

stability compared with corresponding systems which lack a tertiary amine.

The catalyst system according to the invention comprises a source of a Group VIII metal. The source of a Group VIII metal may be the metallic element or, preferably, a Group VIII metal compound.

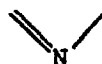
Examples of Group VIII metals are iron, cobalt, nickel, ruthenium, rhodium, palladium, iridium and platinum.

The catalyst system according to the invention preferably comprises a source of a palladium compound.

Examples of compounds of Group VIII metals include salts, for example salts of nitric acid; sulphuric acid; sulphonic acids; phosphonic acids; perhalic acids; carboxylic acids such as alkane carboxylic acids having not more than 12 carbon atoms, e.g. acetic acid; and hydrohalic acids. Since halide ions can be corrosive, salts of hydrohalic acids are not preferred. Other examples of compounds of Group VIII metals include complexes, such as complexes with acetylacetonate, phosphines and/or carbon monoxide. For example the compound of a Group VIII metal may be palladium acetylacetonate, tetrakis-triphenylphosphinepalladium, bis-tri-o-tolylphosphinepalladium acetate, bis-diphenyl-2-pyridylphosphinepalladium acetate, tetrakis-diphenyl-2-pyridylphosphinepalladium, bis-di-o-tolylpyridylphosphinepalladium acetate, or bis-diphenylpyridylphosphinepalladium sulphate.

The catalyst system used in the process according to the invention further comprises a phosphine having an aromatic substituent which contains an imino nitrogen atom.

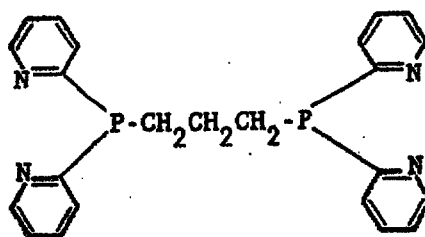
As used herein, the term "imino nitrogen atom" means a nitrogen atom which may be represented in the structural formula of the aromatic substituent containing it by the formula



For example, if the aromatic substituent is a pyridyl group, the structural formula of the aromatic substituent is



The phosphine preferably comprises one or two phosphorus atoms. Each phosphorus atom has three substituents. At least one of these substituents is an aromatic substituent which contains an imino nitrogen atom. The remaining substituents are preferably selected from optionally substituted aliphatic and aromatic hydrocarbyl groups. When the phosphine comprises more than one phosphorus atom, it is possible for one substituent to be shared by more than one phosphorus atom, as for example in



The aromatic substituent which contains an imino nitrogen is preferably a 6-membered ring containing one, two or three nitrogen atoms. The aromatic substituent may itself be optionally substituted.

When a substituent is said to be optionally substituted in this specification, unless otherwise stated, the substituent may be unsubstituted or substituted by one or more substituents. Examples of suitable substituents include halogen atoms; alkyl groups; alkoxy groups; haloalkyl groups; haloalkoxy groups; acyl groups; acyloxy groups; amino groups, preferably alkyl or dialkylamino groups; hydroxy groups; nitrile groups; arylamino groups; and aromatic hydrocarbyl groups.

An aliphatic hydrocarbyl group is preferably an alkyl group, for example a C₁₋₄ alkyl group; or a cycloalkyl group, for example a C₃₋₆ cycloalkyl group.

An aromatic hydrocarbyl group is preferably a phenyl group.

A halogen atom, as such or in a haloalkyl group, is preferably a fluorine, chlorine or bromine atom.

An acyl group in an acyl, acyloxy or acylamino group is preferably a C₂₋₅ alkanoyl group such as acetyl.

Examples of aromatic substituents containing an imino nitrogen atom are pyridyl, pyrazinyl, quinolyl, isoquinolyl, pyrimidinyl, pyridazinyl, cinnolinyl, triazinyl, quinoxaliny, and quinazolinyl. Preferred substituents are pyridyl and pyrimidyl.

An imino group in an aromatic substituent containing an imino nitrogen atom is preferably connected to a phosphorus atom through a single bridging carbon atom. For example, if the aromatic substituent is a pyridyl group, it is preferably connected through the carbon atom at the 2-position in the pyridyl group. Accordingly, examples of preferred aromatic substituents containing an imino nitrogen atom are 2-pyridyl; 2-pyrazinyl; 2-quinolyl; 1-isoquinolyl; 3-isoquinolyl; 2-pyrimidinyl; 3-pyridazinyl; 3-cinnolinyl; 2-triazinyl; 2-quinoxaliny; and 2-quinazolinyl. 2-Pyridyl, 2-pyrimidyl and 2-triazinyl are particularly preferred.

When the phosphine contains one phosphorus atom, it may conveniently be represented by the general formula



in which R¹ represents an aromatic substituent containing an imino nitrogen atom, and R² and R³, which may be the same or different, represent a group R¹ or an optionally substituted aliphatic or aromatic hydrocarbonyl group.

Particularly preferred phosphines are:

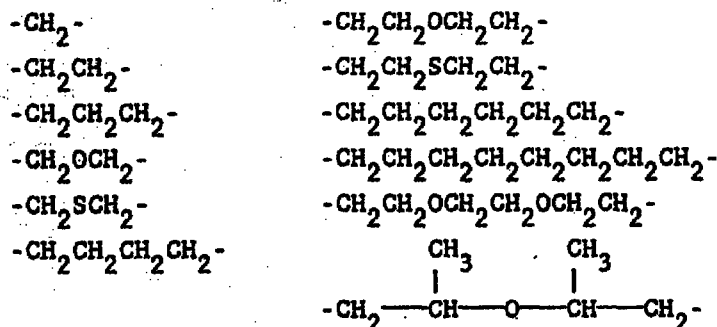
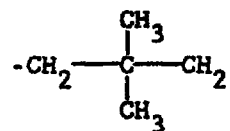
bisphenyl-(2-pyridyl)phosphine,
bis(2-pyridyl)phenylphosphine,
tris(2-pyridyl)phosphine,
diphenyl(6-methoxy-2-pyridyl)phosphine,
bis(6-ethoxy-2-pyridyl)phenylphosphine,
bis(6-chloro-2-pyridyl)phenylphosphine,
bis(6-bromo-2-pyridyl)phenylphosphine,
tris(6-methyl-2-pyridyl)phosphine,
bis(6-methyl-2-pyridyl)phenylphosphine,
bisphenyl(6-methyl-2-pyridyl)phosphine,
bis(3-methyl-2-pyridyl)phenylphosphine,
bisphenyl(4,6-dimethyl-2-pyridyl)phosphine,
di(n-butyl)-2-pyridylphosphine,
dimethyl-2-pyridylphosphine,
methyl phenyl-2-pyridylphosphine,
n-butyl tert-butyl 2-pyridylphosphine,
n-butyl(4-methoxyphenyl)(2-pyridyl)phosphine, and
methyl di(2-pyridyl)phosphine.

