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(71) Applicants *(for all designated States except US)*: DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: WISSING, Elmo [NL/NL]; Troelstraweg 17, NL-3732 CA De Bilt (NL). TEUNISSEN, Antonius, Jacobus, Josephus, Maria [NL/NL]; Van Ostadestraat 42, NL-6165 XM Geleen (NL). HANSEN, Carolina, Bernedette [NL/NL]; Rolandsweg 27A, NL-6136 BT Sittard (NL). VAN LEEUWEN, Petrus, Wilhelmus, Nicolaas, Maria [NL/NL]; Roerdomp 45, NL-3628 CA Kockengen (NL). VAN ROOY, Annemiek [NL/NL]; Ouddiemerlaan 7', NL-1111 GS Diemen (NL). BURGERS, Dennis [NL/NL]; Prinseneiland 93, NL-1013 LM Amsterdam (NL).

(74) Agent: CRAMWINCKEL, Michiel; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).

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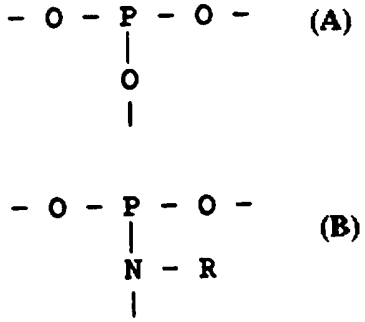
(54) Title: PROCESS FOR THE PREPARATION OF AN ALDEHYDE

(57) Abstract

Process for preparing an aldehyde compound by hydroformylation of an ethylenically unsaturated organic compound in the presence of a catalyst system comprising of a multidentate phosphorous ligand and a Group 8-10 metal, wherein the multidentate phosphorus amide ligand consists essentially of a multivalent bridging organic group connected to at least two trivalent phosphorus-containing groups of formulas (A) and (B) provided that at least one group of formula (B) is present, wherein R is hydrogen, an organic group, or $-SO_2R^1$, wherein R^1 is a C_{1-12} organic group, and wherein remaining free bonds of said trivalent phosphorus groups are linked to a mono- or divalent organic group.



(A)

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PROCESS FOR THE PREPARATION OF AN ALDEHYDE

The invention relates to a process for preparing an aldehyde compound by hydroformylation of an ethylenically unsaturated organic compound in the presence of a catalyst system comprising of a multidentate phosphorus ligand and a Group 8-10 metal.

With hydroformylation is meant the reaction of an unsaturated compound with hydrogen and carbon monoxide in the presence of a catalyst.

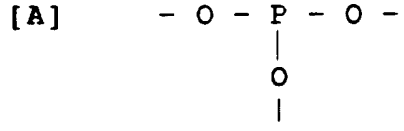
Such a process is described in US-A-4769498. US-A-4769498 describes the hydroformylation of 2-butene in the presence of a homogeneous catalyst system consisting of rhodium and a bidentate phosphite ligand.

A disadvantage of such a process is that the selectivity to aldehydes is too low for a commercially interesting process.

An object of this invention is a hydroformylation process to prepare aldehydes with a higher selectivity to aldehydes than is achieved with the catalyst system of US-A-4769498.

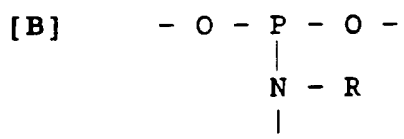
This object of the invention is achieved in that the multidentate phosphorus amide ligand consists of a multivalent bridging organic group connected to at least two trivalent phosphorus-containing groups of the formula

[A]



and

[B]



provided that at least one group of formula [B] is present, wherein R is hydrogen, an organic group, or -SO_2R^1, wherein R^1 is a C_{1-12} organic group, and wherein remaining free bonds of said trivalent phosphorus groups are linked to a mono- or di-valent organic group.

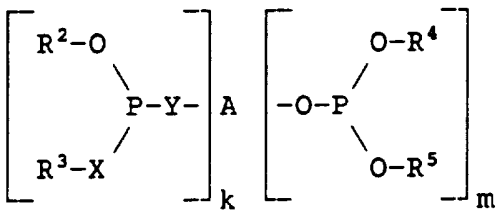
It has been found that when an aldehyde is prepared with the process according to the invention the selectivity to aldehyde is higher than the selectivity achieved with the process of US-A-4769498.

Some of the compounds that can be used as bidentate phosphorus amide ligands according to the invention are described in US-A-5147910, US-A-5147909 and US-A-5075483. All of these references describe phosphorus amide compounds with chemical structures comprising trivalent $P(N(R)-)(O-)_2$ groups to be effective in stabilizing organic materials such as polymers. None of these references suggest that these phosphorus amide compounds could be advantageously used as part of a catalyst system for the hydroformylation of ethylenically unsaturated organic compounds.

Phosphorus amide compounds, which are used as ligands, are described in WO-A-9303839. In this patent application the asymmetric hydroformylation of styrene is described in which a catalyst system is used consisting of rhodium and a bidentate phosphorus diamide ((N,N'-diphenyl-ethylenediamine-P)$_2$-2S,4S-pentanediol). This bidentate phosphorus diamide ligand contains structural groups in which two nitrogen atoms, in contrast to the $P(N(R)-)(O-)_2$ group(s) of the ligands according to the invention, are directly bonded to a phosphorus atom of the ligand. It appears however that when this kind of phosphorus diamide ligand is used the selectivity to aldehydes does not improve compared to the process of US-A-4769498. Furthermore, WO-A-9303839 is dedicated to a process for the stereo specific preparation of optically active aldehyde

compounds by using one specific stereo-isomer of the phosphorus amide ligand.

The phosphorus amide compound used as ligand in the process according to the invention may for example be represented by the following formula:

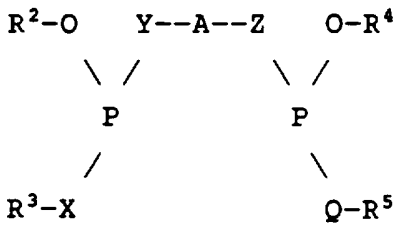


(1)

in which R^2, R^3, R^4 and R^5 are the same or different and in which either one of X or Y is a N(R) group while the other group is oxygen, A is a multivalent (multi is equal to k+m) organic group with 2 to 30 carbon atoms, k is at least 1, m can be 0-5 and k+m is 2-6, R^2 and R^3 together and/or R^4 and R^5 together form one, optionally substituted, divalent organic group with 2 to 30 carbon atoms or R^2, R^3, R^4 and R^5 are independently, optionally substituted, monovalent organic groups with 1 to 20 carbon atoms.

R is hydrogen or an organic group with 1 to 11 carbon atoms or $-SO_2R^1$ in which R^1 is an organic group with 1 to 12 carbon atoms. Preferably R is hydrogen or a C_1-C_{11} alkyl group, phenyl, for example methyl, ethyl, propyl or substituted or unsubstituted aryl groups, for example phenyl and tolyl or a $-SO_3R^1$ group as defined before.

One class of bidentate phosphorus amide compounds used as ligand in the process according to the invention can be represented by formula (1) in which k+m is equal to 2 or by the following formula:



(2)

in which at least one of X, Y, Z or Q is a N(R) group, the remaining of X, Y, Z and Q being oxygen, in which one or both phosphor atom(s) is at most bonded to only one nitrogen atom, A is a divalent organic group with 2 to 30 carbon atoms and in which R^2, R^3, R^4, R^5 and R are the same as defined above.

The bridging group (A) may be for example a multivalent organic group with 2 to 30 carbon atoms. The number of valencies is in principle not bound to an upper limit. An example of a multivalent bridging group are dendrimer like compounds as described in WO-A-9314147. A preferred dendrimer bridging compound has reactive $-NH_2$ groups which can easily react with a bis(alkoxy) or bis(aryloxy)phosphorus chloride compound to yield the ligand which can be used in the process according to the invention.

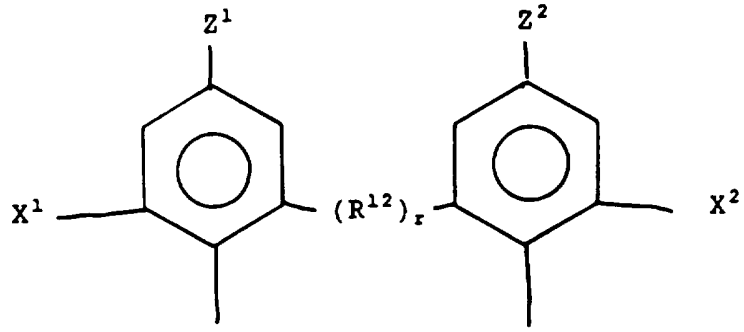
In general the amount of valencies will be 2-6. An example of a tetravalent organic group is pentaerythritetraryl.

Preferred divalent organic groups are alkylene, alkylene-oxy-alkylene, arylene, arylene-$(CH_2)_y$-$(R^6)_n$-$(CH_2)_y$-arylene, in which y is 0 or 1, n is 0 or 1 and each arylene is the same or different, substituted or unsubstituted divalent aryl radical and R^5 individually represents a divalent group selected from the group consisting of $-CR^7R^8-$, $-O-$, $-S-$, $-NR^9-$, $-SiR^{10}R^{11}-$ and $-CO-$, in which R^7 and R^8 individually represents hydrogen, C_1-C_{12} alkyl, phenyl, tolyl, anisyl or methoxyphenyl, wherein each R^9, R^{10} and R^{11} group individually represents hydrogen or a C_1-C_{12} organic group for example ethyl, propyl, butyl, benzyl and by

preference hydrogen, methyl or phenyl.

Examples of possible divalent organic bridging groups (A) include substituted and unsubstituted radicals selected from the group consisting of alkylene, alkylene-oxy-alkylene, phenylene, naphthylene, phenylene-$(CH_2)_y$-$(R^6)_n$-$(CH_2)_y$-phenylene and naphthylene-$(CH_2)_y$-$(R^6)_n$-$(CH_2)_y$-naphthylene-radicals, R^6, n and y are the same as defined above. More specific examples of divalent radicals A are $-CH_2CH_2OCH_2CH_2-$, 1,4-phenylene, 2,3-phenylene, 1,3-phenylene, 1,4-naphthylene, 1,5-naphthylene, 1,8-naphthylene, 2,3-naphthylene, 1,1' biphenyl-2,2'-diyl, 2,2' biphenyl-1,1'-diyl, 1,1' biphenyl-4,4'-diyl, 1,1' binaphthyl-2,2'-diyl, 2,2'-binaphthyl-1,1'-diyl, phenylene-CH_2-phenylene, phenylene-S-phenylene, CH_2-phenylene-CH_2 and phenylene-$CH(CH_3)$-phenylene.

Preferably the divalent bridging group (A) has the following formula:



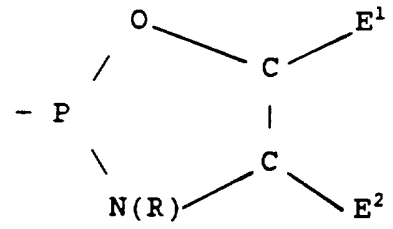
(3)

in which R^{12} is - CY^1Y^2- wherein each Y^1 and Y^2 radical individually represents hydrogen, C_1-C_{12} alkyl, for example methyl, propyl, isopropyl, butyl, isodecyl, dodecyl; phenyl, methoxyphenyl, tolyl and anisyl and r has a value of 0 to 1; wherein each X^1, X^2, Z^1, and Z^2 group individually is hydrogen, an alkyl radical having from 1 to 18 carbon atoms, substituted or unsubstituted

aryl, alkaryl, aralkyl or alicyclic groups as defined and exemplified hereinabove, for example phenyl, benzyl, cyclohexyl and 1-methylcyclohexyl; cyano, halogen, for example Cl, Br, I; nitro, trifluoromethyl, hydroxy, carbonyloxy, amino, acyl, phosphonyl, oxycarbonyl, amido, sulfinyl, sulfonyl, silyl, alkoxy or thionyl. Preferably both X^1 and X^2 are groups having a steric hindrance, for example isopropyl, or more preferably tert-butyl, or greater and Z^1 and Z^2 are hydrogen, an alkyl radical, especially tert-butyl, a hydroxy radical or an alkoxy radical, especially methoxy. Preferably R^{11} represents a methylene($-CH_2-$) bridging group or an alkylidene($-CHR^{13}-$) bridging group wherein R^{13} is an alkyl radical of 1 to 12 carbon atoms as defined above for Y^1. R^{13} is preferably methyl (R^{12} is $-CHCH_3-$) or a substituted aryl group, for example methoxyphenyl.

Divalent organic groups for R^2 and R^3 together and/or R^4 and R^5 together can be the same as described above for bridging group (A). The preferences for the bridging group also apply for these divalent groups. Preferably the divalent group is defined according to formula (3).

More preferred divalent organic groups for R^2 and R^3 in case X is a N(R) group and/or for R^4 and R^5 in case Q is a N(R) group in formula (2) are represented by the following formula (presented with the N(R), P and -O- groups)

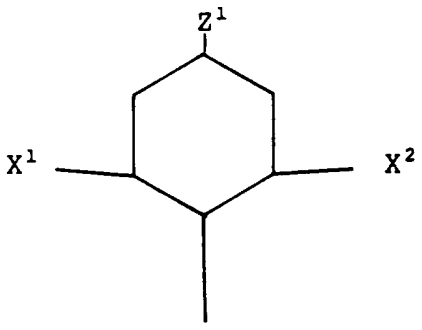


(3a)

in which E^1 and E^2 are the same or different and in which E^1 en E^2 are hydrogen or a monovalent organic

group with 1 to 11 carbon atoms or in which E^1 and E^2 together are one divalent organic group with 3 to 11 carbon atoms or R and E^2 together are one divalent organic group with 3 to 12 carbon atoms and E^1 is hydrogen or a monovalent organic group as defined above. The possible remaining group bonded to the carbon atom(s) in formula (3a) is hydrogen. Possible monovalent organic groups are alkyl, aralkyl, alkaryl or aryl groups, for example methyl, ethyl, propyl, tert-butyl, phenyl, benzyl or tolyl. Divalent groups for E^1 and E^2 can be C_3-C_5 alkylene groups, for example propylene or butylene or can be so choosen that E^1, E^2 and the two carbon atoms of formula (3a) form a conjugated ring structure of 6 carbon atoms which ring may be substituted with for example methyl, ethyl, propyl or phenyl groups. Examples for divalent organic groups for R and E^2 are, optionally substited, C_3-C_{10} alkylene groups, for example propylene, butylene or pentylene.

