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(54) **Title**: OLIGOMERIZATION OF OLEFINS

(57) **Abstract**: Transition metal compound comprising at least one ligand system L with a nitrogen-phosphorus-nitrogen-structural element wherein phosphorus is pentavalent, catalyst system for the oligomerization of olefins comprising such a transition metal complex and process for oligomerization of olefinic monomers carried out in the presence of the catalyst system.

Oligomerization of Olefins

Field of the Invention

The present invention relates to oligomerization of olefins, including oligomerization process, catalyst system for oligomerization and a transition metal complex which can be used in a catalyst system for oligomerization of olefins.

Background of the invention

Oligomers, and especially α-olefins, are used in polymerization processes often as monomers or comonomers to prepare polyolefins having interesting properties. Unfortunately, very few efficient processes are known which selectively produce a specifically desired oligomer.

Conventional ethylene oligomerization technologies produce a range of olefins following either a Schulz-Flory or Poisson product distribution. By definition, these mathematical distributions limit the mass percentage of the dimer, trimer or tetramer that can be formed and make a distribution of products.

In US patents 3,676,523 and 3,635,937, the so-called SHOP process is disclosed which today is used for the synthesis of a statistical mixture of α-olefins, which can be fractioned for being marketed for a range of commercial applications. In these patents catalyst systems comprising Ni complexes with chelating ligands, e.g. 2-diphenyl phosphino benzoic acid, are reported.

But there also have been developed processes for producing selectively trimers as e.g. disclosed in US 2002/0035029 A1, wherein pyrrazolyl chromium complexes are disclosed as precatalysts. Further examples are WO 2002/04119 A1 disclosing a catalyst for trimerization of ethylene which comprises a source of chromium, molybdenum and tungsten and a ligand containing at least one phosphorous, arsenic or antimony atom bound to at least one heterohydrocarbyl group. Further examples are disclosed in US 5,811,618 A1, WO 03/004158 A2, WO 03/053890 A1, WO 04/056479 A1.

In WO 2004/056478 A1 and WO 2004/056479 A1 a process for preparing 1-octene as the major component is disclosed, wherein a complex comprises a ligand having a phosphorus-nitrogen-phosphorus basic structure. A discussion of the catalytic process is described in J. Am. Chem. Soc., 2004, 126 (45), 14712-14713 and J. Am. Chem. Soc., 2005, 127 (30),

10723-10730. Catalysts having similar basic structures are also disclosed in Organometallics 2006, 25 (3), 715-718 and Organometallics 2007, 26 (10), 2782-2787. The cocatalyst influence on one of these complexes has been examined in Organometallics 2007, 26(10), 2561-2569.

Recently, in WO 2009/006979 A1 a process for di-, tri- and tetramerization of ethylene has been published. In this process a catalyst is used which comprises chromium complexes with a ligand having a phosphorus-nitrogen-phosphorus structure. In the examples good yields of di- and trimers are disclosed.

In Angew. Chem. Int. Ed. 2008, 47, 5816-5819 and in Organometallics 2008, 27 5708-5711 an anionic nitrogen-phosphorus-nitrogen ligand (*t*-Bu)NPN(*t*-Bu) is described, wherein phosphorus is trivalent. When activation was carried out with $AliBu_3$ the complex $[(t\text{-Bu})NPN(t\text{-Bu})]_2Cr$ leads to a selective trimerization system producing 99.9 % 1-hexene in view of total amount of oligomers. However, the catalyst system nonetheless leads to production of polyethylene.

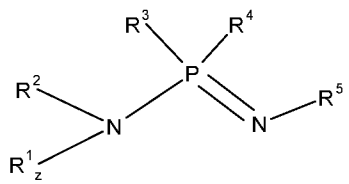
Summary of the Invention

A general problem of nearly all oligomerization processes is the production of polymer additionally to the oligomers leading to reactor fouling during industrial set-ups for oligomerization systems.

Thus, it is an object of the present invention to produce oligomers and avoid poymer production as a side reaction.

We have found that this object is achieved by a transition metal complex comprising at least one ligand system L with a nitrogen-phosphorus-nitrogen-structural element wherein phosphorus is pentavalent, a catalytic system comprising the transition metal compound, and a process for oligomerization carried out in the presence of this catalyst system.

Preferably the ligand system L is represented by the following formula (A)



(A)

wherein

R^1, R^2, R^3, R^4, and R^5 are identical or different and are each, independently of one another, hydrogen, halogen, C_1-C_{50}-alkyl, C_2-C_{50}-alkenyl, C_6-C_{50}-aryl, alkylaryl or arylalkyl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, C_1-C_{50}–alkoxy, or C_6-C_{50}–aryloxy, wherein the organic radicals R^1, R^2, R^3, R^4, and R^5 may also be substituted by halogens, C_1-C_{50}–alkoxy, C_6-C_{50}–aryloxy or SiR^6_3 and the radicals R^1, R^2, R^3, R^4, and R^5 and their substituents may also contain heteroatoms selected from N, P, O or S,

R^6 are each, independently of one another, hydrogen, C_1-C_{50}-alkyl, C_2-C_{50}-alkenyl, C_6-C_{50}-aryl, arylalkyl or alkylaryl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, C_1-C_{50}–alkoxy or C_6-C_{50}–aryloxy and two radicals R^6 may also be joined to form a five- or six-membered ring, and

z is 0 or 1.

R^1, R^2, R^3, R^4, and R^5 are identical or different and are each, independently of one another, hydrogen, halogen, C_1-C_{50}-alkyl, preferably C_1-C_{10}-alkyl, C_2-C_{50}-alkenyl, preferably C_2-C_{10}-alkenyl, C_6-C_{50}-aryl, preferably C_5-C_{14}-aryl, C_1-C_{50}–alkoxy, preferably C_1-C_{10}–alkoxy, or C_6-C_{50}–aryloxy, preferably C_6-C_{14}–aryloxy or alkylaryl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, preferably from 1 to 10 carbon atoms in the alkyl part and from 6 to 14 carbon atoms in the aryl part. Each alkyl moiety and each alkenyl moiety may be branched or unbranched. The organic radicals R^1, R^2, R^3, R^4, and R^5 may also be substituted by halogens, .i.e. by fluorine, bromine, chlorine, or iodine, C_1-C_{50}–alkoxy, preferably C_1-C_{10}–alkoxy, C_6-C_{50}–aryloxy preferably C_6-C_{14}–aryloxy or SiR^6_3 and R^1, R^2, R^3, R^4, and R^5 and their substituents may also contain heteroatoms selected from N, P, O or S.

Preferably R^2 and R^5 are identical or different and are each, independently of one another C_1-C_{50}-alkyl, preferably C_1-C_{10}-alkyl, C_2-C_{50}-alkenyl, preferably C_2-C_{10}-alkenyl, C_6-C_{50}-aryl, preferably C_6-C_{14}-aryl, or alkylaryl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, preferably from 1 to 10 carbon atoms in the alkyl part and from 6 to 14 carbon atoms in the aryl part. Each alkyl moiety and each alkenyl moiety may be branched or unbranched. The organic radicals R^2 and R^5 may also be substituted by halogens, .i.e. by fluorine, bromine, chlorine, or iodine, C_1-C_{50}–alkoxy, preferably C_1-C_{10}–alkoxy, C_6-C_{50}–aryloxy preferably C_6-C_{14}–aryloxy or SiR^6_3 and R^2 and R^5 and their substituents may also contain heteroatoms selected from N, P, O or S. Especially preferred are R^2 and R^5 being tert-buty, isopropyl or phenyl.

z may be 0 or 1. If z is 0 the ligand is anionic, while in case z is 1 the ligand is neutral. In case z is 1, R^1 is preferably hydrogen. Preferably z is 0.

