylthio)propylamine (29 mg, 0.276 mmol) and triethylamine (0.2 ml) in dichloromethane (3 ml) at room temperature (r.t.) was added a solution of chlorodiethylphosphine (70 mg, 0.56 mmol) in dichloromethane (2 ml). The resulting solution was stirred for 20 h, the dichloromethane evaporated to dryness and 5ml of toluene added. The suspension was filtered through a layer of celite to remove the triethylammonium salt formed. The product $Et_2PN(CH_2CH_2CH_2SCH_3)PEt_2$ (1c) (64 mg, 0.228 mmol, 84 % yield) was isolated as an colorless oil after removed the solvent. 31P NMR ($CDCl_3$): δ 58.55.

Example 1d): Preparation of $Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$ (1d)

To a mixture of 3-(methylthio)propylamine (60 mg, 0.571 mmol) and triethylamine (0.6 ml) in dichloromethane (4 ml) at room temperature (r.t.) was added a solution of chlorodiphenylphosphine (251 mg, 1.14 mmol) in dichloromethane (4 ml). The resulting solution was stirred for 20 h, the dichloromethane evaporated to dryness and 5 ml of toluene added. The suspension was filtered through a layer of celite to remove the triethylammonium salt formed. The product $Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$ (1d) (261 mg, 0.552 mmol, 97 % yield) was isolated as a white solid.

Example 1e): Preparation of $Et_2PN(CH_2CH_2CH_2OCH_2CH_3)PEt_2$ (1e)

To a mixture of 3-ethoxypropylamine (37 mg, 0.359 mmol) and triethylamine (0.2 ml) in dichloromethane (4 ml) at room temperature (r.t.) was added a solution of

chlorodiethylphosphine (90 mg, 0.722 mmol) in dichloromethane (4 ml). The resulting solution was stirred for 20 h, the dichloromethane evaporated to dryness and 5 ml of toluene added. The suspension was filtered through a layer of celite to remove the triethylammonium salt formed. The product $Et_2PN(CH_2CH_2CH_2OCH_2CH_3)PEt_2$ (1e) (92 mg, 0.33 mmol, 91 % yield) was isolated as an colorless oil after removed the solvent.

Example 1f): Preparation of $Et_2PN(CH_2CH_2CH_2OCH_2CH_2CH_2CH_3)PEt_2$ (1f)

To a mixture of 3-butoxypropylamine (47 mg, 0.359 mmol) and triethylamine (0.2 ml) in dichloromethane (4 ml) at room temperature (r.t.) was added a solution of chlorodiethylphosphine (90 mg, 0.722 mmol) in dichloromethane (4 ml). The resulting solution was stirred for 20 h, the dichloromethane evaporated to dryness and 5 ml of toluene added. The suspension was filtered through a layer of celite to remove the triethylammonium salt formed. The product $Et_2PN(CH_2CH_2CH_2OCH_2CH_2CH_2CH_3)PEt_2$ (1f) (97 mg, 0.316 mmol, 87 % yield) was isolated as an colorless oil after removed the solvent.

Example 1g): Preparation of $Et_2PN(CH_2CH_2C_5H_4N)PEt_2$ (1g)

To a mixture of 2-(2-aminoethyl)pyridine (141 mg, 1.157 mmol) and triethylamine (0.8 ml) in dichloromethane (4 ml) at room temperature (r.t.) was added a solution of chlorodiethylphosphine (288 mg, 2.313 mmol) in dichloromethane (4 ml). The resulting solution was stirred for 20 h, the dichloromethane evaporated to dryness and 5 ml of toluene added. The suspension was filtered through a layer of celite to remove the

triethylammonium salt formed. The product $Et_2PN(CH_2CH_2C_5H_4N)PEt_2$ (336 mg, 1.128 mmol, 97 % yield) was isolated as an colorless oil after removed the solvent. 31P NMR ($CDCl_3$): δ 58.41.

Preparation of catalysts in situ in the stock solution

The catalysts were prepared in situ in 1 ml toluene as shown in Table 1. The mixture was shaken up for 2 min before use.