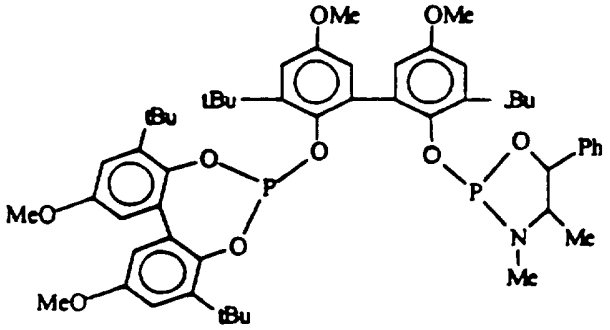
Monovalent organic groups for R^2, R^3, R^4 and R^5 can more specifically be monovalent alkyl groups of 1 to 20 carbon atoms, cycloalkyl groups of 5 to 12 carbon atoms, aryl groups of 5 to 20 carbon atoms and alkaryl groups of 6 to 20 carbon atoms. Examples of the monovalent organic group are methyl, ethyl, isopropyl, butyl, isodecyl, dodecyl, phenyl, tolyl and anisyl. Preferably the monovalent group has the following structure:



(4)

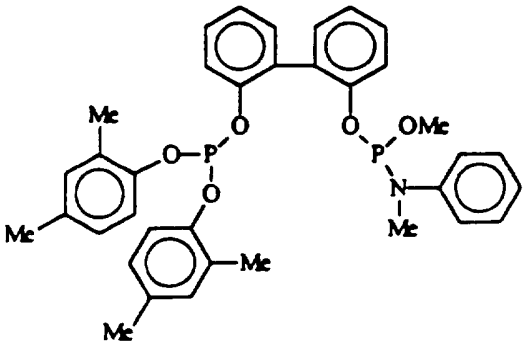
in which X^1, X^2 and Z^1 are groups as defined above.

Examples of compounds to be used as ligands in the process according to the invention are Ligand (1) to (24) as presented below. Ph is a phenyl group, Me is a methyl group, tBu is a tert-butyl group and OMe is a methoxy group in these formulas.

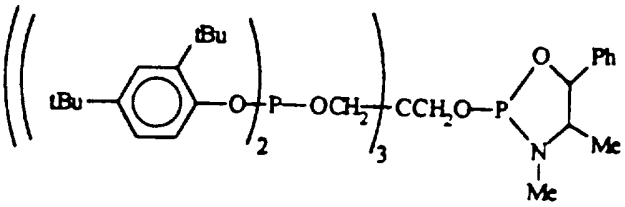


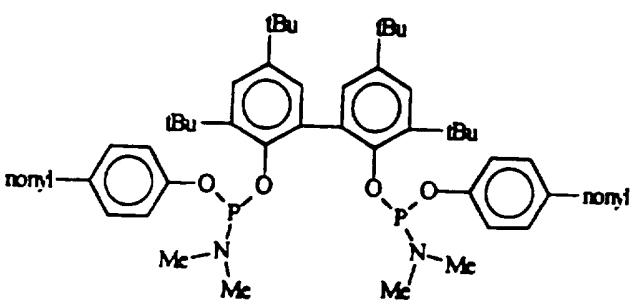
Ligand (1)

Ligand (2)



Ligand (3)





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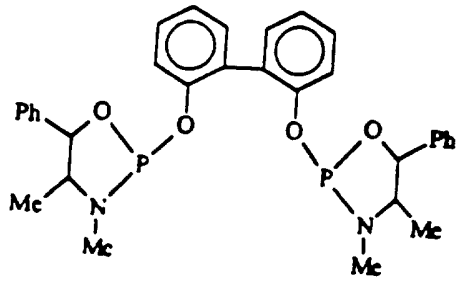

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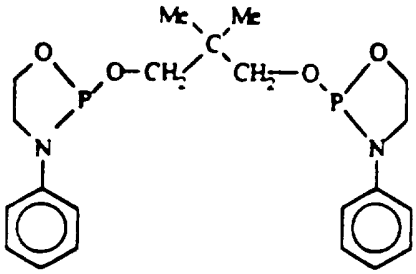

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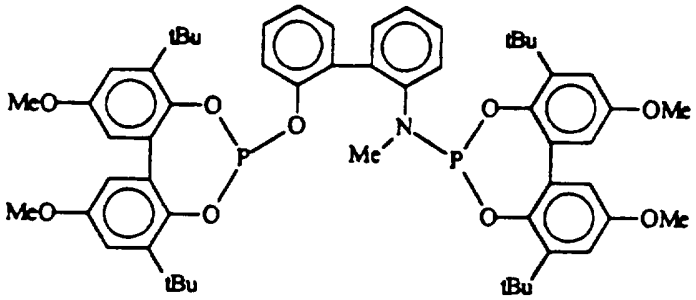

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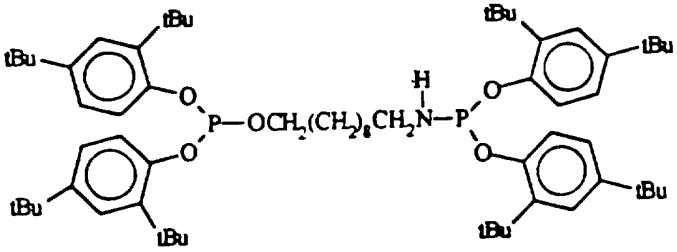

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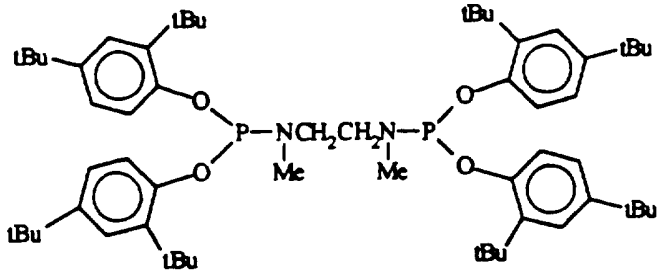

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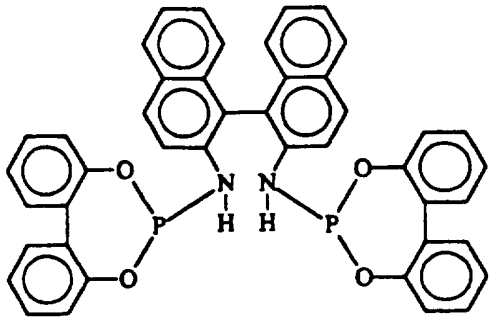

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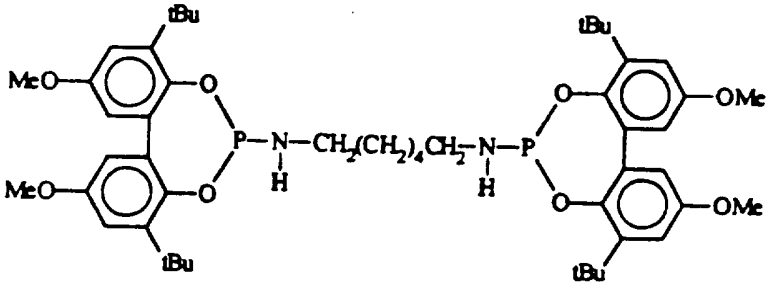

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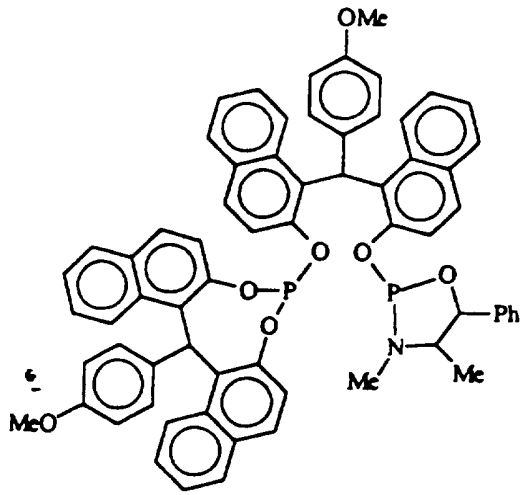

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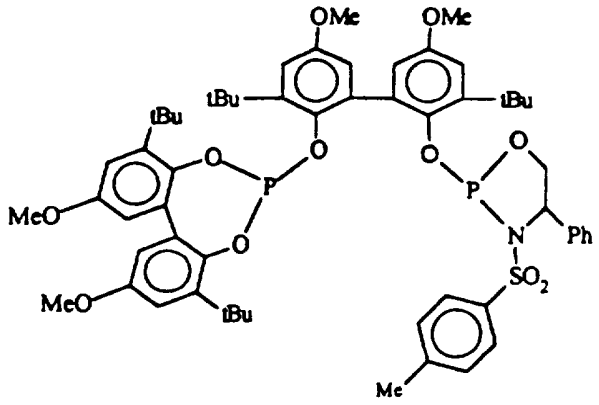

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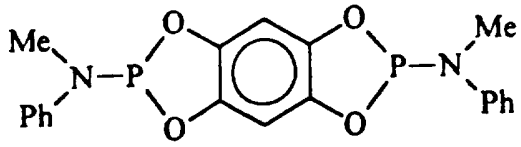

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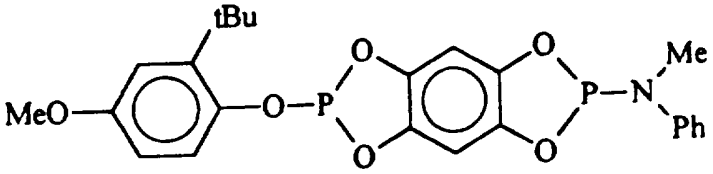

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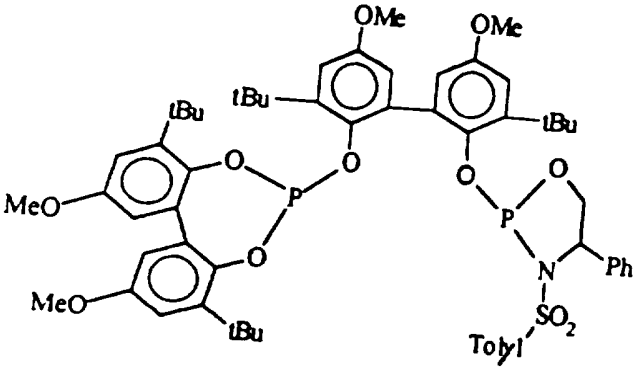

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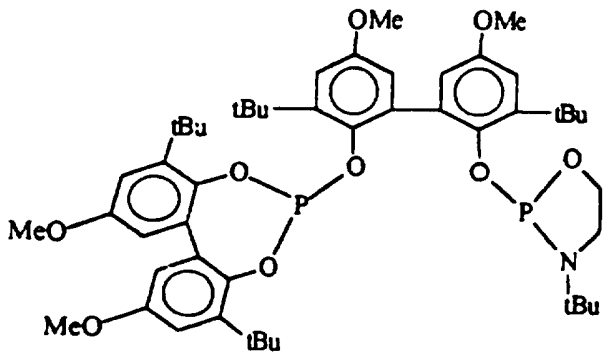

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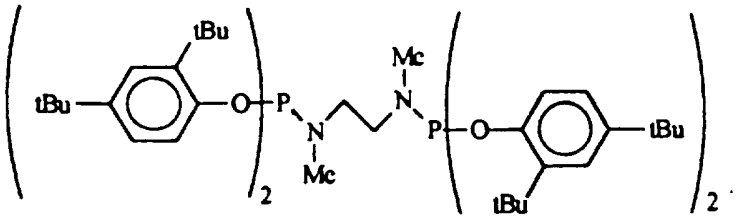

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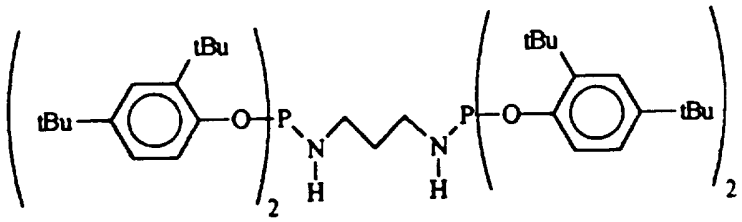

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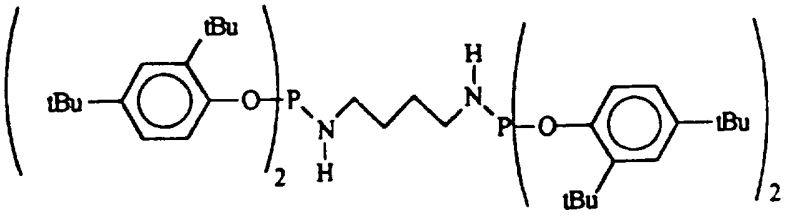
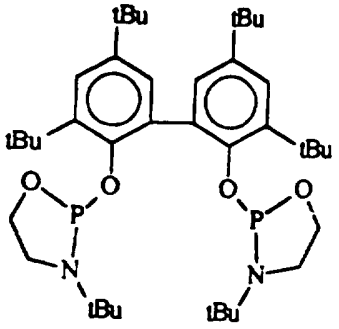
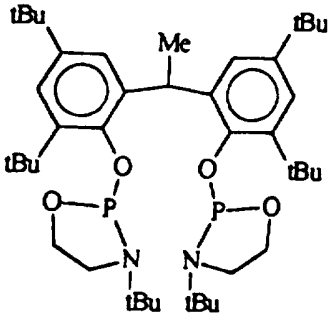


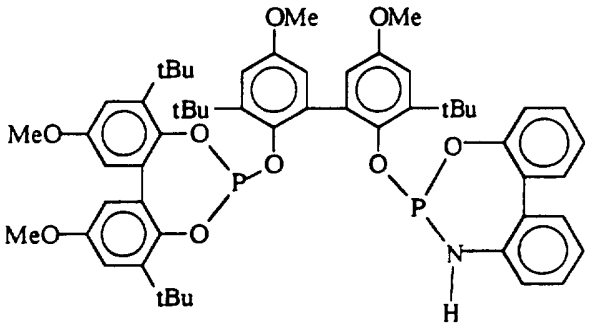
Ligand (20)



Ligand (21)



Ligand (22)



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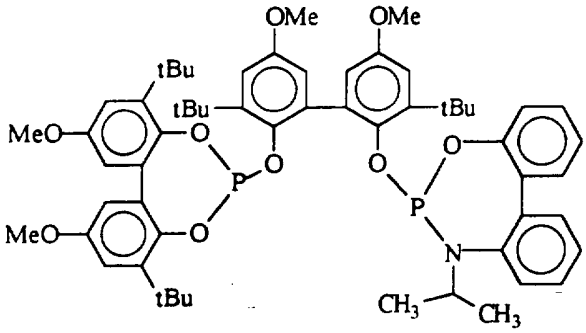


Ligand (24)

The phosphorus amide compounds which are used as ligands in this invention can be prepared as described in EP-A-42359 and in S.D. Pastor et al., J. Am. Chem. Soc. 110, 6547 (1988) and S.D. Pastor et al., Helv. Chim. Acta 76, 900 (1991).

The ethylenically unsaturated organic compound used in the preparation of an aldehyde compound through hydroformylation is not specially limited so long as it has at least one ethylenically (C=C) bond in the molecule. The ethylenically unsaturated organic compound has usually 2 to 20 carbon atoms. Examples of possible ethylenically unsaturated organic compound are linear terminal olefinic hydrocarbons for example ethylene, propylene, 1-butene, 1,3-butadiene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene and 1-dodecene; branched terminal olefinic hydrocarbons for example isobutene and 2-methyl-1-butene; linear internal olefinic hydrocarbons for example cis- and trans-2-butene, cis- and trans-2-hexene, cis- and trans-3-hexene, cis- and trans-2-octene and cis- and trans-3-octene; branched internal olefinic hydrocarbons for example 2,3-dimethyl-2-butene, 2-methyl-2-butene and 2-methyl-2-pentene; mixtures of terminally olefinic and internally olefinic hydrocarbons for example octenes prepared by dimerization of butenes, olefin oligomer isomer mixture (of from dimer to tetramer) of lower olefins including propylene, n-butene, isobutene or the like; and cycloaliphatic olefinic hydrocarbons for example cyclopentene, cyclohexene, 1-methylcyclohexene, cyclooctene and limonene.

Examples of the olefinic compound substituted with a hydrocarbon group containing an unsaturated hydrocarbon group include olefinic compounds containing an aromatic substituent such as styrene, α-methylstyrene and allylbenzene; and diene compounds

such as 1,5-hexadiene, 1,7-octadiene and norbornadiene.

The ethylenically unsaturated organic compound can be substituted with one or more functional groups containing a heteroatom, for example oxygen, sulfur, nitrogen and phosphor. Examples of these substituted ethylenically unsaturated organic compounds are vinyl methyl ether, methyl oleate, allyl alcohol, oleyl alcohol, 3-methyl-3-buten-1-ol, methyl 3-pentenoate, methyl 4-pentenoate, 3-pentenoic acid, 4-pentenoic acid, 3-pentenenitrile, 4-pentenenitrile, 3-hydroxy-1,7-octadiene, 1-hydroxy-2,7-octadiene, 1-methoxy-2,7-octadiene, 7-octen-1-al, hexa-1-en-1-ol, acrylonitrile, acrylic acid esters for example methylacrylate, methacrylic acid esters for example methylmethacrylate, vinyl acetate and 1-acetoxy-2,7-octadiene.

The advantages of the invention regarding improved aldehyde selectivity are more pronounced when starting from internally ethylenically unsaturated organic compounds and even more pronounced when these compounds are substituted with one or more functional groups containing a hetero atom as described above. Examples of these compounds are described above.

Preferred substrates are pentenenitrile, pentenoic acid and C_1-C_6 alkyl pentenoate ester compounds, for example 3-pentene nitrile, 3-pentenoic acid, methyl-3-pentenoate, ethyl-3-pentenoate and methyl 4-pentenoate. These compounds are preferred because the resulting terminal aldehyde compounds can be advantageously used in the preparation of Nylon-6 and Nylon-6.6 intermediates. An example of such use is described in US-A-4731445. The branched aldehyde compounds obtained by the process according to the invention can be used to prepare branched lactams in an analogous method as described in the aforementioned US patent.

The catalyst system can be prepared by mixing

a suitable Group 8-10 (according to the new IUPAC notation) metal compound with the phosphorus amide compound optionally in a suitable solvent in accordance with well known complex-forming methods. The solvent will generally be the solvent used in the hydroformylation. Suitable Group 8-10 metal compounds are hydrides, halides, organic acid salts, inorganic acid salts, oxides, carbonyl compounds and amine compounds of these metals. Examples of suitable Group 8-10 metals are cobalt, ruthenium, rhodium, palladium, platinum, osmium and iridium. Examples of Group 8-10 metal compounds are ruthenium compounds for example $Ru_3(CO)_{12}$, $Ru(NO_3)_3$, $RuCl_3(Ph_3P)_3$ and $Ru(acac)_3$; palladium compounds for example $PdCl_2$, $Pd(OAc)_2$, $Pd(acac)_2$, $PdCl_2(COD)$ and $PdCl_2(Ph_3P)_2$; osmium compounds for example $Os_3(CO)_{12}$ and $OsCl_3$; iridium compounds for example $Ir_4(CO)_{12}$ and $IrSO_4$; platinum compounds for example K_2PtCl_4, $PtCl_2(PhCN)_2$ and $Na_2PtCl_6.6H_2O$; cobalt compounds for example $CoCl_2Co(NO_3)_2$, $Co(OAc)_2$ and $Co_2(CO)_8$; and rhodium compounds for example $RhCl_3$, $Rh(NO_3)_3$, $Rh(OAc)_3$, Rh_2O_3, $Rh(acac)(CO)_2$ $[Rh(OAc)(COD)]_2$, $Rh_4(CO)_{12}$,, $Rh_6(CO)_{16}$, $RhH(CO)(Ph_3P)_3$, $[Rh(OAc)(CO)_2]_2$ and $[RhCl(COD)]_2$ (wherein "acac" is an acetylacetonate group; "Ac" is an acetyl group; "COD" is 1,5-cyclooctadiene; and "Ph" is a phenyl group). However, it should be noted that the Group 8-10 metal compounds are not necessarily limited to the above listed compounds.

Preferably rhodium is used as Group 8-10 metal because the speed of reaction is higher than in case one of the other metals is used.

The amount of Group 8-10 metal (compound) is not specially limited, but is optionally selected so that favourable results can be obtained in respect of catalyst activity and economy. In general the concentration of Group 8-10 metal in the reaction medium is between 10 and 10.000 ppm and more preferably

between 100-1000 ppm calculated as free metal.

The molar ratio multidentate phosphorus amide ligand to Group 8-10 metal of the catalyst system is not specially limited, but is preferably selected so that favorable results can be obtained in respect to catalyst activity and aldehyde selectivity. This ratio is generally from about 0.5 to 100 and preferably from 1 to 10 (mol ligand/mol metal).

The choice of an optional solvent is not critical. The reaction medium may be the mixture of reactants of the hydroformylation itself, such as the starting unsaturated compound, the aldehyde product and/or by-products. If an extra solvent is used suitable examples are saturated hydrocarbons such as naphtha, kerosine, mineral oil and cyclohexane and aromatics, for example toluene, benzene, xylene, ethers, for example diphenyl ether, tetrahydrofuran, ketones, for example cyclohexanone and nitriles, for example benzonitrile and texanol® (Union Carbide).

The reaction conditions to conduct the hydroformylation according to the invention are the same as used in a conventional process, described for example in US-A-4769498, and will be dependent of the particular starting ethylenically unsaturated organic compound. For example, the temperature can be from room temperature to 200 °C and preferably from 50 to 150 °C. The pressure is from normal pressure to 20 MPa and preferably from 0.15 to 10 MPa and more preferably from 0.2 to 5 MPa. The pressure is generally the result of the combined hydrogen and carbon monoxide partial pressure. Extra inert gasses may however be present. The molar ratio hydrogen : carbon monoxide is generally between 10:1 and 1:10 and preferably between 1:1 and 6:1.

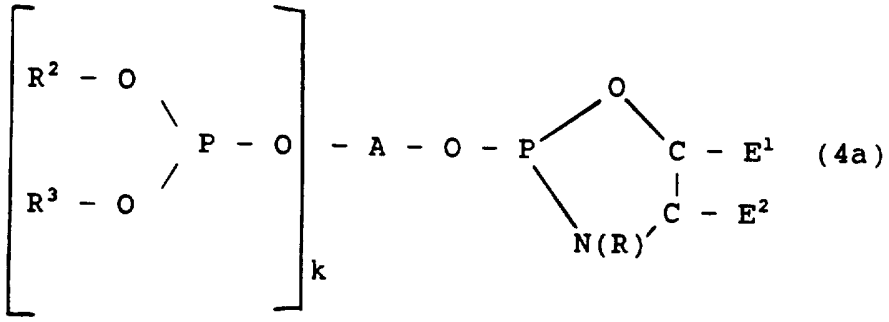
The invention also relates to a catalyst system comprising a Group 8-10 metal and, by preference a racemic mixture of, the multidentate phosphorus amide

ligand as here described.

The phosphorus amide compounds used as ligands of this catalyst system can be represented by formula (1-2). The groups X, Y, Z, Q, A, R, R^1-R^{13} and E^1-E^2 can be the same as defined above. A preferred catalyst system according to the invention is a catalyst system comprising the phosphorus amide ligand in which the Group 8-10 metal is rhodium. These catalyst systems are advantageous when used for hydroformylating internally ethylenically unsaturated organic compounds to aldehydes as explained above.

The catalyst system can also for example be used as a hydrogenation-, polymerisation-, isomerisation- and carbonylation catalyst.

The invention is also directed to a new group of phosphorus amide compounds, which can be advantageously used as ligands in the homogeneously catalysed hydroformylation of ethylenically unsaturated organic compounds as described above. This new group of phosphorus amide compounds can be represented by the following general formula



(4a)

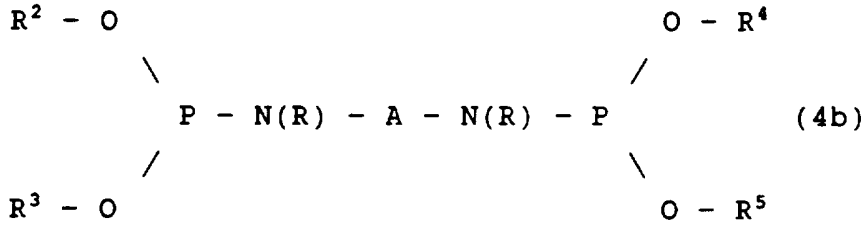
in which R^2, R^3, A, R, E^1 and E^2 are the same as defined above and k is 1-5. The end group consisting of N(R), C, C, E^1, E^2 and O in formula (4a) is the same as the corresponding group of formula (3a).

Examples of these new compounds are the above described Ligands (1), (3) and (12). A preferred compound is Ligand (12).

The compounds according to formula (4a) can

be for example prepared in an analogous manner as described in Example 13 of US-A-4748261 in which instead of two equivalent of the phenol derivative (p-chlorophenol) an equal molar amount of an amino-alcohol derivative, for example ephedrine is used.

Another class of new phosphorus amide compounds to which this invention is directed can be represented by the following formula



(4b)

in which R^2, R^3, $R3^4$, R^5 and A are the same as defined above. These compounds can be advantageously used as ligands in the homogeneously catalysed hydroformylation of ethylenically unsaturated organic compounds as described above. Examples of these new compounds are the above described Ligands (9), (10) and (11) and the compounds which are used as ligands in Example IV of this invention.

Compounds according to formula (4b) can be prepared by mixing in an organic solvent a phosphorus halogenide compound (corresponding with the $(R^1O)(R^2O)P$- or $(R^3O)(R^4O)P$-group) with 2 equivalents of an alkylamine, for example triethylamine, and 0.5 equivalent of a diamine which corresponds with the -N(R)-A-N(R)-group of formula (4b), for example N,N'-dimethylethylenediamine. After filtration and evaporation of the solvent the compounds are obtained as white solids. Subsequent crystallization results in a pure white crystalline compound.

The invention will be elucidated with the following non limiting examples.

The compounds used as ligands in the Examples

and experiments were prepared as described below. Some compounds are well known from literature and/or are commercially available. Therefore their preparation is not described in detail.

Ligand (1)

Ligand (1) (see the description for a reference to Ligand (1) and other Ligands used in the Examples) was prepared in an analogous manner as described in Example 13 of US-A-4748261 in which instead of 2 molar amounts of para-chlorophenol, an equal molar amount of ephedrine was used. The triethylamine-hydrochloride precipitate, formed in the final step of the reaction was removed by filtration. The residue was washed with two 50 ml portions of toluene. The combined filtrate and washes was concentrated to give an offwhite solid. The solid was crystallized from toluene/acetonitrile to give a 71% yield of the ligand according formula of ligand (1).

Ligand (3)

Ligand (3) was prepared by dissolving 18.6 gr of 2.4-di-tert-butyl phenol in 500 ml of toluene, of which 50 ml was distilled off azeotropically to remove traces of moisture. The solution was cooled to room temperature and 1 molar equivalent of triethyl amine (9.1 g) was added. To the mechanically stirred mixture 0.5 equivalent of PCl_3 (6.2 g) were added. The immediately formed suspension was stirred for 3 hours at 60°C. Subsequently, 4.55 g of triethyl amine and 2.04 g of pentaerythritol was added to the mixture and additionally stirred for 16 hours at 60°C. The suspension was cooled to room temperature and 3.44 g of 2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxaza-phospholidine (such as described by S.D. Pastor et al., Helv. Chim. Acta 74, 1175 (1991)) was added. Ligand (3) was formed upon stirring the mixture at 40°C for 20

hrs. The work-up procedure was the same as described for the Ligand (1). After two crystallizations the ligand (3) was obtained as a white solid in a 75% yield.

Ligand (9)

The synthesis of Ligand (9) starts similar to the synthesis of Ligand (3). To the mixture of bis(2,4-di-tert-butyl phenoxy) phosphorus chloride and triethylamine-hydrochloride was added 1 equivalent of triethylamine and 0.5 equivalent of N,N-dimethyl-ethylenediamine. Ligand (9) was formed upon stirring the mixture at 50°C for 4 hours. The work-up procedure was the same as described for Ligand (1). After crystallization Ligand (9) was obtained as white solid in 89% yield.

Ligand (12)

Ligand (12) was prepared from p-anisylidene-1,1-bis(2-naphtol) in an analogous manner as described for Ligand (1). The ligand (12) was obtained as a white solid in 84% yield.

Ligand (16)

Ligand (16) was prepared in an analogous manner as described for ligand (1) using N-tosyl-2-amino-2-phenylethanol as aminoalcohol.

Ligand (17)

Ligand (17) was prepared in an analogous manner as described for ligand (1) using N-tert-butyl 2-aminoethanol.

Ligand (18)

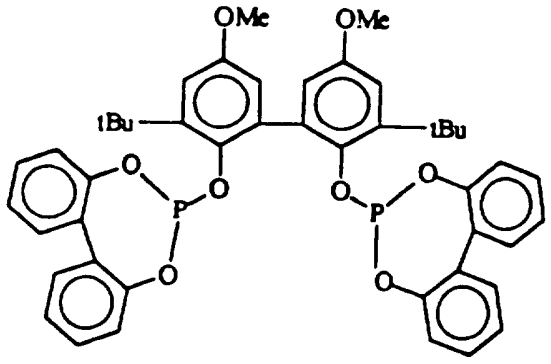
Ligand (18) was prepared in an analogous manner as described for ligand (9) using 2,4-di-tert-butylphenol and N,N'-dimethylethanediamine.

Example I

A 150 ml Hastelloy-C-steal autoclave (Parr) was charged with a mixture of 5.8 mg (2.25×10^{-5} mol) of rhodium dicarbonyl acetylacetonate and 45 mg (4.80×10^{-5} mol) of the phosphorus amide Ligand (1) in 60 ml toluene under nitrogen atmosphere. The autoclave was heated to 90°C in 1 hour and pressurized to 0.5 MPa with a H_2/CO (2/1 (mol/mol)) mixture. Subsequently, a mixture of 5.1 g (45 mmol) of methyl 3-pentenoate and 1 g of nonane (internal standard) with toluene (total volume of 15 ml) was injected into the reactor. The reactor pressure was kept constant during the hydroformylation at 0.5 MPa with H_2/CO (2/1; mol/mol). The composition of the reaction mixture was analysed by gas chromatography and the results are presented in Table 1.

Comparative Experiment A

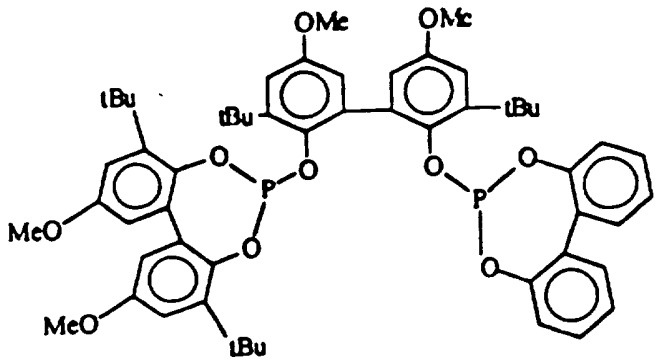
Example I was repeated with a bisphoshite ligand (A) as also used in example 14 of US-A-4769498. The results are presented in Table 1. Bisphosphite ligand (A) used:



Ligand (A)

Comparative Experiment B

Example I was repeated with a bisphosphite ligand (B) as shown below (see also US-A-4769498). The results are presented in Table 1.



Ligand (B)

Table 1

Example	Ligand	L/Rh (1)	S_{ald} (2)	conversion (%) (3)
I	1	2.1	79.5	93.1 (28h)
A	A	2.1	69.0	98.4 (21h)
B	B	2.2	74.9	94.3 (28h)

(1) L/Rh is molar ratio of ligand and rhodium

(2) S_{ald} is selectivity in % to aldehyde calculated as molar amount of aldehyde on total mol of products formed

(3) conversion is molar amount of reacted unsaturated compound on total mol of starting compound expressed in %.

The numbers between brackets refer to the reaction time in hours.

Example IIa

Example I was repeated with a phosphorus amide ligand, Ligand (3), in which the pressure was 1.0 MPa (H_2/CO = 1/1 (mol/mol)) and the ligand/Rh ratio of 2.8 (mol/mol). After 46 hours the conversion was 75% and the selectivity to aldehydes (S_{ald}) was 84.5%.

Example IIb

Example IIa was repeated with a phosphorus amide ligand, Ligand (12) and a ligand/Rh ratio of 2.9.

After 22 hours the conversion was 86.2% and the selectivity to aldehydes (S_{ald}) was 91.6%.

Comparative Example C

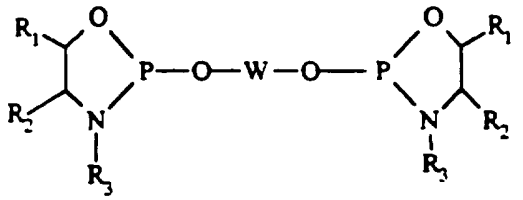
Example II was repeated with the phosphorus diamide ligand of Example 7 of WO-A-9303839:

Ligand (C)

The ligand/rhodium ratio was 2.1/1 mol/mol. S_{ald} = 76.6% at 28.2% conversion after 40 hours reaction time.

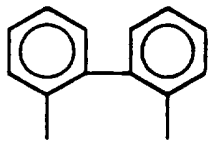
Example IIIa-d

Example IIa was repeated with the phosphorus amide ligands of the general structure according to formula 8a-8d. The synthesis of Ligand 8a-8d are described in S.D. Pastor et al., J. Am. Chem. Soc. 110, 6547 (1988) and S.D. Pastor et al., Helv. Chim. Acta 76, 900 (1991).



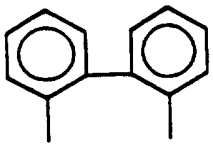
(8)

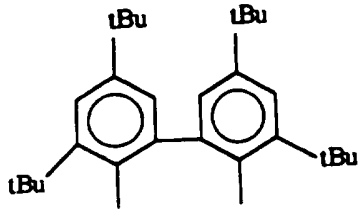
W =

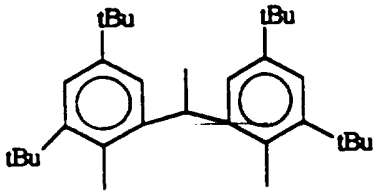


R_1 = Ph
R_2 = R_3 = Me

(8a)

W =  $R_1 = R_2 = H$, $R_3 = tBu$ (8b)

W =  $R_1 = R_2 = H$, $R_3 = tBu$ (8c)

W =  $R_1 = R_2 = H$, $R_3 = tBu$ (8d)

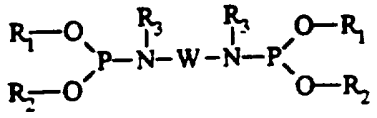
The results are presented in Table 2.

Table 2

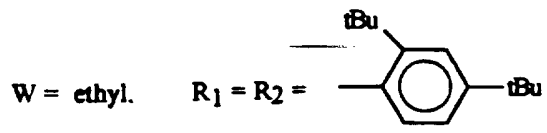
Example	Ligand	L/Rh	S_{ald}	conversion %
IIIa	**8a**	1.9	91.2	22.4 (6 h)
IIIb	**8b**	2.0	75.6	27.4 (16.5 h)
IIIc	**8c**	2.1	82.5	19.1 (16.5 h)
IIId	**8d**	2.2	81.0	47.7 (16.5 h)

Example IVa-d

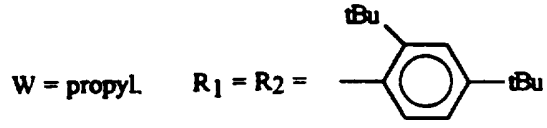
Example IIa was repeated with the phosphorus amide ligands of the general structure according to formula 9 and with various ligand/Rh ratios (mol/mol). The synthesis of the ligands according to the general formula (9) were all prepared in a similar manner as described for Ligand (9) by using the appropriate diamine bridge corresponding with the -N(R)-A-N(R)- group of formula (3c). The ligand/Rh ratio and the results are presented in Table 3.



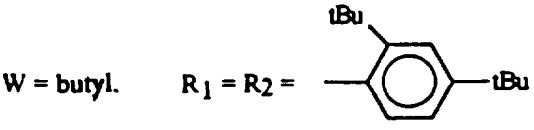
(9)



(9a)



(9b)



(9c)

Table 3

Example	ligand	L/Rh	S_{ald}	conversion %
IVa	**9a**	5	85.5	45 (21h)
IVb	**9b**	2	80.1	70 (21h)
IVc	**9c**	2	79.1	55.4 (20h)

Example Va-b

Example IIa was repeated with 2.5 g of a mixture of cis and trans 2-octene (22 mmol) instead of methyl 3-pentenoate. The results are given in Table 4.

Table 4

Example	Ligand	L/Rh	S_{ald}	conversion %
Va	**1**	2.2	100	19.0 (5h)
Vb	**9b**	2.2	99.3	49.6 (2h)

Example VIa-c

A 181 ml stainless steel autoclave was filled with 2 ml of a toluene solution containing 0.008 mmol $Rh(CO)_2acac$, 5 equivalents of the used ligand (see Example III for ligand 8b, 8c and 8d) and 18 ml toluene. The autoclave was pressurized to 1.5 MPa CO/H_2 (1/1 mol/mol) and the temperature was raised to 80°C. After stabilization of the temperature 20 mmol 1-octene and 1 ml decane (internal standard) was injected into the reactor. The pressure was further increased to 2.0 MPa CO/H_2 (1/1 mol/mol). The reaction was performed

batchwise and no additional CO or H_2 was added during the reaction. The composition was analyzed by gas chromatography and the results are presented in Table 5.

Table 5

Example	Ligand	L/Rh	S_{ald}	conversion %
VIa	8b	5	99	49 (2h)
VIb	8c	5	87	72 (2h)
VIc	8d	5	88	48 (2.5h)

Example VII a-c

Example I was repeated at 1.0 MPa (CO/H_2 = 1/1 mol/mol) with (a) Ligand (16), (b) Ligand (17) and (c) Ligand (18). The ligand/rhodium ratio varied in which the rhodium concentration was kept the same as in Example I.
The results are presented in Table 6.

Table 6

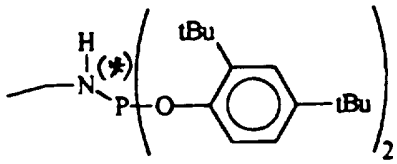
Example	Ligand	L/Rh	S_{ald}	conversion %
VIIa(*)	16	2.1	88.4	93.2 (48h)
VIIb	17	2.2	85.7	86.2 (22h)
VIIc	18	5	85.5	44.9 (21h)

T= 90°C, pressure = 0.25 MPa

Example VIII

A ligand with a dendrimer bridging compound with 32 end groups as represented with the following formula (10) was prepared as follows.

To 6.08 g (29.5 mmol 2,4-di-tert-butylphenol) in 350 ml toluene which was dried azeotropically, 10 ml of triethyl amine and subsequently 2.02 g (14.7 mmol) PCl_3 were added. After stirring overnight 5 ml triethylamine and 0.307 mmol of dendrimer PA 32 (as prepared in Example VII of WO-A-9314147) in 250 ml of toluene were added. After stirring overnight, the reaction mixture was filtered over Al_2O_3 twice. The solvent was evaporated and the ligand was purified by crystallistion from acetonitril and ethanol (twice). On average 90% of the N-groups were linked with the below group in the resulting compound.



(10)

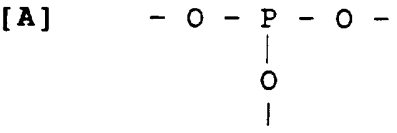
(*) one of the 32 N-groups of the fourth generation dendrimer compound.

Example IX

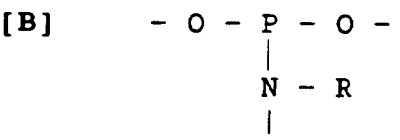
Example VII was repeated with a ligand according to formula (10). The phosphorus/rhodium (mol atoms P/mol rhodium) ratio was 4. The selectivity to aldehydes was 97% at 5% conversion after 18.5 hours of reaction.

C L A I M S

1. Process for preparing an aldehyde compound by hydroformylation of an ethylenically unsaturated organic compound in the presence of a catalyst system comprising of a multidentate phosphorus ligand and a Group 8-10 metal, characterized in that the multidentate phosphorus amide ligand consists of a multivalent bridging organic group connected to at least two trivalent phosphorus-containing groups of the formula

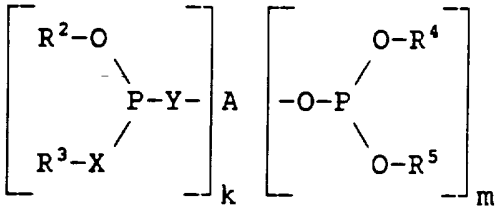


and



provided that at least one group of formula [B] is present, wherein R is hydrogen, an organic group, or $-SO_2R^1$, wherein R^1 is a C_{1-12} organic group, and wherein remaining free bonds of said trivalent phosphorus groups are linked to a mono- or di-valent organic group.

2. Process according to claim 1, characterized in that the phosphorus amide ligand is represented by the following formula:



(1)

in which each X, Y, R^2, R^3, R^4 and R^5 are the same

or different and in which either one of X or Y is a N(R) group while the other group is oxygen, A is a multi-valent (multi is equal to k+m) organic group with 2 to 30 carbon atoms, k is at least 1, m can be 0-5 and k+m is 2-6, R^2 and R^3 together and/or R^4 and R^5 together form one, optionally substituted, divalent organic group with 2 to 30 carbon atoms or R^2, R^3, R^4 and R^5 are independently, optionally substituted, monovalent organic groups with 1 to 20 carbon atoms.

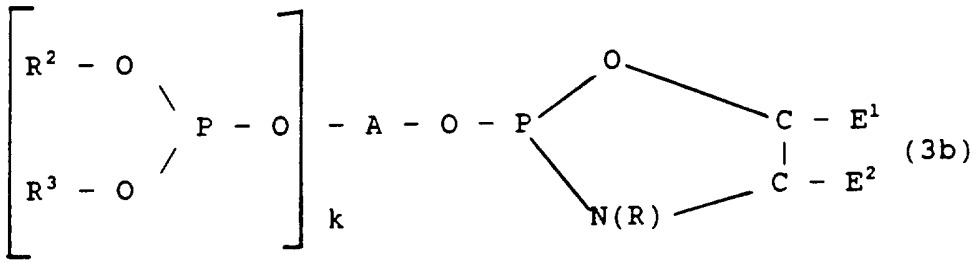
3. Process according to claim 2, characterized in that the phosphorus amide ligand is a bidentate phosphorus amide ligand with k+m is equal to 2.

4. Process according to any one of claims 1-3, characterized in that the Group 8-10 metal is rhodium.

5. Process according to any one of claims 1-4, characterized in that the ethylenically unsaturated organic compound is an internally ethylenically unsaturated organic compound.

6. Process according to claim 5, characterized in that the internally ethylenically unsaturated organic compound is a pentenenitrile, pentenoic acid or a C_1-C_6 alkyl pentenoate ester.

7. Multidentate phosphorus amide compound, characterized in that the compound is represented by the following general formula

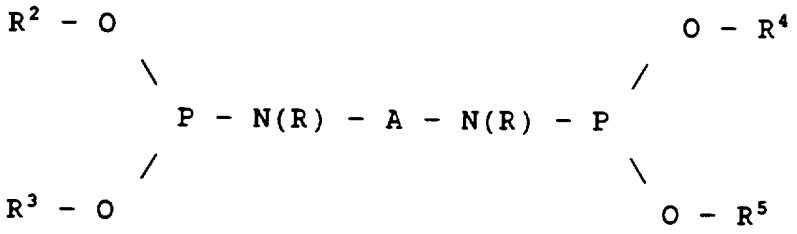


(3b)

in which R^2, R^3, A and R are as defined in claim 2, k is 1-5 and E^1 and E^2 are the same or different and in which E^1 and E^2 are hydrogen or a monovalent

organic group with 1 to 11 carbon atoms or in which E^1 and E^2 are one divalent organic group with 3 to 11 carbon atoms or R and E^2 are one divalent organic group with 3 to 12 carbon atoms and E^1 is hydrogen or a monovalent organic group with 1 to 11 carbon atoms, in which the possible remaining group bonded to the carbon atoms (C) is hydrogen.

8. Bidentate phosphorus amide compound, characterized in that the compound is represented by the following general formula



(3c)

in which R^2, R^3, A, R^4 and R^5 are the same as defined in claim 2.

9. Catalyst system comprising a Group 8-10 metal and a multidentate phosphorus amide ligand as described in any one of claims 1-3 or claims 7-8.

10. Catalyst system according to claim 9, characterized in that the Group 8-10 metal is rhodium.

INTERNATIONAL SEARCH REPORT

Inter ıal Application No
PCT/NL 95/00393

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C45/50 C07F9/6584 C07F9/6571

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)
IPC 6 C07C C07F

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 214 622 (UNION CARBIDE CORPORATION) 18 March 1987 cited in the application see claims ---	1
A	EP,A,0 473 543 (CIBA-GEIGY AG) 4 March 1992 cited in the application see claims ---	7
A	EP,A,0 540 025 (HIMONT INCORPORATED) 5 May 1993 see claims -----	8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date

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"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.

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Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer
Bonnevalle, E

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter nal Application No
PCT/NL 95/00393

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-214622	18-03-87	US-A-	4668651	26-05-87
		AU-B-	597593	07-06-90
		AU-B-	6237386	12-03-87
		CA-A-	1281704	19-03-91
		DE-A-	3685276	17-06-92
		JP-C-	1765977	11-06-93
		JP-B-	4051531	19-08-92
		JP-A-	62116535	28-05-87
		US-A-	4769498	06-09-88
EP-A-473543	04-03-92	US-A-	5075481	24-12-91
		US-A-	5075484	24-12-91
		US-A-	5075483	24-12-91
		JP-A-	4244093	01-09-92
		US-A-	5147911	15-09-92
		US-A-	5147910	15-09-92
		US-A-	5147909	15-09-92
EP-A-540025	05-05-93	IT-B-	1251754	23-05-95
		IT-B-	1251722	23-05-95
		AU-B-	2740692	06-05-93
		CA-A-	2081883	01-05-93
		FI-A-	924933	01-05-93
		JP-A-	6049086	22-02-94
		US-A-	5352830	04-10-94