Preferably R^3 and R^4 are identical or different and are each, independently of one another, C_6-C_{50}-aryl, preferably C_6-C_{14}-aryl, or alkylaryl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, preferably from 1 to 10 carbon atoms in the alkyl part and from 6 to 14 carbon atoms in the aryl part. Each alkyl moiety and each alkenyl moiety may be branched or unbranched. The organic radicals R^3 and R^4 may also be substituted by halogens, .i.e. by fluorine, bromine, chlorine, or iodine, C_1-C_{50}–alkoxy, preferably C_1-C_{10}–alkoxy, C_6-C_{50}–aryloxy preferably C_6-C_{14}–aryloxy, or SiR^6_3, and R^3 and R^4 and their substituents may also contain heteroatoms selected from N, P, O or S. Especially preferred are R^3 and R^4 being phenyl.

The radicals R^6 in organosilicon substituents SiR^6_3 can be the same or different are each, independently of one another, hydrogen, C_1-C_{50}-alkyl, preferably C_1-C_{10}-alkyl, C_2-C_{50}-alkenyl, preferably C_2-C_{10}-alkenyl, C_6-C_{50}-aryl, C_6-C_{14}-aryl, arylalkyl or alkylaryl having from 1 to 50, preferably 1 to 10 carbon atoms in the alkyl part and 6 to 50, preferably 6 to 14 carbon atoms in the aryl part, C_1-C_{50}–alkoxy, preferably C_1-C_{10}–alkoxy or C_6-C_{50}–aryloxy, preferably C_6-C_{14}–aryloxy, where two radicals R^6 may also be joined to form a 5- or 6-membered ring. Examples for the radicals R^6 are trimethylsilyl, triethylsilyl, butyldimethylsilyl, tributylsilyl, tritert-butylsilyl, triallylsilyl, triphenylsilyl or dimethylphenylsilyl. Preferred radicals R^6 are hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, methoxy, ethoxy, propoxy, butoxy, benzyl, phenyl, ortho-dialkyl- or dichloro-substituted phenyls, trialkyl- or trichloro-substituted phenyls, naphthyl, biphenyl and anthranyl.

In the above formula (A) and below formula (B) as well as throughout the whole specification the terms have the following meanings:

The term "alkyl" as used herein refers to a branched or unbranched saturated hydrocarbon group containing 1 to 50 carbon atoms, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, octyl, decyl, and the like, as well as cycloalkyl groups such as cyclopentyl, cyclohexyl and the like. Generally, alkyl groups herein may contain 1 to 10 carbon atoms.

The term "alkenyl" as used herein refers to a branched or unbranched, cyclic or acyclic hydrocarbon group containing 2 to 50 carbon atoms and at least one double bond, such as

ethenyl, n-propenyl, isopropenyl, n-butenyl, isobutenyl, octenyl, decenyl, and the like. Generally, alkenyl groups herein contain 2 to 10 carbon atoms.

The term "aromatic" is used in its usual sense, including unsaturation that is delocalized across several bonds around a ring. The term "aryl" as used herein refers to a group containing an aromatic ring. Aryl groups herein include groups containing a single aromatic ring or multiple aromatic rings that are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. More specific aryl groups contain one aromatic ring or two or three fused or linked aromatic rings, e.g. phenyl, naphthyl, biphenyl, anthracenyl, or phenanthrenyl. Aryl groups include 6 to 50 atoms other than hydrogen, typically 6 to 14 atoms other than hydrogen. In some embodiments herein, multi-ring moieties are substituents and in such embodiments the multi-ring moiety can be attached at an appropriate atom. For example, "naphthyl" can be 1-naphthyl or 2-naphthyl; "anthracenyl" can be 1-anthracenyl, 2-anthracenyl or 9-anthracenyl; and "phenanthrenyl" can be 1-phenanthrenyl, 2-phenanthrenyl, 3-phenanthrenyl, 4-phenanthrenyl, or 9-phenanthrenyl.

The term "alkoxy" as used herein intends an alkyl group bound through a single, terminal ether linkage; that is, an "alkoxy" group may be represented as -O-alkyl where alkyl is as defined above. The term "aryloxy" is used in a similar fashion, and may be represented as -O-aryl, with aryl as defined below. The term "hydroxyl" refers to -OH.

The terms "halo" and "halogen" are used in the conventional sense to refer to a chloro, bromo, fluoro or iodo radical.

The term “contain heteratoms selected from N, P, O or S” refer to a molecule or molecular fragment in which one or more carbon atoms is replaced with a heteroatom. Thus, for example, in view of "alkyl" it refers to an alkyl substituent that is heteroatom-containing. In respect of “cycles” containing a heteroatom one or more carbon atoms in a ring is replaced with a heteroatom, that is, an atom other than carbon, i.e. nitrogen, oxygen, sulfur, phosphorus. The term "aryl containing heteroatoms" refers to an aryl radical that includes one or more heteroatoms in the aromatic ring. Specific heteroaryl groups include groups containing heteroaromatic rings such as thiophene, pyridine, pyrazine, isoxazole, pyrrazole, pyrrole, furan, thiazole, oxazole, imidazole, isothiazole, oxadiazole, triazole, and benzo-fused analogues of these rings, such as indole, carbazole, benzofuran, benzothiophene and the like.

By "pentavalent" as in "phosphorus is pentavalent" is meant that phosphorus is bound at five points to molecules or moieties, such as nitrogen, alkyl etc with the five bonding points being covalent bonds. In this sense a double bond is regarded as two bonding points.

Special preference is given to an transition metal compound of formula (B),

$$[(M^1L_oX_m)_n]^{p-} \qquad (B)$$

wherein

M^1 is an element of group 3 to 10 of the Periodic Table of the Elements,

L is a ligand system with a nitrogen-phosphorus-nitrogen-structural element wherein phosphorus is pentavalent,

o is 1 or 2,

X are the same or different and are each halogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{22}-aryl, alkylaryl or arylalkyl group having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 22 carbon atoms in the aryl radical, -OR^7 or –NR^7R^8, wherein two radicals X may also be joined to one another, and wherein R^7 and R^8 are each independently C_1-C_{10}-alkyl, C_6-C_{14}-aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 22, carbon atoms in the aryl radical,

m is a natural number from 0 to 5,

n is 1, 2, or 3;

p is 0 or 1.

M^1 is a transition metal of group 3 to 10 of the periodic table of the elements or the lanthanides, M^1 is preferably an element of group 3, 4, 5 or 6 of the Periodic Table of the Elements or the lanthanides, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum or tungsten, preferably chromium, molybdenum or tungsten, particularly preferably chromium.

The radicals X are identical or different, preferably identical, with two radicals X also being able to be joined to one another. X is preferably halogen, for example fluorine, chlorine, bromine, iodine, most preferably chlorine, C_1-C_{20}-, preferably C_1-C_4-alkyl, in particular methyl, C_2-C_{20}-, preferably C_2-C_4-alkenyl, C_5-C_{22}-, preferably C_5-C_{10}-aryl, an alkylaryl or arylalkyl group having from 1 to 10, preferably from 1 to 4, carbon atoms in the alkyl radical and from 5 to 22, preferably from 5 to 10, carbon atoms in the aryl radical, -OR^7 or –NR^7R^8,

preferably $-OR^7$, where two radicals X, preferably two radicals $-OR^7$, may also be joined to one another. It is also possible for two radicals X to form a substituted or unsubstituted diene ligand, in particular a 1,3-diene ligand. The radicals R^7 and R^8 are each C_1-C_{10}-, preferably C_1-C_4-alkyl, C_5-C_{15}-, preferably C_5-C_{10}-aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl each having from 1 to 10, preferably from 1 to 4, carbon atoms in the alkyl radical and from 5 to 22, preferably from 5 to 10, carbon atoms in the aryl radical. Most preferably X is chlorine, methyl, or 1,3-butadiene.