Table 1: Preparation of catalysts

	Ligands	Cr(III)
Example 2a	$Et_2PN(CH_2CH_2SCH_3)PEt_2$ (1.6 mg, 0.006 mmol)	$Cr(acac)_3$ (1 mg, 0.003 mmol)
Example 2b	$Et_2PN(CH_2CH_2SCH_2CH_3)PEt_2$ (1.6 mg, 0.006 mmol)	$Cr(acac)_3$ (1 mg, 0.003 mmol)
Example 2c	$Et_2PN(CH_2CH_2CH_2SCH_3)PEt_2$ (1.6 mg, 0.006 mmol)	$Cr(acac)_3$ (1 mg, 0.003 mmol)
Example 2d	$Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$ (2.7 mg, 0.006 mmol)	$Cr(acac)_3$ (1 mg, 0.003 mmol)
Example 2e	$Et_2PN(CH_2CH_2CH_2OCH_2CH_3)PEt_2$ (1.6 mg, 0.006 mmol)	$Cr(acac)_3$ (1 mg, 0.003 mmol)
Example 2f	$Et_2PN(CH_2CH_2CH_2OCH_2CH_2CH_2CH_3)PEt_2$ (1.8 mg, 0.006 mmol)	$Cr(acac)_3$ (1 mg, 0.003 mmol)
Example 2g	$Et_2PN(CH_2CH_2C_5H_4N)PEt_2$ (1.7 mg, 0.006 mmol)	$CrCl_3 \cdot 3THF$ (1 mg, 0.003 mmol)

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Example for ethylene tetramerization reactions

The catalytic activities were screened by Endeavor™ Parallel Pressure Reactor from AAPPTEC LLC of Louisville, Kentucky United States of America, following recommended procedure:

1. Glass liners were prepared with toluene as solvent. The total volume of toluene was 4 ml. This can be summarized by the following equation:
2. 0.125 ml (Cr solution) + 3.75 ml (toluene) + 0.1 ml (MAO solution) = 4 ml
3. n-Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID.
4. The catalyst solution (125 µl, 0.125 mg, 0.36 µmol) and activator solution were injected into the reactor chamber.
5. The stirrer top was secured with impellers to the reactor block.
6. The reaction temperature, pressure, volume 4 ml, run time and reaction sequence were input using Endeavor™ Advanced Software. The temperature was set to a target of 80°C while the pressure was set to 30 Bar (3MPa). The total reaction time was 3 hours.
7. Start Endeavor™ software on PC
8. Click "Start" on Endeavor™ software on PC.
9. After the desired reaction time, the vessel was cooled down as low as possible and depressurized.

The reaction mixture was cooled to 0 °C and terminated by addition of 10 % hydrochloride acid in water. A small sample of the upper-layer solution was filtered through a layer of celite and analyzed by GC. The individual products of oligomerization were identified by GC-MS. The remainder of the upper-layer solution was filtered to isolate the solid polymeric

products. The solid products was suspended in 10 % hydrochloride acid in water and stirred for 24 h, dried under reduced pressure before the final mass was weighted.

Table 2: Ethylene tetramerization runs:[a]

Run (ligand)	Activity[b]	Total product mg	Solids (%)	Liquids (%)	Liquid product distribution (%)				1-C_8 Selectivity (%)
					C_6	C_8	C_{10}	C_{11+}	
1 (1a)	41 505	772	11.1	88.9	25.9	49.3	1.3	24.5	97.7
2 (1b)	53 602	997	24.3	75.7	18.0	36.8	1.6	43.3	98.5
3 (1c)	43 978	818	4.9	95.1	26.7	55.5	1.2	16.2	98.5
4 (1d)[d]	18 602	346	62.4	37.6	9.2	33.3	1.9	54.8	97.0
5 (1e)	61 021	1135	26.9	73.1	17.3	35.3	1.8	45.4	97.8
6 (1f)	48 871	909	26.4	73.6	17.9	37.8	1.8	42.2	97.5
7 (1g)	30 538	569	23.4	77.6	11.7	19.3	2.3	66.2	96.2

[a]Standard reaction conditions: 0.36 µmol $Cr(acac)_3$, 2 equiv of ligands, 440 equiv of MAO, 4 ml toluene, 30 bar ethylene, 3 h. [b] (run 7; $CrCl_3 \cdot 3THF$). Activity = g prod./g Cr. [c] % = weight %. [d] 1 h.

It can be seen from Table 2 that a high proportion of the liquid product were in the C_8 fraction. Furthermore, the selectivity for 1-C_8 was very high with all experiments showing more than 96% selectivity for 1-Octene. The selectivity for 1-C_8 was experimentally measured by GC/MS obtained using different GC columns.

It can also be seen that the activity of the catalysts 1-7 were all maintained and did not substantially reduce after use. This was despite the fact that the catlaysts were subject to temperatures of at least 80°C, pressures of about 30 Bar (3 MPa) for 3 hours. Hence, the data of Table 2 indicates that the catalysts are still active under these thermal conditions and therefore it can be inferred that the catalysts are thermally stable.

Applications

The disclosed catalyst system is useful for oligomerization of olefins, primarily α-olefins. More advantageously, the disclosed catalyst system is shown to have high selectivity for 1-Octene. Typical selectivity for 1-Octene has been shown to be more than 50%. The catalyst system may therefore provide a useful catalyst for the production of 1-Octene on a commercial scale.