When the phosphine contains two phosphorus atoms, it may conveniently be represented by the general formula:

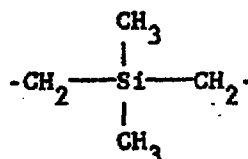


in which at least one of R⁴, R⁵, R⁶ and R⁷ represents an aromatic substituent containing an imino nitrogen atom, the remainder of R⁴, R⁵, R⁶ and R⁷ independently represent an optionally substituted hydrocarbonyl or heterocyclic group, and X represents a divalent bridging group containing from 1 to 10 atoms in the bridge.

The bridging group represented by X is preferably a hydrocarbon, an ether or a thio-ether residue. For example, the bridging group may be an alkylene chain which is optionally interrupted by one or more oxygen and/or sulphur atoms, as in:



It may also be a silane residue, as in



The bridging group preferably contains from 2 to 8 atoms in the bridge, more preferably from 3 to 5 atoms. For example, when the bridging group is a propane residue, the bridge contains 3 atoms.

Particularly high reaction rates have been obtained using organic diphosphines of general formula (II) in which X represents a dialkyl ether residue. Accordingly, the use of such compounds is preferred in the process according to the invention.

The remainder of R⁴, R⁵, R⁶ and R⁷ are preferably optionally substituted alkyl or optionally substituted phenyl groups. Most preferably they are optionally substituted phenyl groups.

Examples of organic diphosphines which may be used in the process according to the invention are:

bis[(2-pyridyl)phenylphosphino]methane,
 1,2-bis[(2-pyridyl)phenylphosphino]ethane,
 1,3-bis[(2-pyridyl)phenylphosphino]propane,
 1,5-bis[(2-pyridyl)phenylphosphino]-3-oxapentane,
 1,8-bis[(2-pyridyl)phenylphosphino]-3,6-dioxaoctane,
 1,3-bis[(2-pyridyl)butylphosphino]propane, and
 1,3-bis[di-(2-pyridyl)phosphino]propane.

The catalyst system used in the process according to the invention further comprises a protonic acid. The function of the protonic acid is to provide a source of protons. Accordingly, the protonic acid may be generated *in situ*.

Preferably the protonic acid is selected from acids having a non-coordinating anion. Examples of such acids include sulphuric acid; a sulphonic acid, e.g. an optionally substituted hydrocarbylsulphonic acid such as benzenesulphonic acid, p-toluenesulphonic acid, naphthalenesulphonic acid; an alkylsulphonic acid such as methanesulphonic acid or tert-butylsulphonic acid, or 2-hydroxypropanesulphonic acid, trifluoromethanesulphonic acid, chlorosulphonic acid or fluorosulphonic acid; a phosphonic acid, e.g. orthophosphonic acid, pyrophosphonic acid or benzenephosphonic acid; a carboxylic acid, e.g. chloroacetic acid, dichloroacetic acid, trichloroacetic acid, trifluoroacetic acid, oxalic acid or terephthalic acid; or a perhalic acid such as perchloric acid. The protonic acid may also be an acidic ion exchange resin.

The catalyst system used in the process according to the invention may be homogeneous or heterogeneous. Preferably it is homogeneous.

The ratio of the number of moles of phosphine per gram atom of Group VIII metal is not critical. Preferably it is in the range of from 1 to 1000, more preferably from 2 to 500, especially from 10 to 100.

The ratio of the number of moles of phosphine per mole of protonic acid is not critical. The function of the protonic acid is to provide a source of protons. Accordingly, the protonic acid may be generated *in situ*. Preferably it is in the range of from 0.1 to 50, more preferably from 0.5 to 5.

Examples of tertiary amines include optionally substituted aromatic, heterocyclic tertiary amines such as pyridines, quinolines, isoquinolines, pyrimidines, pyrazines, triazoles, triazines, pyridazines, purines, thiazoles, benzimidazoles, oxazoles, pyrazoles and isothiazoles; aliphatic tertiary amines such as dialkylamines, e.g. dimethylamine or diethylamine; and optionally substituted tertiary anilines such as, N,N-dialkylanilines, e.g. N,N-

dimethylaniline.

Preferably the tertiary amine is a pyridine or an N,N-dialkylaniline.

Preferred examples of pyridines are pyridine, alkyl-substituted pyridines such as 2,6-dimethylpyridine and polyvinylpyridine.

The number of equivalent of tertiary amine present per mole of protons is preferably at least 0.5, more preferably at least 1, even more preferably at least 2, especially at least 5. Depending upon the particular carbonylation process in which the catalyst system is to be used, the tertiary amine is preferably present in catalytic quantities or in solvent quantities.

When the tertiary amine is present in catalytic quantities, the number of equivalent of tertiary amine per mole of protons is preferably in the range of from 0.1 to 200, more preferably 0.5 to 100, especially 1 to 50.

When the tertiary amine is present in solvent quantities, the number of equivalents of tertiary amine per mole of protons is preferably in the range of from 1 to 2,500, more preferably 1.5 to 1500, especially 10 to 1000.

For the avoidance of doubt, the tertiary amine may not be a phosphine, for example the phosphine having an aromatic substituent containing an imino nitrogen atom.

Our co-pending British patent application number 9002491.0 discloses and claims:

a carbonylation catalyst system, which comprises:

- a) a source of a Group VIII metal;
- b) a source of a phosphine having an aromatic substituent containing an imino nitrogen atom;
- c) a source of protons; and
- d) a source of an alkylsulphonate anion, and the use of such a catalyst composition in the carbonylation of an unsaturated compound.

Our co-pending British patent application number 9002508.1 discloses and claims a catalyst system, which comprises

- a) a source of a Group VIII metal, and
- b) a phosphine of general formula:



in which R¹, R² and R³ are independently selected from an optionally substituted aryl group and a group of general formula:



wherein each of A, X, Y and Z is independently selected from a nitrogen atom, a CH group and a group of formula CR, wherein R represents a hydroxyl group, an amino group, an amido group, a cyano group, an acyl group, an acyloxy group, a halogen atom, an optionally substituted hydrocarbyl group or an optionally substituted hydrocarbyloxy group, it also being possible for two adjacent CR groups to form a ring, provided that at least one of R¹, R² and R³ represents a group of formula (III), in which at least one of A and Z represents a group of formula CR; or an acid addition salt thereof, and the use of such a catalyst composition in the carbonylation of an olefinically or acetylenically unsaturated compound.

Our co-pending British patent application number 9002509.9 discloses and claims:

a catalyst system, which comprises:

- a) a Group VIII metal compound, and
- b) a phosphine of formula



wide limits and generally lies within the range of 0.01:1 to 100:1.

The carbon monoxide required for the process according to the present invention may be used in a practically pure form or diluted with an inert gas, for example nitrogen. The presence of more than small quantities of hydrogen in the gas stream is undesirable on account of the hydrogenation of the unsaturated hydrocarbon which may occur under the reaction conditions. In general, it is preferred that the quantity of hydrogen in the gas stream supplied is less than 5 vol%.

The catalyst systems used in the process according to the invention are constituted in a liquid phase. They may be prepared by any convenient method. Thus they may be prepared by combining a separate Group VIII metal compound, the phosphine (I), the protonic acid and the tertiary amine in a liquid phase. Alternatively, they may be prepared by combining a Group VIII metal compound and an acid addition salt of the phosphine and the tertiary amine in a liquid phase. Alternatively, they may be prepared from a Group VIII metal compound which is a complex of a Group VIII metal with the phosphine, the protonic acid and the tertiary amine in a liquid phase. Alternatively they may be prepared by combining a Group VIII metal compound, the phosphine and an acid addition salt of the tertiary amine in a liquid phase.

The liquid phase may conveniently be formed by one or more of the reactants with which the catalyst system is to be used. Alternatively it may be formed by a solvent. It may also be found by one of the components of the catalyst system, for example a tertiary amine.

Phosphines having an aromatic substituent which contains an imino nitrogen atom are known in the art. They are conveniently prepared by reacting a phosphorus halide or alkali metal phosphide with a appropriate alkali metal or halide derivative of an aromatic compound containing an imino nitrogen atom.

Organic diphosphines having at least one aromatic substituent containing an imino nitrogen atom may be prepared, for example, according to the methods described in European patent application publication number EP-A2-0305012. Thus, for example, they may be prepared by reacting an appropriate alkali metal phosphide with an appropriate dihalo compound.

The invention will now be illustrated by the following examples.

Preparation 1

Preparation of diphenyl-(6-methyl-2-pyridyl)-phosphine

All manipulations were carried out in an inert atmosphere (nitrogen or argon). Solvents were dried and distilled prior to use. 36 ml of a 1.6M n-butyllithium solution in hexane was added to 40 ml diethyl ether, and the mixture was cooled to -40 °C. To the stirred mixture was added in the course of 20 minutes a solution of 10 g 2-bromo-6-methylpyridine in 15 ml diethyl ether; during this addition, the temperature was kept at -40 °C. After the addition, the temperature was raised to -5 °C, kept there for 5 minutes, and then lowered again to -40 °C. A solution of 12.8 g chlorodiphenylphosphine in 15 ml diethyl ether was added in the course of 15 minutes to the stirred mixture. After the addition, the mixture was warmed to room temperature, the solvents were removed in vacuo, and 50 ml water and 50 ml dichloromethane were added. After 5 minutes of vigorous stirring, the dichloromethane layer was separated. The water layer was extracted with two 50 ml portions of dichloromethane, the organic fractions were combined, and the solvent removed in vacuo. The residue was crystallized from toluene/hexane to afford 12 g (75%) of diphenyl-(6-methyl-2-pyridyl)-phosphine as off-white crystals. The product was characterized by ^{31}P NMR: $\delta_p = -5.6$ ppm.

Preparation 2

Preparation of diphenyl-(3-methyl-2-pyridyl)-phosphine

This compound was prepared as described in Preparation 1, but using 10.0 g 2-bromo-3-methylpyridine instead of the 2-bromo-6-methylpyridine. It was characterized by ^{31}P NMR: $\delta_p = -8.1$ ppm.

Preparation 3

Preparation of phenyl-bis(6-methyl-2-pyridyl)-phosphine

This compound was prepared as described in Preparation 1, but using 5.2 g phenyldichlorophosphine instead of the chlorodiphenylphosphine. It was characterized by ^{31}P NMR: $\delta_p = -5.1$ ppm.

Preparation 4Preparation of tris(6-methyl-2-pyridyl)-phosphine

This compound was prepared as described in Preparation 1, but using 2.7 g phosphorus trichloride instead of the chlorodiphenylphosphine. It was characterized by ^{31}P NMR: $\delta_p = -3.8$ ppm.

Preparation 5Preparation of diphenyl-(4,6-dimethyl-2-pyridyl)-phosphine

This compound was prepared as described in Preparation 1, but using 10.8 g 2-bromo-4,6-dimethylpyridine instead of the 2-bromo-6-methylpyridine. It was characterized by ^{31}P NMR: $\delta_p = -5.6$ ppm.

Preparation 6Preparation of diphenyl-(6-methoxy-2-pyridyl)-phosphine

2.7 g Sodium was added to 100 ml liquid ammonia at -80°C , and then 15.2 g triphenylphosphine was added in 6 portions with stirring. The solution was slowly warmed to -40°C , kept at that temperature for 30 min, and then cooled again to -80°C . Then, 3.1 g ammonium chloride was added to the stirred solution, followed by 10.9 g 2-bromo-6-methoxypyridine in three portions. The cooling bath was removed and the ammonia was allowed to evaporate. The residue was worked up with water/dichloromethane as described in Preparation 1. Crystallization from hexane afforded 7 g of a somewhat impure product (characterized by ^{31}P NMR: $\delta_p = -4.4$ ppm) which was used as such in the following Examples.

Preparation 7Preparation of di(n-butyl)-2-pyridyl phosphine

To a magnetically stirred solution of 2.5 g phenyl(2-pyridyl) $_2\text{P}$ in 20 ml tetrahydrofuran, cooled to -80°C , was added in the course of 10 min 5.9 ml of a 1.6 M solution of n-butyliLi in hexane. The resulting deep-red solution was allowed to warm to room temperature, and analysis of the solution by ^{31}P NMR showed it to contain the phosphide (n-butyl)(2-pyridyl)PLi as the only phosphorus-containing compound ($\delta_p = -16.3$ ppm).

The solution was cooled to -40°C and a solution of 1.3 g 1-bromobutane in 10 ml tetrahydrofuran was added. The mixture was again warmed to room temperature, the solvents were removed in vacuo, and 25 ml of diethylether and 10 ml of water were added. After 10 min of stirring, the organic layer was separated and the water layer was extracted with 10 ml of ether. The organic layers were combined and the solvent was removed in vacuo (66 Pa). The resulting light-yellow liquid was analyzed by ^1H , ^{13}C and ^{31}P NMR and shown to consist of a 1:1 (molar ratio) mixture of 2-phenylpyridine and (n-butyl) $_2$ (2-pyridyl)P ($\delta_p = -19.5$ ppm).

Preparation 8Preparation of dimethyl 2-pyridyl phosphine and methylphenyl-2-pyridyl phosphine

The method of Preparation 7 was repeated, except that a 1.6 M solution of methylLi in diethylether was used instead of the n-butyliLi solution, and 1.3 g iodomethane instead of the bromobutane. The reaction product was a mixture of (methyl) $_2$ 2-pyridylP, methyl phenyl 2-pyridylP and 2-phenyl pyridine in the approximate ratio 70:30:60, from which the (methyl) $_2$ (2-pyridyl)P was isolated by distillation.

The physical characteristics of the products were $\delta_p = -41.2$ ppm (dimethyl-2-pyridylphosphine) and $\delta_p = -24.1$ ppm (methylphenyl-2-pyridylphosphine).

Preparation 9Preparation of n-butyl tert-butyl 2-pyridyl phosphine

The method of Preparation 7 was repeated, except that 5.6 ml of a 1.7 M solution of t-butyliLi in pentane was used instead of the n-butyliLi solution. The final product was identified as n-butyl t-butyl 2-pyridylP by NMR

analysis ($\delta_p = -7.4$ ppm).

Preparation 10

Preparation of dimethyl 2-pyridylphosphine

The method of Preparation 8 was repeated, except that 1.91 g methyl(2-pyridyl)₂P and only 0.7 g iodomethane were used. Workup as described in Preparation 1 afforded dimethyl 2-pyridyl phosphine, which was further purified by distillation (65% yield). ($\delta_p = -41.2$ ppm).

Preparation 11

Preparation of n-butyl(4-methoxyphenyl)(2-pyridyl)phosphine

All manipulations were carried out in an inert atmosphere (nitrogen or argon). Solvents were dried and distilled prior to use. 18 ml of a 1.6M n-butyllithium solution in hexane was added to 30 ml diethyl ether, and the mixture was cooled to -40°C . To the stirred mixture was added in the course of 20 minutes a solution of 4.6 g 2-bromopyridine in 15 ml diethyl ether; during this addition, the temperature was kept at -40°C . After the addition, the temperature was raised to -5°C , kept there for 5 minutes, and then lowered again to -40°C . The resulting solution was added to a cooled (-40°C) solution of 7.6 g 4-methoxyphenyl-bis(2-pyridyl)-phosphine in 30 ml THF. The mixture was warmed to room temperature. After stirring for 10 minutes, the solvents were removed in vacuo. Water (25 ml) and dichloromethane (25 ml) were added. After 5 minutes of vigorous stirring, the dichloromethane layer was separated. The water layer was extracted with two 25-ml portions of dichloromethane, the organic fractions were combined, and the solvent removed in vacuo. The residue was distilled, giving 4.7 g (60%) of (n-butyl)(4-methoxyphenyl)(2-pyridyl)phosphine as a yellowish liquid. The product was characterized by ^{31}P NMR: $\delta_p = -14.9$ ppm.

In this experiment, n-butyllithium is believed to react with 2-bromopyridine to afford a mixture of n-butyllithium bromide and 2-pyridyllithium. Then the 2-pyridyllithium reacts with 4-methoxy-bis(2-pyridyl)phosphine to afford 4-methoxyphenyl(2-pyridyl)lithium phosphide (and 2,2'-bipyridine). The lithium phosphide then reacts with n-butyllithium bromide to afford (n-butyl)(4-methoxyphenyl)(2-pyridyl)phosphine.

Preparation 12

Preparation of methyl di(2-pyridyl)phosphine

All manipulations were carried out in an inert atmosphere (nitrogen or argon). Solvents were dried and distilled prior to use. 36 ml of a 1.6M n-butyllithium solution in hexane was added to 40 ml diethyl ether, and the mixture was cooled to -40°C . To the stirred mixture was added in the course of 20 minutes a solution of 9.2 g 2-bromopyridine in 15 ml diethyl ether; during this addition, the temperature was kept at -40°C . After the addition, the temperature was raised to -5°C , kept there for 5 minutes, and then lowered again to -40°C . A solution of 3.4 g methylchlorophosphine in 15 ml diethyl ether was added to the stirred mixture. After the addition, the mixture was warmed to room temperature, the solvents were removed in vacuo, and 50 ml water and 50 ml dichloromethane were added. After 5 minutes of vigorous stirring, the dichloromethane layer was separated. The water layer was extracted with two 50-ml portions of dichloromethane, the organic fractions were combined, and the solvent removed in vacuo. The residue was distilled, giving 4.0 g (68%) of methyl-bis(2-pyridyl)phosphine as a yellowish liquid. The product was characterized by ^{31}P NMR: $\delta_p = -20.5$ ppm.

Example 1

A 250 ml stainless steel magnetically stirred autoclave was filled with 0.1 mmol palladium(II)acetate, 5 mmol bisphenyl(2-pyridyl)phosphine, 4 mmol paratoluenesulphonic acid, 50 ml (620 mmol) pyridine and 10 ml (65 mmol) triethylsilanol. Air was then evacuated from the autoclave, and then carbon monoxide (30 bar) and ethylene (20 bar) were added. The autoclave was then sealed and heated to a temperature of 110°C . After a reaction time of 4.5 hours, a sample of the contents of the autoclave was withdrawn and analysed by gas liquid chromatography.

Triethylsilylpropionate was formed with a selectivity of 60% (based on silanol). Di-triethylsilyl ether was also formed, with a selectivity of about 40% (based on silanol). The mean conversion rate was calculated to 200 mol ethene/gram atom Pd/hour.

Comparative Example A

The method of Example 1 was repeated, but using triphenylphosphine instead of bisphenyl(2-pyridyl)phosphine, and withdrawing a sample of the contents of the autoclave after 5 hours instead of 4.5 hours. Only traces of triethylsilyl propionate were detected.

Comparative Example B

The method of Comparative Example A was repeated, but using 50 ml methylpropionate instead of 50 ml pyridine and heating to 80 °C instead of 110 °C. Di(triethylsilyl)ether was formed with a selectivity of >90%. Only traces of triethylsilylpropionate were detected.

Example 2

A 250 ml stainless steel, magnetically stirred autoclave was filled with 0.1 mmol palladium(II)acetate, 5 mmol bisphenyl(2-pyridyl)phosphine, 4 mmol p-toluenesulphonic acid, 40 ml (500 mmol) pyridine, 20 ml methanol and 5 g paraformaldehyde. Air was then evacuated from the autoclave, and then carbon monoxide (30 bar) and ethene (20 bar) were added. The autoclave was then sealed and heated to a temperature of 110 °C. After a reaction time of 5 hours, a sample of the contents of the autoclave was withdrawn and analysed by gas liquid chromatography. Two products were found; methoxymethylpropionate, which had been formed with a selectivity of 10%, and methylpropionate, which had been formed with a selectivity of 90%. The mean reaction rate was calculated to be 200 mol ethene/gram atom Pd/hour.

Comparative Example C

The method of Example 2 was repeated, but using triphenylphosphine instead of bisphenyl(2-pyridyl)phosphine. Only traces of carbonylated products were observed.

Comparative Example D

The method of Example 2 was repeated, but using no pyridine, and 50 ml methanol instead of 20 ml methanol. The sample of the contents of the autoclave was withdrawn after a reaction time of 2 hours. Only traces of methoxymethylpropionate were observed. Methylpropionate was found to have been formed with a selectivity of >95%. The mean reaction rate was calculated to be 1000 mol ethene/gram atom Pd/hour.

Example 3

The method of Example 2 was repeated, but using 40 ml (350 mmol) 2,6-dimethylpyridine instead of 40 ml pyridine, heating to 125 °C instead of 110 °C, and analysing a sample of the contents of the autoclave after 4.5 hours instead of 5 hours. Methoxymethylpropionate was found to have been formed with a selectivity of 35%, and methylpropionate with a selectivity of 60%. The mean reaction rate was calculated to be 150 mol ethene/gram atom Pd/hour.

Example 4

The method of Example 2 was repeated, but using 40 ml (350 mmol) 2,6-dimethylpyridine instead of pyridine, 10 ml methanol instead of 20 ml methanol and heating to 125 °C instead of 110 °C. Methoxymethylpropionate was found to have been formed with a selectivity of 60%, and methyl propionate with a selectivity of 30%. The mean reaction rate was calculated to be 100 mol ethene/gram atom Pd/hour.

Example 5

A 250 ml stainless steel magnetically stirred autoclave was filled with 0.1 mmol palladium(II)acetate, 2 mmol bisphenyl(2-pyridyl)phosphine, 10 mmol paratoluenesulphonic acid, 40 ml (500 mmol) pyridine and 20 ml methanol. Air was then evacuated from the autoclave and then 20 bar ethene and 30 bar carbon monoxide were added. The autoclave was then sealed and heated to 110 °C. After a reaction time of 5 hours, a sample of the contents of the autoclave was withdrawn and analysed by gas liquid chromatography. Methylpropionate was found to have been formed. The mean reaction rate was calculated to be 300 mol ethene/gram atom Pd/hour. No methyltriphenyl-

phosphonium tosylate was detected, indicating that the catalyst had remained stable during the course of the reaction.

5 Comparative Example E

The method of Example 5 was repeated, but using triphenylphosphine instead of bisphenyl(2-pyridyl)phosphine. Methyl propionate was detected, but the mean reaction rate was calculated to be less than 10 mol ethene/gram atom Pd/hour.

10

Comparative Example F

The method of Example 5 was repeated, but using tris(p-chlorophenyl)phosphine instead of bisphenyl(2-pyridyl)phosphine, 4 mmol paratoluenesulphonic acid, heating to 130 °C, and withdrawing a sample from the autoclave after 4 hours. Methyl propionate was detected. The mean reaction rate was calculated to be less than 10 mol ethene/gram atom Pd/hour.

15

Example 6

The method of Example 5 was repeated, but using 40 ml (320 mmol) N,N-dimethylaniline instead of 40 ml pyridine, heating to 100 °C instead of 110 °C, and withdrawing a sample from the autoclave after 1½ hour instead of 5 hours. Methyl propionate had been formed. The mean reaction rate was calculated to be 700 mol ethene/gram atom Pd/hour.

20

25 Example 7

The method of Example 5 was repeated, but using 20 ml (270 mmol) propionic acid instead of 20 ml methanol, and heating to 90 °C instead of 110 °C. Propionic anhydride was formed. The mean reaction rate was calculated to be 250 mol ethene/gram atom Pd/hour.

30

Example 8

The method of Example 5 was repeated, but using 5 mmol bisphenyl(2-pyridyl)phosphine, 4 mmol paratoluenesulphonic acid, 30 ml methanol, and heating for 3 hours instead of 5 hours. Methyl propionate was formed. The mean conversion rate was calculated to be 800 mol ethene/gram atom Pd/hour.

35

Example 9

The method of Example 5 was repeated, but using 5 mmol bisphenyl(2-pyridyl)phosphine, 4 mmol trifluoromethanesulphonic acid, and withdrawing a sample of the contents of the autoclave after 3 hours. Methyl propionate was formed. The mean reaction rate was calculated to be 1000 mol ethene/gram atom Pd/hour.

40

Example 10

The method of Example 5 was repeated, but using 5 mmol bisphenyl(2-pyridyl)phosphine, 4 mmol paratoluenesulphonic acid, 50 ml methanol instead of 20 ml, and 10 g (95 mmol) poly-4-vinylpyridine (cross-linked) instead of 40 ml pyridine. Methyl propionate was formed. The mean reaction rate was calculated to be 400 mol ethene/gram atom Pd/hour.

45

50 Example 11

A 300 ml magnetically-stirred stainless steel autoclave was successively filled with 0.025 mmol palladium(II)acetate, 1 mmol bisphenyl (6-methyl-2-pyridyl) phosphine, 2 mmol 2-methyl-2-propylsulphonic acid, 30 ml methyl methacrylate as solvent, 30 ml methanol and 10 mmol dimethylaniline. Air was then evacuated from the autoclave, and then 30 ml propyne containing 0.4% allene was added. Carbon monoxide was then added to a pressure of 60 bar. The autoclave was then sealed and heated to a temperature of 60 °C. After a reaction time of 0.1 hour at 60 °C, a sample of the contents of the autoclave was analyzed by gas liquid chromatography. From the results of the analysis, the selectivity to methyl methacrylate was calculated to be 99.94% and the mean conversion rate was calculated to be 90,000 mol propyne/gram atom Pd/hour.

55

Examples 12 to 18 and Comparative Example G

The method of Example 11 was repeated using different tertiary amines, and different amounts of allene in the propyne. The results are summarized in Table 1.

The results demonstrate that the inhibitory effect of allene on the catalyst can be counteracted by using tertiary amines.

10

15

20

25

30

35

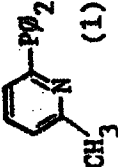
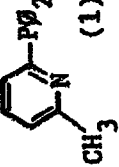
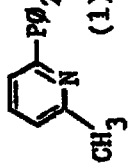
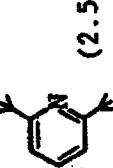
40

45

50

55

Table 1
 Carbonylation of Propyne and Methanol to give methyl methacrylate

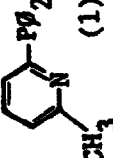
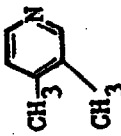
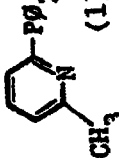
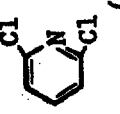
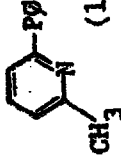
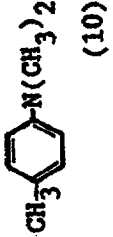
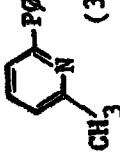
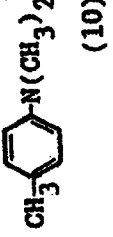
Example	Ligand (mmol)	Acid (mmol)	Solvent	Promoter (mmol)	% allene	Temp (°C)	Selectivity (%)	Mean Conversion rate (mol propyne/gat. Pd/hr)
11	 (1)	CH ₃ SO ₃ H (2)	MMA	 (10)	0.4	60	99.94	90,000
12	 (1)	CH ₃ SO ₃ H (2)	MMA	 (2.5)	0.4	60	99.0	67,000
13	 (1)	CH ₃ SO ₃ H (2)	MMA	 (20)	0.4	60	99.94	18,000
14	 (1)	CH ₃ SO ₃ H (2)	MMA	 (2.5)	0.4	60	99.9	30,000

Key

MMA Methylmethacrylate

Ø Phenyl group

Table 1 (Cont'd)

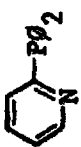
Example	Ligand (mmol)	Acid (mmol)	Solvent	Promoter (mmol)	% allene	Temp (°C)	Selectivity (%)	Mean Conversion rate (mol propyne/gat. Pd/hr)
15	 (1)	CH ₃ SO ₃ H (2)	MMA	 (2.5)	0.4	60	99.9	9,000
16	 (1)	CH ₃ SO ₃ H (2)	MMA	 (2.5)	0.4	60	99.9	15,000
17	 (1)	CH ₃ SO ₃ H (2)	MMA	 (10)	2.0	60	99.9	7,000
18	 (3)	(CH ₃) ₃ CSO ₃ H (2)	MMA	 (10)	7.0	45	99.9	6,000

Key

MMA Methylmethacrylate

Ø Phenyl group

Table 1 (Cont'd)

Example	Ligand (mmol)	Acid (mmol)	Solvent	Promoter (mmol)	% allene	Temp (°C)	Selectivity (%)	Mean Conversion rate (mol propyne/gat. Pd/hr)
G		CH ₃ SO ₃ H	MMA	None	0.4	60	98.9	7,000
	(1)	(2)						

Key

MMA Methylmethacrylate

Ø Phenyl group

**Claims****Claims for the following Contracting States : BE, DE, FR, GB, IT, NL**

1. A catalyst system, which comprises:
 - a) a source of a Group VIII metal;
 - b) a phosphine having an aromatic substituent which contains an imino nitrogen atom;
 - c) a source of protons; and
 - d) a tertiary amine.
2. A catalyst system as claimed in claim 1, in which the source of a Group VIII metal is a palladium compound.
3. A catalyst system as claimed in claim 1 or 2, in which an imino group in an aromatic substituent containing an imino nitrogen atom is linked to a phosphorus atom through a single bridging carbon atom.
4. A catalyst system as claimed in claim 3, in which the phosphine is a 2-pyridyl, 2-pyrimidyl or 2-triazinyl-phosphine.
5. A catalyst system as claimed in any one of claims 1 to 4, in which the tertiary amine is an optionally substituted heterocyclic tertiary amine, an aliphatic tertiary amine or an optionally substituted tertiary aniline.
6. A catalyst system as claimed in claim 5, in which the tertiary amine is a pyridine or an N,N-dialkylaniline.
7. A catalyst system as claimed in any one of claims 1 to 6, in which the number of equivalents of tertiary amine per mole of protons is at least 1.
8. A catalyst system as claimed in claim 7, in which the number of equivalents of tertiary amine per mole of protons is in the range of from 1.5 to 1,500.
9. The use of a catalyst system as defined in claim 1 in the carbonylation of an acetylenically or olefinically unsaturated compound.
10. A process for the carbonylation of an acetylenically or olefinically unsaturated compound, which comprises reacting an acetylenically or olefinically unsaturated compound in the presence of a catalyst system as defined in claim 1.
11. A process as claimed in claim 10, in which a nucleophilic compound having a removable hydrogen atom is present.
12. A process as claimed in claim 11, in which the nucleophilic compound having a removable hydrogen atom is a hydroxyl-containing compound.
13. A process as claimed in claim 12, in which the hydroxyl-containing compound is an alcohol, water, a carboxylic acid or a silanol.
14. A process as claimed in claim 13 in which the hydroxyl-containing compound is a tertiary alkanol or a silanol.

Claims for the following Contracting State : ES

1. A process for preparing a catalyst system, which comprises combining:
 - a) a source of a Group VIII metal;
 - b) a phosphine having an aromatic substituent which contains an imino nitrogen atom;
 - c) a source of protons; and
 - d) a tertiary amine.
2. A process as claimed in claim 1, in which the source of a Group VIII metal is a palladium compound.
3. A process as claimed in claim 1 or 2, in which an imino group in an aromatic substituent containing an imino nitrogen atom is linked to a phosphorus atom through a single bridging carbon atom.



4. A process as claimed in claim 3, in which the phosphine is a 2-pyridyl, 2-pyrimidyl or 2-triazinylphosphine.
5. A process as claimed in any one of claims 1 to 4, in which the tertiary amine is an optionally substituted heterocyclic tertiary amine, an aliphatic tertiary amine or an optionally substituted tertiary aniline.
6. A process as claimed in claim 5, in which the tertiary amine is a pyridine or an N,N-dialkylaniline.
7. A process as claimed in any one of claims 1 to 6, in which the number of equivalents of tertiary amine per mole of protons is at least 1.
8. A process as claimed in claim 7, in which the number of equivalents of tertiary amine per mole of protons is in the range of from 1.5 to 1,500.
9. The use of a catalyst system as prepared by the process of claim 1 in the carbonylation of an acetylenically or olefinically unsaturated compound.
10. A process for the carbonylation of an acetylenically or olefinically unsaturated compound, which comprises reacting an acetylenically or olefinically unsaturated compound in the presence of a catalyst system as defined in claim 1.
11. A process as claimed in claim 10, in which a nucleophilic compound having a removable hydrogen atom is present.
12. A process as claimed in claim 11, in which the nucleophilic compound having a removable hydrogen atom is a hydroxyl-containing compound.
13. A process as claimed in claim 12, in which the hydroxyl-containing compound is an alcohol, water, a carboxylic acid or a silanol.
14. A process as claimed in claim 13 in which the hydroxyl-containing compound is a tertiary alkanol or a silanol.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB, IT, NL

1. Ein Katalysatorsystem, welches umfaßt:
 - a) eine Quelle für ein Metall der Gruppe VIII;
 - b) ein Phosphin mit einem aromatischen Substituenten, der ein Iminostickstoffatom enthält;
 - c) eine Quelle für Protonen; und
 - d) ein tertiäres Amin.
2. Ein Katalysatorsystem, wie in Anspruch 1 beansprucht, in welchem die Quelle für ein Metall der Gruppe VIII eine Palladiumverbindung ist.
3. Ein Katalysatorsystem, wie in Anspruch 1 oder 2 beansprucht, in welchem eine Iminogruppe in einem aromatischen Substituenten mit einem Iminostickstoffatom über ein einzelnes Brücken-Kohlenstoffatom an ein Phosphoratom gebunden ist.
4. Ein Katalysatorsystem, wie in Anspruch 3 beansprucht, in welchem das Phosphin ein 2-Pyridyl-, 2-Pyrimidyl- oder 2-Triazinylphosphin ist.
5. Ein Katalysatorsystem, wie in einem der Ansprüche 1 bis 4 beansprucht, in welchem das tertiäre Amin ein gegebenenfalls substituiertes heterocyclisches tertiäres Amin, ein aliphatisches tertiäres Amin oder ein gegebenenfalls substituiertes tertiäres Anilin ist.
6. Ein Katalysatorsystem, wie in Anspruch 5 beansprucht, in welchem das tertiäre Amin ein Pyridin oder ein N,N-Dialkylanilin ist.



7. Ein Katalysatorsystem, wie in einem der Ansprüche 1 bis 6 beansprucht, in welchem die Anzahl an Äquivalenten des tertiären Amins je Mol Protonen mindestens 1 ist.
8. Ein Katalysatorsystem, wie in Anspruch 7 beansprucht, in welchem die Anzahl an Äquivalenten des tertiären Amins je Mol Protonen im Bereich von 1,5 bis 1500 liegt.
9. Die Verwendung eines Katalysatorsystems, wie in Anspruch 1 beansprucht, beim Carbonylieren einer acetylenisch oder olefinisch ungesättigten Verbindung.
10. Ein Verfahren zum Carbonylieren einer acetylenisch oder olefinisch ungesättigten Verbindung, welches das Umsetzen einer acetylenisch oder olefinisch ungesättigten Verbindung in Gegenwart eines Katalysatorsystems, wie in Anspruch 1 definiert, umfaßt.
11. Ein Verfahren, wie in Anspruch 10 beansprucht, in welchem eine nukleophile Verbindung mit einem entfernbaren Wasserstoffatom vorliegt.
12. Ein Verfahren, wie in Anspruch 11 beansprucht, in welchem die nukleophile Verbindung mit einem entfernbaren Wasserstoffatom eine hydroxylhaltige Verbindung ist.
13. Ein Verfahren, wie in Anspruch 12 beansprucht, in welchem die hydroxylhaltige Verbindung ein Alkohol, Wasser, eine Carbonsäure oder ein Silanol ist.
14. Ein Verfahren wie in Anspruch 13 beansprucht, in welchem die hydroxylhaltige Verbindung ein tertiäres Alkanol oder ein Silanol ist.

Patentansprüche für folgenden Vertragsstaat : ES

1. Ein Verfahren zur Herstellung eines Katalysatorsystems, welches das Kombinieren
- a) einer Quelle für ein Metall der Gruppe VIII;
 - b) eines Phosphins mit einem aromatischen Substituenten, der ein Iminostickstoffatom enthält;
 - c) einer Quelle für Protonen; und
 - d) eines tertiären Amins umfaßt.
2. Ein Verfahren, wie in Anspruch 1 beansprucht, in welchem die Quelle für ein Metall der Gruppe VIII eine Palladiumverbindung ist.
3. Ein Verfahren, wie in Anspruch 1 oder 2 beansprucht, in welchem eine Iminogruppe in einem aromatischen Substituenten mit einem Iminostickstoffatom über ein einzelnes Brücken-Kohlenstoffatom an ein Phosphoratom gebunden ist.
4. Ein Verfahren, wie in Anspruch 3 beansprucht, in welchem das Phosphin ein 2-Pyridyl-, 2-Pyrimidyl- oder 2-Triazinylphosphin ist.
5. Ein Verfahren, wie in einem der Ansprüche 1 bis 4 beansprucht, in welchem das tertiäre Amin ein gegebenenfalls substituiertes heterocyclisches tertiäres Amin, ein aliphatisches tertiäres Amin oder ein gegebenenfalls substituiertes tertiäres Anilin ist.
6. Ein Verfahren, wie in Anspruch 5 beansprucht, in welchem das tertiäre Amin ein Pyridin oder ein N,N-Dialkylanilin ist.
7. Ein Verfahren, wie in einem der Ansprüche 1 bis 6 beansprucht, in welchem die Anzahl an Äquivalenten des tertiären Amins je Mol Protonen mindestens 1 ist.
8. Ein Verfahren, wie in Anspruch 7 beansprucht, in welchem die Anzahl an Äquivalenten des tertiären Amins je Mol Protonen im Bereich von 1,5 bis 1500 liegt.
9. Die Verwendung eines Katalysatorsystems, wie in Anspruch 1 beansprucht, beim Carbonylieren einer acetylenisch oder olefinisch ungesättigten Verbindung.
10. Ein Verfahren zum Carbonylieren einer acetylenisch oder olefinisch ungesättigten Verbindung, welches



das Umsetzen einer acetylenisch oder olefinisch ungesättigten Verbindung in Gegenwart eines Katalysatorsystems, wie in Anspruch 1 definiert, umfaßt.

- 6 11. Ein Verfahren, wie in Anspruch 10 beansprucht, in welchem eine nukleophile Verbindung mit einem entfernbaren Wasserstoffatom vorliegt.
12. Ein Verfahren, wie in Anspruch 11 beansprucht, in welchem die nukleophile Verbindung mit einem entfernbaren Wasserstoffatom eine hydroxylhaltige Verbindung ist.
- 10 13. Ein Verfahren, wie in Anspruch 12 beansprucht, in welchem die hydroxylhaltige Verbindung ein Alkohol, Wasser, eine Carbonsäure oder ein Silanol ist.
14. Ein Verfahren wie in Anspruch 13 beansprucht, in welchem die hydroxylhaltige Verbindung ein tertiäres Alkanol oder ein Silanol ist.

Revendications

Revendications pour les Etats contractants suivants : BE, DE, FR, GB, IT, NL

- 20 1. Un système catalytique, qui comprend
 - a) une source d'un métal du groupe VIII ;
 - b) une phosphine ayant un substituant aromatique qui contient un atome d'azote de groupe imino ;
 - c) une source de protons ; et
 - 25 d) une amine tertiaire.
2. Un système catalytique selon la revendication 1, dans lequel la source d'un métal du groupe VIII est un composé du palladium.
- 30 3. Un système catalytique selon la revendication 1 ou 2, dans lequel un groupe imino dans un substituant aromatique contenant un atome d'azote de groupe imino est lié à un atome de phosphore par un seul atome de carbone formant pont.
- 35 4. Un système catalytique selon la revendication 3, dans lequel la phosphine est une 2-pyridyl, 2-pyrimidyl ou 2-triazinylphosphine.
5. Un système catalytique selon l'une quelconque des revendications 1 à 4, dans lequel l'amine tertiaire est une amine tertiaire hétérocyclique éventuellement substituée, une amine tertiaire aliphatique ou une aniline tertiaire éventuellement substituée.
- 40 6. Un système catalytique selon la revendication 5, dans lequel l'amine tertiaire est une pyridine ou une N,N-dialcoylaniline.
7. Un système catalytique selon l'une quelconque des revendications 1 à 6, dans lequel le nombre d'équivalents d'amine tertiaire par mole de protons est d'au moins 1.
- 45 8. Un système catalytique selon la revendication 7, dans lequel le nombre d'équivalents d'amine tertiaire par mole de protons est compris entre 1,5 et 1 500.
9. L'utilisation d'un système catalytique tel que défini dans la revendication 1 dans la carbonylation d'un composé acétyléniquement ou oléfiniquement insaturé.
- 50 10. Un procédé pour la carbonylation d'un composé acétyléniquement ou oléfiniquement insaturé, qui comprend la réaction d'un composé acétyléniquement ou oléfiniquement insaturé en présence d'un système catalytique tel que défini dans la revendication 1.
- 55 11. Un procédé selon la revendication 10, dans lequel un composé nucléophile ayant un atome d'hydrogène enlevable est présent.
12. Un procédé selon la revendication 1, dans lequel le composé nucléophile ayant un atome d'hydrogène



enlevable est un composé hydroxylé.

13. Un procédé selon la revendication 12, dans lequel le composé hydroxylé est un alcool, l'eau, un acide carboxylique ou un silanol.
14. Un procédé selon la revendication 13, dans lequel le composé hydroxylé est un alcool tertiaire ou un silanol.

Revendications pour l'Etat contractant suivant : ES

1. Un procédé pour la préparation d'un système catalytique, qui comprend la combinaison de :
a) une source d'un métal du groupe VIII ;
b) une phosphine ayant un substituant aromatique qui contient un atome d'azote de groupe imino ;
c) une source de protons ; et
d) une amine tertiaire.
2. Un procédé selon la revendication 1, dans lequel la source d'un métal du groupe VIII est un composé du palladium.
3. Un procédé selon la revendication 1 ou 2, dans lequel un groupe imino dans un substituant aromatique contenant un atome d'azote de groupe imino est lié à un atome de phosphore par un seul atome de carbone formant pont.
4. Un procédé selon la revendication 3, dans lequel la phosphine est une 2-pyridyl, 2-pyrimidyl ou 2-triazolylphosphine.
5. Un procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'amine tertiaire est une amine tertiaire hétérocyclique éventuellement substituée, une amine tertiaire aliphatique ou une aniline tertiaire éventuellement substituée.
6. Un procédé selon la revendication 5, dans lequel l'amine tertiaire est une pyridine ou une N,N-dialcoylaniline.
7. Un procédé selon l'une quelconque des revendications 1 à 6, dans lequel le nombre d'équivalents d'amine tertiaire par mole de protons est d'au moins 1.
8. Un procédé selon la revendication 7, dans lequel le nombre d'équivalents d'amine tertiaire par mole de protons est compris entre 1,5 et 1 500.
9. L'utilisation d'un système catalytique tel que préparé par le procédé de la revendication 1 dans la carbonylation d'un composé acétyléniquement ou oléfiniquement insaturé.
10. Un procédé pour la carbonylation d'un composé acétyléniquement ou oléfiniquement insaturé, qui comprend la réaction d'un composé acétyléniquement ou oléfiniquement insaturé en présence d'un système catalytique tel que défini dans la revendication 1.
11. Un procédé selon la revendication 10, dans lequel un composé nucléophile ayant un atome d'hydrogène enlevable est présent.
12. Un procédé selon la revendication 11, dans lequel le composé nucléophile ayant un atome d'hydrogène enlevable est un composé hydroxylé.
13. Un procédé selon la revendication 12, dans lequel le composé hydroxylé est un alcool, l'eau, un acide carboxylique ou un silanol.
14. Un procédé selon la revendication 13, dans lequel le composé hydroxylé est un alcool tertiaire ou un silanol.