The variable m is a number from 0 to 5. The number m of the ligands X depends on the oxidation state of the transition metal M^1. The oxidation state of the transition metals M^1 in catalytically active complexes is usually known to those skilled in the art. E.g. chromium, molybdenum and tungsten are very probably present in the oxidation state +3 and titanium, zirconium, hafnium and vanadium in the oxidation state 4, with titanium and vanadium also being able to be present in the oxidation state 3. However, it is also possible to use complexes whose oxidation state does not correspond to that of the active catalyst. Such complexes can then be appropriately reduced or oxidized by means of suitable activators. M^1 is preferably chromium in the oxidation states 2, 3 and 4.

The complex may have more than one metal center, i.e. a di- or trimetallic cluster may be formed. In case R^1 is present the complex generally is neutral, i.e. p is 0. In case R^1 is not present, the ligand has a negative charge. The complex may comprise a countercation, which may be retained as a part of the complex or cluster. The countercation may be partially solvated. However, it is also possible that a countercation unconnected to the cluster is present.

Thus, in case the complex of formula (B) is anionic a further possible description of an embodiment of the complex is as follows:

$$(M^1L_oX_m)_nM^2Y_q \qquad \text{(BII)}$$

wherein

M^1 is an element of group 3 to 10 of the Periodic Table of the Elements,

L is a ligand system with a nitrogen-phosphorus-nitrogen-structural element wherein phosphorus is pentavalent,

o is 1 or 2,

X are the same or different and are each halogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{22}-

aryl, alkylaryl or arylalkyl group having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 22 carbon atoms in the aryl radical, -OR^7 or –NR^7R^8, wherein two radicals X may also be joined to one another, and wherein R^7 and R^8 are each independently C_1-C_{10}-alkyl, C_6-C_{14}-aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 22, carbon atoms in the aryl radical,

m is a natural number from 0 to 5,

n is 1, 2, or 3;

M^2 is an element of group 1 of the Periodic Table of the Elements,

Y is a neutral ligand, and

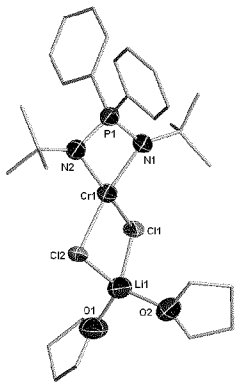
q is a number from 0 to 3.

The complex may further comprise neutral ligands which solvate the countercation and are represented by Y in formula (BII). Examples for preferred ligands Y are selected from the groups of nitriles, isocyanides, alcohols, ethers, amines, acid amides, lactames and sulfones; e.g. acetonitrile (CH_3CN), diethylether (DEE), dimethylether (DME), water (H_2O), or acetone. Also cyclic ligands can be used, e.g. tetrahydrofurane (THF), dioxane, pyridine, imidazole or thiophene. Mixed systems with different types of ligands are also possible. Especially preferred is THF.

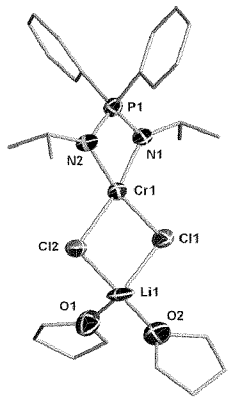
In formula (BII) M^2 is an element of group 1 of the Periodic Table of the Elements, i.e. Li, Na, K, Rb, Cs, wherein M^2 preferably is Li.

Examples for especially preferred compounds are

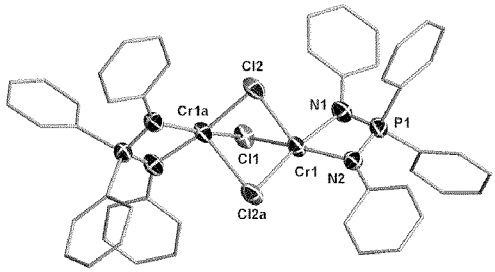
[(^{t}Bu)NP(Ph)$_2$N(^{t}Bu)]CrCl$_2$Li·2THF **(1)**



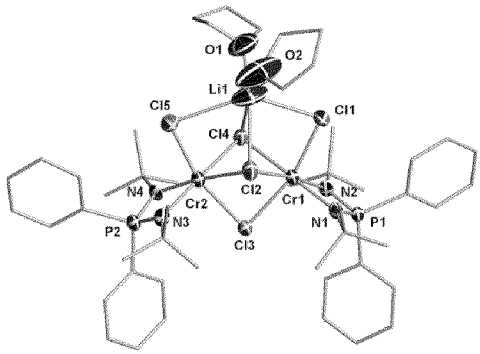
[(^{i}Pr)NP(Ph)$_2$N(^{i}Pr)]CrCl$_2$Li·2THF **(2)**



{[(Ph)N-P(Ph)$_2$-N(Ph)]Cr}$_2$(μ-Cl)$_2$Li **(3)**



{[(^{t}Bu)N-P(Ph)$_2$-N(^{t}Bu)]CrCl$_2$}$_2$LiCl·2THF **(4)**,



And {[(^{t}Bu)N-P(Ph)$_2$-N(^{t}Bu)]CrC}$_3$[η^2,η^4,η^4-CH$_2$CHCHCH$_2$] **(5)**.

The R-NP(Ph)$_2$N(H)-R [R = t-Bu, i-Pr, Ph] ligands, bearing pentavalent phosphorus, can be prepared according to literature procedure (e.g. as described by Henri-Jean Cristau, Jouanin, Isabelle, and Taillefer, Marc in Journal of Organometallic Chem. 584 (1999), 68-72 and by Cristau, Henri-Jean and Garcia, Chantal in Synthesis (Stuttgart) 1990, 315-317) followed by a double deprotonated with n-butyl lithium. The resulting dianion was reacted with a divalent chromium salt affording the corresponding complexes. The structures of complexes [(^{t}Bu)NP(Ph)$_2$N(^{t}Bu)]CrCl$_2$Li **(1)**, [(^{i}Pr)N-P(Ph)$_2$-N(^{i}Pr)]CrCl$_2$Li **(2)**, and {[(Ph)N-P(Ph)$_2$-N(Ph)]Cr}$_2$-(μ-Cl)$_2$Li **(3)** were authenticated by crystal structures and showed closely related connectivities. All the three complexes contained a divalent chromium atom. In complexes **1** and **2** the metal is in the standard square-planar coordination geometry with the ligand chelating the chromium atom in a bidentate bonding mode and two chlorine atoms bridging a lithium countercation. Complex **3** is instead dimeric with three chlorine atoms bridging the two transition metals. The chromium metal displays a square pyramidal coordination geometry.

The present invention further refers to a catalyst system for the oligomerization of olefins, which comprises

- at least one transition metal compound comprising a ligand system L with a nitrogen-phosphorus-nitrogen-structural element wherein phosphorus is pentavalent and
- at least one cocatalyst which is able to convert the transition metal compound into a species which is oligomerization-active toward at least one α-olefin.

It will be appreciated that the above catalyst system may either be formed prior to use in an oligomerization reaction, or it may be formed in situ by adding the individual components thereof to the reaction mixture.

The oligomerization catalyst system may also be formed in-situ by mixing

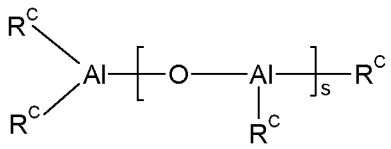
- a transition metal precursor of a transition metal of group 3 to 10 of the Periodic Table of the Elements,
- a ligand L with a nitrogen-phosphorus-nitrogen-structural element wherein phosphorus is pentavalent, and
- further component or components.