Use of the disclosed catalyst system may provide a useful alternative to known catalysts in the oligomerization of ethylene to 1-Octene. Indeed, the disclosed catalyst has shown to have produce higher 1-Octene yields and higher 1-Octene selectivity compared to some known and currently commercially available catalysts.

Advantageously, the disclosed catalysts have been shown to have relatively high thermal stability. This is particularly important as it demonstrates that the catalyst is capable of being used in an industrial process for the production of 1-Octene, in which relatively high temperatures and pressures are required to produce 1-Octene.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

CLAIMS

1. A catalyst system for oligomerization of olefins comprising:

a) a metal compound; and

b) a ligand of general formula:

$(R_1)_nX_1-Z(B-A)-X_2(R_2)_m$

wherein:

X_1 and X_2 are independently selected from the elements of Group 14, Group 15 and Group 16 of the Periodic Table of Elements;

Z is an element selected from Group 15 of the Periodic Table of Elements;

B is a linking group;

A is a nucleophilic group;

R_1 and R_2 are independently optionally substituted hydrocarbyl groups or heterohydrocarbyl groups; and

n and m respectively for R_1 and R_2 are independently determined by the respective valence and oxidation state of X_1 and X_2.

2. A catalyst system as claimed in claim 1, wherein at least one of X_1 and X_2 are selected from the group consisting of nitrogen, phosphorous, arsenic, antimony, bismuth, oxygen, sulfur, and selenium.

3. A catalyst system as claimed in claim 2, wherein at least one of X_1 and X_2 are phosphorous.

4. A catalyst system as claimed in claim 3, wherein X_1 and X_2 are both phosphorous.

5. A catalyst system as claimed in claim 1, wherein B is an optionally substituted hydrocarbyl or an optionally substituted heterohydrocarbyl.

6. A catalyst system as claimed in claim 5, wherein the linking group B is an optionally substituted, straight, branched and cyclic alkyl, alkenyl, alkynyl, aryl, aryloxy, diaryl, and heteroaryl.

7. A catalyst system as claimed in claim 6, wherein said linking group B has up to 8 carbon atoms.

8. A catalyst system as claimed in claim 6, wherein said linking group B is one of methyl, ethyl, propyl, butyl, pentyl , hexyl, heptyl and octyl.

9. A catalyst system as claimed in claim 1, wherein said linking group B is selected to be a single atom spacer.

10. A catalyst system as claimed in claim 1, wherein A is selected from the group consisting of optionally substituted hydroxyl, ethers, cycloethers, thioethers, imino, imine, amine, amino, carbene, aromatic heterocyclic and phosphines.

11. A catalyst system as claimed in claim 10, wherein said ether is a primary ether.

12. A catalyst system as claimed in claim 11, wherein said primary ether is a diethylether group or a dipropylether group.

13. A catalyst system as claimed in claim 10, wherein said thioether is selected from the group consisting of dialkyl thioethers, methyl-ethyl-thioether, diethyl-thioether, diaryl thioethers, dialkaryl thioethers, diaralkyl thioethers, alkyl aryl thioethers, alkyl alkaryl thioethers, alkyl aralkyl thioethers, aryl alkaryl thioethers, aryl aralkyl thioethers and alkaryl aralkyl thioethers.

14. A catalyst system as claimed in claim 10, wherein said amino is selected from the group consisting of a primary amine, secondary amine and a tertiary amine.

15. A catalyst system as claimed in claim 10, wherein said aromatic heterocyclic is selected from the group consisting of thiophene, pyrrole, imidazole, pyrazole, thiazole, isothiazole, oxazole, triazole, pyridine, pyrazine, pyrimidine, pyridazine, benzothiazole, benzothiophene, indole, isoindole and benzoxazole.

16. A catalyst system as claimed in claim 1, wherein R_1 and R_2 are independently optionally substituted, straight, branched and cyclic alkyl, alkenyl, alkynyl, aryl, aryloxy, diaryl and heteroaryl.

17. A catalyst system as claimed in claim 16, wherein R_1 and R_2 are independently straight chain or branched chain alkyls.

18. A catalyst system as claimed in claim 17, wherein R_1 and R_2 are independently selected from the group consisting of methyl, ethyl, propyl and butyl.

19. A catalyst system as claimed in claim 16, wherein R_1 and R_2 are independently selected from the group consisting of benzyl, phenyl, tolyl, xylyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, diethylamino, methylethylamino, thiophenyl, pyridyl, thioethyl, thiophenoxy, trimethylsilyl, dimethylKydrazyl, methyl, ethyl, ethenyl, propyl, butyl, propenyl, propynyl, cyclopentyl, cyclohexyl, ferrocenyl and tetrahydrofuranyl group.