In the case of the transition metal precursor being a chromium precursor, examples for a metal precursor of the present invention are chromium salts in oxidation state +II or +III , preferably THF adducts of chromium(II) and chromium(III) salts. Examples for these chromium precursors are $(THF)_3CrMeCl_2$, $(THF)_3CrCl_3$, $(Mes)_3Cr(THF)$, $[\{TFA\}_2Cr(OEt_2)]_2$, $(THF)_3CrPh_3$, $Cr(NMe_3)_2Cl_3$, $CrCl_3$, $Cr(acac)_3$, Cr(2-ethylhexanoate)$_3$, Cr(neopentyl)$_3$(THF)$_3$, $Cr(CH_2\text{-}C_6H_4\text{-}o\text{-}NMe_2)_3$, $Cr(TFA)_3$, $Cr(CH(SiMe_3)_2)_3$, $Cr(Mes)_2(THF)_3$, $Cr(Mes)_2(THF)$, $Cr(Mes)Cl(THF)_2$, $Cr(Mes)Cl(THF)_{0.5}$, Cr(p-tolyl)Cl_2(THF)$_3$, Cr(diisopropylamide)$_3$, Cr(piccolinate)$_3$, $CrCl_2(THF)_2$, $Cr(NO_3)_3$, $CrCl_2$, Cr(hexafluoroacetylacetonato)$_3$, $(THF)_3Cr(\eta^2$-2,2'-Biphenyl)Br as well as mixtures thereof. Especially preferred chromium precursors are $(THF)_3CrCl_3$, $CrCl_3$, $Cr(acac)_3$, $CrCl_2(THF)_2$. The abbreviation used are as follows: THF= tetrahydrofurane; Me= methyl; Mes=mesityl=2,4,6-trimethylphenyl; TFA=trifluoroacetate; Et= ethyl; Ph= phenyl; acac=acetylacetonato.

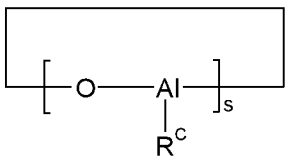
As activating agent a cocatalysts is also present in the invention. Suitable activators for the types of catalyst mentioned are generally known. As cocatalysts Lewis acids or Brönstedt may be used. Examples for Lewis acids are boranes or alanes, such as alkyl aluminum,

aluminum halogenide, aluminum alcoholate, boron organic compounds, boron halogenides, boronic acid esters or boron or aluminum compounds, comprising halogen as well as alkyl, aryl or alcoholate, as well as mixtures thereof or the triphenyl methyl cation. Further cocatalysts to the above are lithium alkyles or magnesium organic compounds, such as Grignard reagents or partly hydrolyzed boron organic compounds.

Preferred cocatalysts are aluminoxanes. It is possible to use, for example, the compounds described in WO 00/31090 1. Particularly suitable aluminoxanes are open-chain or cyclic aluminoxane compounds of the general formulae (CI) or (CII)



(CI)



(CII)

where

R^C is each, independently of one another, a C_1-C_6-alkyl group, preferably a ethyl, butyl or isobutyl group, and

s is an integer from 1 to 40, preferably from 4 to 25.

A particularly suitable aluminoxane compound is methylaluminoxane.

Further preferred cocatalysts are Grignard reagents, especially preferred are unsaturated Gringard reagents such as vinyl magnesium chloride.

Additional to transition metal compound and cocatalyst the catalyst system may also comprise further components. Suitable components are, for example, also strong, uncharged Lewis acids, ionic compounds having Lewis-acid cations or an ionic compounds containing Brönsted acids as cations. Examples are tris(pentafluorophenyl)borane, tetrakis(pentafluorophenyl)borate or salts of N,N-dimethylanilinium.

The catalyst system may further comprise, a metal compound of general formula (D),

$$M^D (R^{D1})_t (R^{D2})_u (R^{D3})_v \qquad (D)$$

where

M^D is lithium, sodium, potassium, beryllium, magnesium, calcium, strontium, barium, boron, aluminum, gallium, indium, thallium, zinc, preferably lithium, sodium, potassium, magnesium, boron, aluminum or zinc and in particular lithium, magnesium, boron or aluminum,

R^{D1} is hydrogen, C_1–C_{10}–alkyl, C_6–C_{15}–aryl, alkylaryl or arylalkyl each having from 1 to 16 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical, preferably C_1–C_{20}–alkyl

R^{D2} and R^{D3} are each hydrogen, halogen, C_1–C_{10}–alkyl, C_6–C_{15}–aryl, alkylaryl, arylalkyl or alkoxy each having from 1 to 20 carbon atoms in the alkyl radical and from 6 to 20 carbon atoms in the aryl radical, or alkoxy with C_1–C_{10}–alkyl or C_6–C_{15}–aryl,

t is an integer from 1 to 3

and

u and v are integers from 0 to 2, with the sum t+u+v corresponding to the valence of M^D.

It is also possible to use mixtures of various metal compounds of the formula (D). Particularly preferred metal compounds of the formula (D) are methyllithium, ethyllithium, n-butyllithium, methylmagnesium chloride, methylmagnesium bromide, ethylmagnesium chloride, ethylmagnesium bromide, butylmagnesium chloride, dimethylmagnesium, diethylmagnesium, dibutylmagnesium, n–butyl–n–octylmagnesium, n–butyl–n–heptyl-magnesium, preferably n–butyl–n-octylmagnesium, tri–n–hexylaluminum, triisobutylaluminum, tri-n-butylaluminum, triethylaluminum, dimethylaluminum chloride, dimethylaluminum fluoride, methylaluminum dichloride, methylaluminum sesquichloride, diethylaluminum chloride and trimethylaluminum and mixtures thereof. The partial hydrolysis products of aluminum alkyls with alcohols can also be used.

If a metal compounds of general formula (D) are used, it is preferably comprised in the catalyst system in such an amount that the molar ratio of M^D from formula (D) to the sum of all metals of catalyst components of formula (B), of cocatalyst and of components of formula (D) is from 3000:1 to 0.1:1, preferably from 800:1 to 0.2:1 and particularly preferably from 100:1 to 1:1.

For carrying out the process of the present invention in gas-phase or in suspension it is often advantageous to use a catalyst system comprising oligomerization catalyst components of formula (B) and the cocatalyst, (e.g. an aluminoxane) in solid form. Accordingly, in an embodiment of the present invention catalyst at least one of transition metal compound and cocatalyst are applied to a solid support.

Transition metal complex, and the cocatalyst can be immobilized independently of one another, e.g. in succession or simultaneously. Thus, the support component can firstly be brought into contact with the cocatalyst or cocatalysts or the support component can firstly be brought into contact with the transition metal complex. Preactivation of the transition metal complex by means of one or more cocatalysts prior to mixing with the support is also possible. The immobilization is generally carried out in an inert solvent which can be removed by filtration or evaporation after the immobilization. After the individual process steps, the solid can be washed with suitably inert solvents such as aliphatic or aromatic hydrocarbons and dried. However, the use of the still moist, supported catalyst is also possible.

As support component, preference is given to using finely divided supports which can be any organic or inorganic solid. In particular, the support component can be a porous support such as talc, a sheet silicate such as montmorillonite, mica or an inorganic oxide or a finely divided polymer powder (e.g. polyolefin or a polymer having polar functional groups). The inorganic support can be subjected to a thermal treatment, e.g. to remove adsorbed water. Such a drying treatment is generally carried out at temperatures in the range from 50 to 1000ºC, preferably from 100 to 600ºC, with drying at from 100 to 200ºC preferably being carried out under reduced pressure and/or under a blanket of inert gas (e.g. nitrogen), or the inorganic support can be calcined at temperatures of from 200 to 1000ºC to produce the desired structure of the solid and/or set the desired OH concentration on the surface. The support can also be treated chemically using customary dessicants such as metal alkyls preferably aluminum alkyls, chlorosilanes or $SiCl_4$, or else methylaluminoxane. Appropriate treatment methods are described, for example, in WO 00/31090 B1.

The invention further refers to a process for olefin oligomerization, especially trimerization, carried out in the presence of a catalyst system as defined above.

In this specification the term "trimerization" means catalytic reaction of a single olefinic monomer or a mixture of olefinic monomers to give products derived from the reaction(s) of three olefinic monomers, as distinct from polymerization. "Trimerization" includes the case where all the monomer units in the trimerization product are identical, where the trimerization product is made from two different olefins (i.e. two equivalents of one monomer react with two equivalents of a second monomer), and also where three different monomer units react to yield the product. A reaction involving more than one monomer is often referred to as co-

trimerization. The term "trimerization" generally refers to the reaction of three, and preferably three identical, olefinic monomer units or α-olefins to yield a linear and/or branched olefin. Under the term α-olefinic monomer units or α-olefins is meant all hydrocarbon compounds with terminal double bonds. This definition includes ethylene, propylene, 1-butene, isobutylene, 1-pentene, 1-hexene, 1-octene and the like. Trimerization of ethylene is preferred.

In analogy the term “tetramerization” means catalytic reaction of a single olefinic monomer or a mixture of olefinic monomers to give products derived from the reaction(s) of four olefinic monomers.

In the present application the term “oligomerization" means catalytic reaction of a single olefinic monomer or a mixture of olefinic monomers to give products enriched in those constituents derived from the reaction(s) of 2 to 15 olefinic monomers.

The cocatalyst or cocatalysts (also referred to as activating compound(s)) can in each case be used in any amounts based on the complexes of the catalyst composition of the invention. They are preferably used in an excess or in stoichiometric amounts, in each case based on the complex which they activate. The amount of cocatalyst(s) to be used depends on the type of the cocatalyst(s). In general, the molar ratio of transition metal complex to cocatalyst can be from 1:0.1 to 1:10000, preferably from 1:1 to 1:2000.

Suitable olefinic monomers, or combinations thereof for use in the trimerization process of the present invention are hydrocarbon olefins, for example, ethylene, C_3-C_{20} α-olefins, internal olefins, vinylidene olefins, cyclic olefins and dienes, propylene, 1-butene, 1-pentene, 1-hexene, 4-methylpentene-1, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, styrene, 2-butene, 2-ethyl-1-hexene, cyclohexene, norbomene, butadiene and 1,5-bexadiene. Olefins with a polar functionality, such as methyl (meth)acrylate, vinyl acetate, α,ω-undecenol and the like, may also be used. The preferred monomer is ethylene. Mixtures of these monomers may also be used, for example a 1-butene unit and two ethylene units may be co-trimerised to form C_8 olefins, or 1-hexene and ethylene co-trimerised to C_{10} olefins, or 1-dodecene and ethylene co-tetramerised to C_{16} olefins. Combinations of these co-trimerization reactions may be performed simultaneously, especially when one or more of the monomers are produced in-situ (e.g. a mixture of ethylene and butene can be used to form mixtures containing predominantly hexenes,

octenes, and decenes.) Techniques for varying the distribution of products from these reactions include controlling process conditions (e.g. concentration, reaction temperature, pressure, residence time) and properly selecting the design of the process and are well known to those skilled in the art.

Olefinic monomers or mixtures of olefinic monomers for oligomerization may be substantially pure or may contain olefinic impurities. One embodiment of the process of the invention comprises the oligomerization, preferably trimerization of olefin-containing waste streams from other chemical processes or other stages of the same process.

When operating under solution or slurry phase conditions, any diluent or solvent that is an olefin, a mixture of olefins, or is substantially inert under oligomerization conditions may be employed. Mixtures of inert diluents, with or without one or more olefins, also could be employed. The preferred diluents or solvents are aliphatic and aromatic hydrocarbons and halogenated hydrocarbons such as, for example, isobutane, pentane, toluene, xylene, ethylbenzene, cumene, mesitylene, heptane, cyclohexane, methylcyclohexane, 1-hexene, 1-octene, chlorobenzene, dichlorobenzene, and the like, and mixtures such as isopar.

The oligomerization can be carried out in a known manner in bulk, in suspension, in the gas phase or in a supercritical medium in the customary reactors used for the oligomerization or polymerization of olefins. It can be carried out batchwise or continuously in one or more stages. High-pressure oligomerization processes in tube reactors or autoclaves, solution processes, suspension processes, stirred gas-phase processes or gas-phase fluidized-bed processes are all possible.

The oligomerizations are usually carried out at temperatures in the range from -60 to 350°C and under pressures of from 0.5 to 4000 bar. The mean residence times are usually from 0.5 to 5 hours, preferably from 0.5 to 3 hours. The advantageous pressure and temperature ranges for carrying out the oligomerizations usually depend on the oligomerization method. In the case of high-pressure oligomerization processes, which are usually carried out at pressures of from 1000 to 4000 bar, in particular from 2000 to 3500 bar, high oligomerization temperatures are generally also set. Advantageous temperature ranges for these high-pressure oligomerization processes are from 200 to 320°C, in particular from 220 to 290°C. In the case of low-pressure oligomerization processes, a temperature which is at least a few degrees below the softening temperature of the oligomer is generally set. In particular, temperatures of from 50 to 180°C, preferably from 70 to 120°C, are set in these

oligomerization processes. The oligomerization temperatures are generally in the range from –20 to 115°C, and the pressure is generally in the range from 1 to 100 bar. The solids content of the suspension is generally in the range from 10 to 80%. The oligomerization can be carried out batchwise, e.g. in stirring autoclaves, or continuously, e.g. in tube reactors, preferably in loop reactors. Particular preference is given to employing the Phillips PF process as described in US-A 3 242 150 and US-A 3 248 179. The gas-phase oligomerization is generally carried out in the range from 30 to 125°C.

There exist a number of options for the oligomerization reactor including batch, semi-batch, and continuous operation. The oligomerization and co-oligomerization reactions of the present invention can be performed under a range of process conditions that are readily apparent to those skilled in the art: as a homogeneous liquid phase reaction in the presence or absence of an inert hydrocarbon diluent such as toluene or heptanes; as a two-phase liquid/liquid reaction; as a slurry process where the catalyst is in a form that displays little or no solubility; as a bulk process in which essentially neat reactant and/or product olefins serve as the dominant medium; as a gas-phase process in which at least a portion of the reactant or product olefin(s) are transported to or from a supported form of the catalyst via the gaseous state. The oligomerization reactions may be performed in the known types of gas-phase reactors, such as circulating bed, vertically or horizontally stirred-bed, fixed-bed, or fluidized-bed reactors, liquid-phase reactors, such as plug-flow, continuously stirred tank, or loop reactors, or combinations thereof. A wide range of methods for effecting product, reactant, and catalyst separation and/or purification are known to those skilled in the art and may be employed: distillation, filtration, liquid-liquid separation, slurry settling, extraction, etc. It is within the scope of this invention that an oligomerization product, preferably a trimerization product might also serve as a reactant (e.g. 1-octene, produced via the trimerization of ethylene, might be converted to tetradecene products via a subsequent co-trimerization reaction with ethylene.

An example of an "in situ" process is the production of branched polyethylene. which is prepared by the oligomerization catalyst added in any order such that the active catalytic species is/are at some point present in a reactor.

In the slurry phase process and the gas phase process, the catalyst is generally supported and metered and transferred into the oligomerization zone in the form of a particulate solid either as a dry powder (e.g. with an inert gas, ethylene or an olefin) or as a slurry. In

addition, an optional cocatalyst can be fed to the oligomerization zone, for example as a solution, separately from or together with the solid catalyst.

Methods for operating gas phase oligomerization processes are well known in the art. Such methods generally involve agitating (e.g. by stirring, vibrating or fluidizing) a bed of catalyst, or a bed of the target polymer (i.e. polymer having the same or similar physical properties to that which it is desired to make in the polymerization process) containing a catalyst, and feeding thereto a stream of monomer (under conditions such that at least part of the monomer oligomerizes in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (e.g. recycled gaseous monomer) and/or volatile liquid (e.g. a volatile inert hydrocarbon, or gaseous monomer which has been condensed to form a liquid). The polymer produced in, and isolated from, gas phase processes forms directly a solid in the oligomerization zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerization zone of a gas phase polymerization process the quantity of liquid in the oligomerization zone is small in relation to the quantity of polymer present. This is in contrast to "solution phase" processes wherein the oligomer is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that monomer is continuously recycled to an agitated oligomerization zone containing oligomerization catalyst, make-up monomer being provided to replace oligomerized monomer, and continuously or intermittently withdrawing produced oligomer from the oligomerization zone at a rate comparable to the rate of formation of the oligomer, fresh catalyst being added to the oligomerization zone to replace the catalyst withdrawn from the oligomerization zone with the produced oligomer.

Methods for operating gas phase fluidized bed processes for making polyethylene, ethylene copolymers, polypropylene and oligomers of ethylene are well known in the art. The process can be operated, for example, in a vertical cylindrical reactor equipped with a perforated distribution plate to support the bed and to distribute the incoming fluidizing gas stream through the bed. The fluidizing gas circulating through the bed serves to remove the heat of oligomerization from the bed and to supply monomer for oligomerization in the bed. Thus the fluidizing gas generally comprises the monomer(s) normally together with some inert gas (e.g. nitrogen or inert hydrocarbons such as methane, ethane, propane, butane, pentane or

hexane) and optionally with hydrogen as molecular weight modifier. The hot fluidizing gas emerging from the top of the bed is led optionally through a velocity reduction zone (this can be a cylindrical portion of the reactor having a wider diameter) and, if desired, a cyclone and or filters to disentrain fine solid particles from the gas stream. The hot gas is then led to a heat exchanger to remove at least part of the heat of oligomerization. Catalysts are preferably fed continuously or at regular intervals to the bed. At start up of the process, the bed comprises flu disable polymer which is preferably similar to the target polymer. Oligomer is produced continuously within the bed by the oligomerization of the monomer(s). Preferably means are provided to discharge oligomer from the bed continuously or at regular intervals to maintain the fluidized bed at the desired height. The process is generally operated at relatively low pressure, for example, at 10 to 50 bars, and at temperatures for example, between 50 and 135°C. The temperature of the bed is maintained below the sintering temperature of the fluidized oligomer to avoid problems of agglomeration.

In the gas phase fluidized bed process for oligomerization of olefins the heat evolved by the exothermic oligomerization reaction is normally removed from the oligomerization zone (i.e. the fluidized bed) by means of the fluidizing gas stream as described above. The hot reactor gas emerging from the top of the bed is led through one or more heat exchangers wherein the gas is cooled. The cooled reactor gas, together with any make-up gas, is then recycled to the base of the bed. In the gas phase fluidized bed oligomerization process of the present invention it is desirable to provide additional cooling of the bed (and thereby improve the space time yield of the process) by feeding a volatile liquid to the bed under conditions such that the liquid evaporates in the bed thereby absorbing additional heat of oligomerization from the bed by the "latent heat of evaporation" effect. When the hot recycle gas from the bed enters the heat exchanger, the volatile liquid can condense out. In one embodiment of the present invention the volatile liquid is separated from the recycle gas and reintroduced separately into the bed. Thus, for example, the volatile liquid can be separated and sprayed into the bed. In another embodiment of the present invention the volatile liquid is recycled to the bed with the recycle gas. Thus the volatile liquid can be condensed from the fluidizing gas stream emerging from the reactor and can be recycled to the bed with recycle gas, or can be separated from the recycle gas and then returned to the bed.

The oligomerization catalyst is preferably (but optionally) added before the polymerization catalyst such that the desired primary monomer to comonomer(s) ratio is established prior to introduction of the polymerization catalyst. The desired comonomer composition at start-up may however be achieved through introduction of fresh comonomer feed or through

judicious initiation of the trimerization reaction before or during oligomerization catalyst introduction.

The present invention is illustrated in the following Examples.

EXAMPLES

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. Molecular weight and molecular weight distributions of the resulting polymers were determined by means of gel permeation chromatography on a PL-GPC210 equipped with a RI- and viscosity detector and a 3 × PLgel 10µm MIXED-B column set at 135 °C using 1,2,4-trichlorobenzene as solvent. The molecular weight of the polyethylenes was referenced to polystyrene (Mw = 65500, PDI = 1.02) standards. The liquid product mixtures were analyzed by using a CP 9000 gas chromatograph (GC) equipped with a 30 mL × 0.32 mm id, capillary CP volamine column and a FID detector. All single-point experiments were performed in duplicate. The yield was determined by ^{1}H-NMR spectroscopy (Varian Mercury 400 MHz spectrometer). Infrared spectra were recorded on an ABB Bomem FTIR instrument from Nujol mulls prepared in a Vacuum-Amosphere dry box. Samples for magnetic susceptibility were pre-weighed inside a dry box equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination were obtained with a Bruker diffractometer equipped with a 1K Smart CCD area detector. Diethyl aluminum chloride and triethyl aluminum were purchased from Strem and were used as received. Methylaluminoxane (MAO, 10% in toluene) and vinyl magnesium bromide (1.6 M in tetrahydrofuran) were purchased from Aldrich.

Example 1:

Preparation of [η^3-(^{t}Bu)NP(Ph)$_2$N(^{t}Bu)]CrCl$_2$Li·2THF

(^{t}Bu)NH-PBr(Ph)$_2$-NH(^{t}Bu) was prepared according to the procedure described by Henri-Jean Cristau, Jouanin, Isabelle, and Taillefer, Marc in Journal of Organometallic Chem. 584 (1999), 68-72 and by Cristau, Henri-Jean and Garcia, Chantal in Synthesis (Stuttgart) 1990, 315-317.

A solution of (^{t}Bu)NH-PBr(Ph)$_2$-NH(^{t}Bu) (0.409 g, 1.0 mmol) in THF (10 mL) was treated with n-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25ºC. The mixture was stirred at room

temperature for 24 h affording a clear yellow solution. The resulting solution was added to a suspension of $CrCl_2(THF)_2$ (0.268 g, 1.0 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature overnight giving a green solution. The solvent was removed *in vacuo* and toluene (10 mL) was added. The solution was centrifuged and the resulting solution was reduced to 4 mL and stored at -35 °C in the freezer for 2 days. The resulting blue crystals were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.39 g, 0.56 mmol, 65%). μ_{eff} = 4.89 μ_B. El. Anal. Calcd. (found) for $C_{28}H_{44}Cl_2CrLiN_2O_2P$: C 55.91 (55.88), H 7.37 (7.21), N 4.66 (4.64).

Example 2

Preparation of $[\eta^3(^iPr)N\text{-}P(Ph)_2\text{-}N(^iPr)]CrCl_2Li\cdot 2THF$ (2)

$(^iPr)NH\text{-}PBr(Ph)_2\text{-}NH(^iPr)$ was prepared according to the procedure described by Henri-Jean Cristau, Jouanin, Isabelle, and Taillefer, Marc in Journal of Organometallic Chem. 584 (1999), 68-72 and by Cristau, Henri-Jean and Garcia, Chantal in Synthesis (Stuttgart) 1990, 315-317.

A solution of $(^iPr)NH\text{-}PBr(Ph)_2\text{-}NH(^iPr)$ (0.381 g, 1.0 mmol) in tetrahydrofuran (10 mL) was treated with nBuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25ºC. The mixture was stirred at room temperature for 24 h affording a clear yellow solution. The resulting solution was added to a suspension of $CrCl_2$.2THF (0.268 g, 1.0 mmol) in tetrahydrofuran (5 mL). The reaction mixture was stirred at room temperature overnight giving a green solution. The solvent was removed *in vacuo* and toluene (10 mL) was added. The solution was centrifuged and the resulting solution was reduced to 4 mL and stored at -35 °C in the freezer for 3 days. The resulting blue crystals were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.296 g, 0.49 mmol, 51%). μ_{eff} = 4.91 μ_B. El. Anal. Calcd. (found) for $C_{26}H_{40}Cl_2CrLiN_2O_2P$: C 54.46 (54.39), H 7.03 (7.07), N 4.89 (4.93).

Example 3

Preparation of $\{[\eta^3(Ph)N\text{-}P(Ph)_2\text{-}N(Ph)]Cr\}_2\text{-}\mu\text{-}Cl_2Li\cdot 3DME$ (3)

$\eta^3(Ph)N\text{-}P(Ph)_2\text{-}N(Ph)$ was prepared according to the procedure described by Henri-Jean Cristau, Jouanin, Isabelle, and Taillefer, Marc in Journal of Organometallic Chem. 584 (1999), 68-72 and by Cristau, Henri-Jean and Garcia, Chantal in Synthesis (Stuttgart) 1990, 315-317.

A solution of $(Ph)NH\text{-}PBr(Ph)_2\text{-}NH(Ph)$ (0.449 g, 1.0 mmol) in dimethoxyethane (10 mL) was treated with n-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25ºC. The mixture was stirred

at room temperature for 24 h affording a clear yellow solution. The resulting solution was added to a suspension of $CrCl_2.(THF)_2$ (0.268 g, 1.0 mmol) in dimethoxyethane (5 mL). The reaction mixture was stirred at room temperature overnight giving a green solution. The solvent was removed *in vacuo* and toluene (10 mL) was added. The suspension was centrifuged and the resulting solution was reduced to 4 mL and stored at -35 °C in the freezer for 3 days. The resulting blue crystals were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.352 g, 0.27 mmol, 55%). μ_{eff} = 4.97 μ_B. El. Anal. Calcd. (found) for $C_{60}H_{70}Cl_3Cr_2LiN_4O_6P_2$: C 58.95 (58.90), H 5.77 (5.68), N 5.58 (5.51).

Example 4

Preparation of $\{[\eta^3(^tBu)N\text{-}P(Ph)_2\text{-}N(^tBu)]CrCl_2\}_2LiCl\cdot 2THF$ (4)

(^{t}Bu)NH-PBr(Ph)$_2$-NH(^{t}Bu) was prepared according to the procedure described by Henri-Jean Cristau, Jouanin, Isabelle, and Taillefer, Marc in Journal of Organometallic Chem. 584 (1999), 68-72 and by Cristau, Henri-Jean and Garcia, Chantal in Synthesis (Stuttgart) 1990, 315-317.

A solution of (^{t}Bu)NH-PBr(Ph)$_2$-NH(^{t}Bu) (0.409 g, 1.0 mmol) in tetrahydrofuran (10 mL) was treated with n-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25ºC. The mixture was stirred at room temperature for 24 h affording a clear yellow solution. The resulting solution was added to a suspension of $CrCl_3.(THF)_3$ (0.375 g, 1.0 mmol) in tetrahydrofuran (5 mL). The reaction mixture was stirred at room temperature overnight giving a purple solution. The solvent was removed *in vacuo* and dimethoxyethane (10 mL) was added. The suspension was centrifuged and the resulting solution was reduced to 4 mL and stored at -35 °C in the freezer for 3 days. The resulting purple crystals were filtered and washed with cold hexanes (10 mL) and dried *in vacuo* (0.398 g, 0.36 mmol, 36%). μ_{eff} = 3.82 μ_B. El. Anal. Calcd. (found) for $C_{48}H_{72}Cl_5Cr_2LiN_4O_2P_2$: C 53.02 (53.00), H 6.67 (6.59), N 5.15 (5.09).

Example 5

Preparation of $\{[(t\text{-}Bu)N\text{-}P(Ph)_2\text{-}N(^tBu)]_2Cr\}_3[\eta^2\ \eta^4\ \eta^4\text{-}CH_2CHCHCH_2]$ (5)

(^{t}Bu)NH-PBr(Ph)$_2$-NH(^{t}Bu) was prepared according to the procedure described by Henri-Jean Cristau, Jouanin, Isabelle, and Taillefer, Marc in Journal of Organometallic Chem. 584 (1999), 68-72 and by Cristau, Henri-Jean and Garcia, Chantal in Synthesis (Stuttgart) 1990, 315-317.

A solution of (^{t}Bu)NH-PBr(Ph)$_2$-NH(^{t}Bu) (0.409 g, 1 mmol) in tetrahydrofuran (10 mL) was treated with n-BuLi (0.84 mL, 2.1 mmol, 2.5 M in hexanes) at 25ºC. The mixture was stirred at room temperature for 24 h affording a clear yellow solution. The resulting solution was added to a suspension of $CrCl_2$ (THF)$_2$ (0.268 g, 1.0 mmol) in tetrahydrofuran (5 mL). The reaction mixture was stirred at room temperature overnight giving a green solution. 2.1 mmol of vinylmagnesium chloride was added and stir the reaction for 18h. The solvent was removed *in vacuo* and hexane (10 mL) was added. The suspension was centrifuged and the resulting solution was reduced to 4 mL and stored at -35°C in the freezer for 4 days. The resulting brown crystals were filtered and washed with cold hexane (10 mL) and dried *in vacuo* to give (0.583 g, 0.47 mmol, 49%). μ_{eff} = 2.83 μ_B. El. Anal. Calcd. (found) for $C_{64}H_{88}Cr_3N_6P_3$: C 64.58 (64.54), H 7.45 (7.46), N 7.06 (7.07).

Comparative Example 6

Preparation of [(*t*BuNPNtBu)$_2$]Cr (6)

The ligand *cis*-{*t*-Bu(H)NP[μ-N]tBu}$_2$PN (H)*t*Bu} was prepared according to Organometallics 2005, 24, 5214.

A solution of *cis*-{*t*-Bu(H)NP[μ-N]tBu}$_2$PN (H)*t*Bu} (0.348 g, 1 mmol) in THF (20 mL) was treated with *n*BuLi (0.84 mL, 2.1 mmol 2.5 M in hexane) at 0°C. The mixture was stirred at room temperature for 18 h. The resulting solution was added to a suspension of [$CrCl_2$(thf)$_2$] (0.268 g, 1 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo and the residue redissolved in toluene. The resulting suspension was centrifuged and the solution was stored at -30°C. Brown crystals of [(*t*BuNPNtBu)$_2$]Cr separated over two days were filtered, washed with cold hexane (10 mL), and dried in vacuo to give analytically pure compound (0.294 g, 74%). μ_{eff}=4.98 μ_B; El. Anal. Calcd. (found) for $C_{16}H_{36}CrN_4P_2$: C 48.23 (48.25), H 9.11 (9.17), N 14.06 (13.91).

Example 7

Oligomerization in an 1 l glass autoclave

Polymerizations were carried out in either 200 mL high-pressure Büchi reactors containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in 100 mL of toluene under N_2 and injected into the preheated reactor already charged with cocatalyst and toluene (total volume 100ml). Solutions were heated using a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. Polymerizations were quenched by releasing the pressure and addition of EtOH and HCl. The polymers obtained were isolated by filtration, sonicated with a solution of HCl, rinsed and thoroughly dried prior to measuring

the mass. The reaction mixture of the oligomerization runs were cooled to 0°C prior to releasing the overpressure and quenching with EtOH and HCl. Process conditions and results are listed in Table 1.

Table 1: Ethylene oligomerization results for 1-6 catalyst systems:

Cata-lyst	Co-Catalyst (equiv)	Co-Cat :Cr	Alkenes (mL)	PE (g)	Activity (mL/mmol Cr·h)	C_6 (mol%)	C_8 (mol%)	C_{10}-C_{16} (mol%)
1	MAO	100	80	0	8000	33	25	42
1	MAO	500	208	0	20800	40	31	29
1	MAO	1000	120	0	12000	37	26	37
1[a]	MAO	500	14	0	1,400	51	40	9
1[b]	MAO	500	20	0	2,000	23	21	56
1	PMAO	500	144	0	14,400	37	23	40
1	DMAO[c]	500	240	0	24,000	36	26	38
1	DMAO[c]	1000	348	0	34800	33	30	37
1	DMAO[c]	2000	420	0	42000	42	30	28
2	MAO	500	112	0	11200	31	30	39
3	MAO	500	100	0	10000	35	25	40
4	MAO	500	16	0	1600	25	27	48
5	CH_2CH_2M	2	4	0	400	99.9	0	0
5	-	-	3	0	300	99.9	0	0
5	MAO	500	6	0	600	25	14	71
Comp 6[d)]	MAO	500	1	3.4	400	44	23	33

Conditions: 100 mL of toluene, loading 10 µmol of complex, 35 bar of ethylene, reaction temperature 60 °C, reaction time 60 min;

[a)] Reaction temperature 20°C

[b)]Reaction temperature 100°C

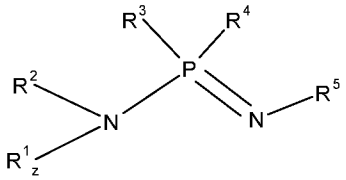
[c)] DMAO= Me_3Al free MAO

[d)] Reaction temperature 50°C,

Claims

1. Transition metal compound comprising at least one ligand system L with a nitrogen-phosphorus-nitrogen-structural element wherein phosphorus is pentavalent.

2. Transition metal complex according to claim 1,
wherein the ligand system L corresponds to formula (A)



(A)

wherein
R^1, R^2, R^3, R^4, and R^5 are identical or different and are each, independently of one another, hydrogen, halogen, C_1-C_{50}-alkyl, C_2-C_{50}-alkenyl, C_6-C_{50}-aryl, alkylaryl or arylalkyl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, C_1-C_{50}–alkoxy, or C_6-C_{50}–aryloxy, where the organic radicals R^1, R^2, R^3, R^4 and R^5 may also be substituted by halogens, C_1-C_{50}–alkoxy, C_6-C_{50}–aryloxy or SiR^6_3 and the radicals R^1, R^2, R^3, R^4, and R^5 and their substituents may also contain heteroatoms selected from N, P, O or S,
R^6 are each, independently of one another, hydrogen, C_1-C_{50}-alkyl, C_2-C_{50}-alkenyl, C_6-C_{50}-aryl, arylalkyl or alkylaryl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, C_1-C_{50}–alkoxy or C_6-C_{50}–aryloxy and two radicals R^6 may also be joined to form a five- or six-membered ring, and
z is 0 or 1.

3. Transition metal compound according to claim 2 or 3, wherein
z is 0, and
R^2 and R^5 are identical or different and are each, independently of one another C_1-C_{50}-alkyl, C_6-C_{50}-aryl, or alkylaryl having from 1 to 50 carbon atoms in the alkyl part and from 6 to 50 carbon atoms in the aryl part, wherein the organic radicals R^2 and R^5 may also be substituted by halogens, C_1-C_{50}–alkoxy, C_6-C_{50}–aryloxy or SiR^6_3 and the radicals R^2 and R^5 and their substituents may also contain heteroatoms selected from N, P, O or S, wherein the radicals R^6 are defined as in claim 2.

4. Transition metal compound according to claim 2 or 3, wherein
R^3 and R^4 are identical or different and are each, independently of one another,

C_5-C_{50}-aryl, alkylaryl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, wherein the organic radicals R^3 and R^4 may also be substituted by halogens, C_1-C_{50}–alkoxy, C_5-C_{50}–aryloxy or SiR^6_3 and the radicals R^3 and R^4 and their substituents may also contain heteroatoms selected from N, P, O or S, wherein the radicals R^6 are defined as in claim 2.

5. Transition metal complex according to one of claims 1 to 4 corresponding to formula (B);

$$[(M^1L_oX_m)_n]^{p-} \qquad (B)$$

wherein

M^1 is an element of group 3 to 10 of the Periodic Table of the Elements,

L is a ligand system with a nitrogen-phosphorus-nitrogen-structural element wherein phosphorus is pentavalent,

o is 1 or 2,

X are the same or different and are each halogen, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_6-C_{22}-aryl, alkylaryl or arylalkyl group having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 22 carbon atoms in the aryl radical, $-OR^7$ or $-NR^7R^8$, wherein two radicals X may also be joined to one another, and wherein R^7 and R^8 are each independently C_1-C_{10}-alkyl, C_6-C_{14}-aryl, alkylaryl, arylalkyl, fluoroalkyl or fluoroaryl each having from 1 to 10 carbon atoms in the alkyl radical and from 6 to 22, carbon atoms in the aryl radical,

m is a natural number from 0 to 5,

n is 1, 2, or 3;

p is 0 or 1.

6. Transition metal complex according to claim 4, wherein

M^1 is chromium, tungsten or molybdenum.

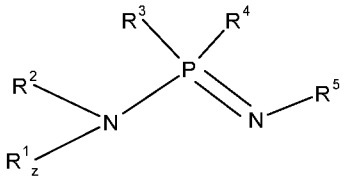
7. A catalyst system for the oligomerization of olefins, which comprises

a) at least one transition metal compound as claimed in one of claims 1 to 5 and

b) at least one cocatalyst which is able to convert the transition metal compound into a species which is oligomerization-active toward at least one olefin.

8. A catalyst system for the oligomerization of olefins, comprising
- a transition metal precursor of a transition metal of group 3 to 10 of the Periodic Table of the Elements and
- at least one ligand system ligand system L according to one of claims 1 to 4, and
- at least one cocatalyst which is able to convert the transition metal compound into a species which is oilgomerization-active toward at least one olefin.

9. A catalyst system according to claim 8, wherein
the ligand system corresponds to formula (A)



(A)

wherein
R^1, R^2, R^3, R^4, and R^5 are identical or different and are each, independently of one another, hydrogen, halogen, C_1-C_{50}-alkyl, C_2-C_{50}-alkenyl, C_6-C_{50}-aryl, alkylaryl or arylalkyl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, C_1-C_{50}–alkoxy, or C_6-C_{50}–aryloxy, where the organic radicals R^1, R^2, R^3, R^4 and R^5 may also be substituted by halogens, C_1-C_{50}–alkoxy, C_6-C_{50}–aryloxy or SiR^6_3 and the radicals R^1, R^2, R^3, R^4, and R^5 and their substituents may also contain heteroatoms selected from N, P, O or S,
R^6 are each, independently of one another, hydrogen, C_1-C_{50}-alkyl, C_2-C_{50}-alkenyl, C_6-C_{50}-aryl, arylalkyl or alkylaryl having from 1 to 50 carbon atoms in the alkyl part and 6 to 50 carbon atoms in the aryl part, C_1-C_{50}–alkoxy or C_6-C_{50}–aryloxy and two radicals R^6 may also be joined to form a five- or six-membered ring, and
z is 0 or 1.

10. A process for oligomerization of olefinic monomers, carried out in the presence of a catalyst system according to one of claims 6 to 9.

11. The process of claim 10 for the oligomerization of ethylene, optionally with other olefin monomers.

12. The process of claim 10 or 11 for trimerization and/or tetramerization.