20. A catalyst system as claimed in claim 1, wherein the metal of said metal compound is a transition metal.

21. A catalyst system as claimed in claim 20, wherein the transition metal has a valence of (+3).

22. A catalyst system as claimed in claim 1, wherein the metal of said metal compound is selected from the group consisting of Group 6 metals and Group 10 metals of the Periodic Table of Elements.

23. A catalyst system as claimed in claim 22, wherein the metal of said metal compound is one of chromium and nickel.

24. A catalyst system as claimed in claim 23, wherein the metal is chromium with a valence of (+3).

25. A catalyst system as claimed in claim 1, wherein the metal compound is selected from a group consisting of a metal inorganic salt and a metal organic salt .

26. A catalyst system as claimed in claim 25, wherein the metal compound is a chromium containing salt.

27. A catalyst system as claimed in claim 1, wherein the ligand is selected from the group consisting of $(C_2H_5)_2PN(CH_2CH_2SCH_3)P(C_2H_5)_2$, $(C_2H_5)_2PN(CH_2CH_2SCH_2CH_3)P(C_2H_5)_2$, $(C_2H_5)_2PN(CH_2CH_2CH_2SCH_3)P(C_2H_5)_2$, $Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$, $(C_2H_5)_2PN(CH_2CH_2CH_2OCH_2CH_3)P(C_2H_5)_2$, $(C_2H_5)_2PN(CH_2CH_2CH_2OCH_2CH_2CH_2CH_3)P(C_2H_5)_2$, $(C_2H_5)_2PN(CH_2CH_2C_5H_4N)P(C_2H_5)_2$.

28. A catalyst system as claimed in claim 1, further comprising an activator.

29. A catalyst system as claimed in claim 28, wherein said activator is selected from the group consisting of organo-aluminium compounds, organo-boron compounds, organic salts and inorganic acids and salts.

30. A catalyst system as claimed in claim 25, wherein said activator is selected from the group consisting of silver and alkali metal salts.

31. A catalyst system as claimed in claim 1, wherein Z is nitrogen.

32. A process for tetramerization of olefins comprising the step of contacting at least one olefinic monomer with the catalyst system as claimed in any one of claims 1 to 31.

33. A process as claimed in claim 32 comprising the step of forming a co-ordination complex of said catalyst system from said metal compound and said ligand before said contacting step.

34. A process as claimed in claim 32 comprising the step of maintaining the pressure during said contacting step in the range of 10 Bar (1MPa) to 50 Bar (5MPa) or in the range of 15 Bar (1.5MPa) to 40 Bar (4MPa).

35. A process as claimed in claim 32 comprising the step of maintaining the temperature during said contacting step in the range of 0°C to 110°C or 50°C to 110°.

36. A process as claimed in claim 33 wherein said forming step comprises the step of providing an amount of said metal compound to said ligand in the molar ratio in the range of from 1:1 to 1:2.5.

37. A method of preparing the catalyst system of any one of claims 1 to 31, comprising the step mixing liquids of said metal compound and said ligands under conditions to form a metal-ligand coordination complex thereof.

38. A kit for preparing a catalyst system as claimed in any one of claims 1 to 31, the kit comprising said metal compounds, said ligands and instructions for mixing said metal compounds and said ligands.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPIDS, JAPIO, CAPLUS: & keywords: olefin, octene, ethylene, oligomeri, tetrameri, catalyst, ligand, chromium, nickel, & similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ELOWE et al. "Nitrogen-linked diphosphine ligands with ethers attached to nitrogen for chromium-catalyzed ethylene tri- and tetramerizations", Organometallics, 2006, vol 25, no 22, pages 5255-5260 See the whole document	1-11,16-26,28-33, 35-38
X	WO 2005/123884 A2 (SASOL TECHNOLOGY PTY LTD) 29 December 2005 See the whole document	1-11,15-26,28-38
X	WO 2007/057458 A1 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ BV) 24 May 2007 See the whole document	1-11,15-26,28-33,35-38

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 October 2007	09 OCT 2007
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **ROBYN KNOCK** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : (02) 6283 3149

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2007/000197

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/123633 A1 (SASOL TECHNOLOGY PTY LTD) 29 December 2005 See the whole document	1-11,15-26,28-33,35-38
X	US 2007/0043181 A1 (KNUDSEN et al) 22 February 2007 See the whole document	1-11,14-26,28,29,31-33,37,38

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/SG2007/000197

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	2005123884	CA	2570056	CN	1993180	EP	1765495
WO	2007057458	US	2007185357				
WO	2005123633	CA	2570054	EP	1756024		
US	2007043181	WO	2007024504				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX