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(54) Titre : PROCEDE DE CARBONYLATION DE COMPOSES A INSATURATION ETHYLENIQUE, COMPOSITION DE DIPHOSPHINE BIDENTATE UTILISEE DANS CE PROCEDE ET PROCEDES DE PREPARATION DE CETTE COMPOSITION DE DIPHOSPHINE BIDENTATE

(54) Title: PROCESS FOR THE CARBONYLATION OF ETHYLENICALLY UNSATURATED COMPOUNDS, BIDENTATE DIPHOSPHINE COMPOSITION USED IN THIS PROCESS AND PROCESSES FOR PREPARATION OF THIS BIDENTATE DIPHOSPHINE COMPOSITION

(57) Abrégé/Abstract:
Process for the carbonylation of optionally substituted ethylenically unsaturated compounds by reaction with carbon monoxide and a coreactant in the presence of a catalyst system. The catalyst system includes (a) a source of Pt group metal cations, (b) a bidentate diphosphine composition. More than 60% w/w of bidentate diphosphine present in the bidentate diphosphine composition has the general formula (II) X^1-R-X^2 wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms. Bidentate diphosphine composition wherein more than 60% w/w of bidentate diphosphine present has the general formula (II)) X^1-R-X^2 wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms, with the proviso that the bidentate diphosphine is not 1,3-PP'bis(9-phosphabicyclo[3.3.1]nonyl)propane. In addition methods to prepare such a bidentate diphosphine composition are described.

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(54) Title: PROCESS FOR THE CARBONYLATION OF ETHYLENICALLY UNSATURATED COMPOUNDS, BIDENTATE DIPHOSPHINE COMPOSITION USED IN THIS PROCESS AND PROCESSES FOR PREPARATION OF THIS BIDENTATE DIPHOSPHINE COMPOSITION

(57) Abstract: Process for the carbonylation of optionally substituted ethylenically unsaturated compounds by reaction with carbon monoxide and a coreactant in the presence of a catalyst system. The catalyst system includes (a) a source of Pt group metal cations, (b) a bidentate diphosphine composition. More than 60% w/w of bidentate diphosphine present in the bidentate diphosphine composition has the general formula (II) X^1-R-X^2 wherein X^1 and X?2 ¿independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms. Bidentate diphosphine composition wherein more than 60% w/w of bidentate diphosphine present has the general formula (II)) X^1-R-X?2 ¿ wherein X^1 and X?2 ¿independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms, with the proviso that the bidentate diphosphine is not 1,3-PP'bis(9-phosphabicyclo[3.3.1]nonyl)propane. In addition methods to prepare such a bidentate diphosphine composition are described.

PROCESS FOR THE CARBONYLATION OF ETHYLENICALLY UNSATURATED COMPOUNDS, BIDENTATE DIPHOSPHINE COMPOSITION USED IN THIS PROCESS AND PROCESSES FOR PREPARATION OF THIS BIDENTATE DIPHOSPHINE COMPOSITION

Background of the invention

The present invention relates to a process for the carbonylation of optionally substituted ethylenically unsaturated compounds by reaction with carbon monoxide and a coreactant in the presence of a catalyst system comprising a source of Pt group metal cations and a bidentate diphosphine having the general formula I

$$Q^1\text{-}Z\text{-}Q^2 \qquad (I)$$

wherein Q^1 and Q^2 represent a phosphabicycloalkyl group, having at least 5 ring atoms; and Z represents a bivalent organic bridging group connecting both phosphorus atoms.

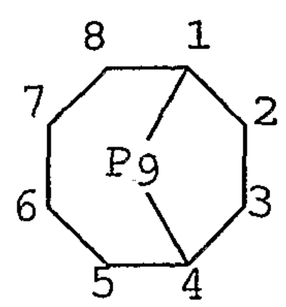
The present invention in particular relates to such a reaction in which the coreactant is hydrogen.

A commercially important carbonylation reaction, using hydrogen as coreactant, is the hydroformylation of olefins, which are reacted with carbon monoxide and hydrogen to form aldehydes and/or alcohols having one carbon atom more than the precursor olefin. Depending on catalyst, reaction conditions and substrates, the hydroformylation can proceed with varying selectivities to the several possible isomeric aldehydes or alcohols in varying yields, as side reactions occur to a smaller or larger extent. Generally only one isomeric product is preferred. For many applications the presence of branched aldehydes or alcohols is undesirable. Moreover, in view of biological degradability, it is considered advantageous to obtain products having a high content of

the linear isomer. The selectivity towards one of several possible isomeric products is called regioselectivity. For hydroformylation a regioselectivity towards reaction at the primary carbon atom, resulting in a linear product, is desirable.

WO-A-95/05354 describes the carbonylation of ethylenically unsaturated compounds by reaction with carbon monoxide and hydrogen, i.e. hydroformylation, in the presence of a catalyst system comprising a Group VIII metal cation, viz. cationic palladium and platinum, and a bidentate ligand, viz. a diphosphine. In the examples amongst others 1,2-bis(1,4-cyclooctylene phosphino)ethane, i.e. in IUPAC nomenclature 1,2-PP'bis(9-phosphabicyclo[4.2.1]nonyl)ethane; 1,3-bis(1,4-cyclooctylene phosphino)propane, i.e. in IUPAC nomenclature 1,3-PP'bis(9-phosphabicyclo[4.2.1]nonyl)-propane; and 1,2-bis(2,6-dimethyl, 1,4-cyclooctylene phosphino)ethane, i.e. in IUPAC nomenclature 1,2-PP'bis(2,6-dimethyl, 9-phosphabicyclo[4.2.1]nonyl)-ethane are used as bidentate diphosphine ligands. The phosphabicyclononyl groups in these ligands are all substituted or non-substituted 1,4-cyclooctylenephosphino groups, i.e. in IUPEC nomenclature 9-phosphabicyclo-[4.2.1]nonyl groups. Such a 9-phosphabicyclo[4.2.1]nonyl group is visualised in Figure A.

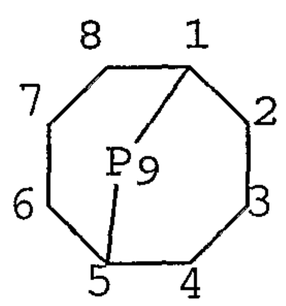
Figure A



As is illustrated by the examples the hydro-formylation of ethylenically unsaturated compounds with a catalyst system containing these diphosphines results in acceptable selectivities towards the linear product.

The 9-phosphabicyclo[4.2.1]nonyl group visualized in Figure A is an example of an asymmetrical phosphabicycloalkyl group. In an asymmetrical phosphabicycloalkyl group the bridges not containing the phosphorus atom have an unequal number of atoms in the bridge. By a symmetrical phosphabicycloalkyl group is understood that the bridges (i.e. the hydrocarbyl groups connecting the tertiary carbon atoms), which do not contain the phosphorus atom, have an equal number of atoms. An example of such a symmetrical group is the 9-phosphabicyclo[3.3.1]nonyl group which is visualised in Figure B.

Figure B



WO-A-00/02375 describes a method to prepare a phosphorus-containing ligand by refluxing a phosphabicyclononane hydride with 1,2-dibromoethane in acetonitrile. After neutralisation with sodium hydroxide a bis-(9-phosphabicyclononyl)ethane can be isolated. The phosphabicyclononane hydride can conveniently be prepared as described by Elsner et al. (Chem. Abstr. 1978, vol. 89, 180154x).

In addition, non-pre-published WO-A-01/87899 describes the preparation of a bidentate diphosphine ligand by reacting P-cyclo-octyl hydride (e.g. phosphabicyclononane hydride) and butyllithium to generate a lithium cyclo-octyl phosphide and subsequently reacting with an appropriate substituted or non-substituted alkane diol sulphate ester. The P-cyclo-octyl hydride can conveniently be prepared as described by Elsner et al. (Chem. Abstr. 1978, vol. 89, 180154x).

In their article entitled "A simple procedure for the separation of the catalytically important phobane isomers" , published in Chemical Communications, 1997, pages 1527-1528, J.H. Downing et al. indicate that to that date there had been no reports of the separation of the symmetrical and asymmetrical isomers of phospha-bicyclononanes, although, by exploiting the difference in reactivity between the isomers, ligands derived from the symmetrical isomer had been isolated.

In the article of J.H. Downing et al. a laborious method is provided for separation of the isomers of phosphabicyclononane. The method comprises:

a) reacting a mixture of both symmetrical and asymmetrical phosphabicyclononane hydride with formaldehyde (CH_2O) in the presence of hydrochloric acid (HCl), yielding phosphonium salts;

b) reacting these phosphonium salts with sodium hydroxide (NaOH), yielding a charged symmetrical phosphine and a neutral asymmetrical phosphine;

c) extracting the neutral asymmetrical phosphine with pentane, leaving relatively pure, charged symmetrical phosphine in an aqueous solution;

d) treating the aqueous solution with sodium hydroxide to obtain the neutral symmetrical phosphine.

The symmetrical phosphabicyclononane is used in the synthesis of 1,3-PP'bis(9-phosphabicyclo[3.3.1]nonyl) propane. The overall yield of this preparation was only 17%. The article does not describe the preparation of any other bidentate diphosphine having general formula I.

Summary of the invention

Although good results with regard to the regio-selectivity towards a linear product are obtained in WO-A-95/05354, there is room for further improvement.

It is therefore an object of the present invention to provide a process for the carbonylation of ethylenically unsaturated compounds by reaction with carbon monoxide and a coreactant, which results in an improved regioselectivity towards a linear product.

It has now surprisingly been found that when a process for the carbonylation of ethylenically unsaturated compounds is characterised by a Pt group metal based catalyst comprising a specific bidentate diphosphine composition wherein a certain amount of bidentate diphosphine with two symmetrical phosphabicycloalkyl groups is present, unexpected advantages with regard to the regioselectivity towards a linear product are obtained.

Accordingly the present invention provides a process for the carbonylation of optionally substituted ethylenically unsaturated compounds by reaction with carbon monoxide and a coreactant in the presence of a catalyst system including:

(a) a source of Pt group metal cations,

(b) a bidentate diphosphine composition

wherein more than 60% w/w of bidentate diphosphine present in the bidentate diphosphine composition has the general formula II

$$X^1\text{-}R\text{-}X^2 \qquad (II)$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms.

The article of J.H. Downing et al. does not indicate any use, nor any expected advantage, for the 1,3-PP'bis(9-phosphabicyclo[3.3.1]nonyl) propane prepared. On the contrary, by means of reference 5,

referring to WO-A-95/05354, the article even indicates a preference for the asymmetrical phosphabicyclononyls.

As will be shown in the examples, however, the use of derivatives of symmetrical phosphabicycloalkane groups is very advantageous for the linearity of the product.

Detailed description of the invention

In the general formula II for component b) of the catalyst system, R preferably represents a bivalent organic bridging group containing from 1 to 10, preferably from 2 to 6, more preferably from 2 to 4, and most preferably 2 to 3 atoms in the shortest connection between both phosphorus atoms. Especially preferred is a bivalent organic bridging group having 2 atoms in this connection. Preferably, the bridging group R represents an alkylene group, but it can also comprise a carbon chain, interrupted by one or more hetero atoms, such as nitrogen, sulphur, silicon or oxygen atom. Preferably the shortest connection between both phosphorus atoms contains 2 or 3 carbon atoms, most preferably 2 carbon atoms.

The shortest connection between both phosphorus atoms can be substituted or non-substituted or can form part of a aliphatic or aromatic ring structure. In a preferred embodiment the connection forms part of an optionally substituted saturated or non-saturated aliphatic ring structure, such as for example a substituted or non-substituted cyclopentane, cyclopentene, cyclohexane or cyclohexene. The cycloaliphatic ring can be interrupted by one or more heteroatoms such as nitrogen, sulphur, silicon or oxygen atoms. The aliphatic ring structure can further be substituted with any kind of substituent, including heteroatoms, alkyl groups, cycloalkyl groups and aryl groups. If the connection forms part of an optionally substituted saturated or non-saturated aliphatic ring

structure the phosphorus atoms are preferably attached at adjacent positions, for example positions 1 and 2.

More preferably the connection is an ethylene or trimethylene group. Most preferably the connection is a ethylene group. The connection can be a substituted alkylene group with at least one substituent and preferably at least two substituents. If the connection is substituted it is preferably substituted with two to four substituents, more preferably with two to three substituents, and most preferably with two substituents.

The substituents can be attached to any part of the connection. In an advantageous embodiment, the carbon atoms of the connection, which are connected to the phosphorus atoms, are substituted. In this case the bidentate diphosphine has two chiral C-atoms and can have the RR, SS, or R,S meso-form. The R,S meso-form is preferred.

The substituents can contain carbon atoms and/or hetero atoms. Substituents which can be used include groups containing hetero-atoms such as halides, sulphur, phosphorus, oxygen and nitrogen. Examples of such groups include chloride, bromide, iodide, thiol, and groups of the general formula H-O-, A^1-O-, -S-A^1, -CO-A^1, $-NH_2$, -NHA^1, -NA^1A^2, -CO-NA^1A^2, -OH, $-PO_4$, $-NO_2$, -NOH, -CO, $-SO_2$, -SOH, in which A^1 and A^2, independently, represent aliphatic groups, preferably having from 1 to 10 carbon atoms, more preferably having from 1 to 4 carbon atoms, like methyl, ethyl, propyl and isopropyl.

Preferably the substituents are hydrocarbyl groups. The hydrocarbyl groups themselves can be aromatic, aliphatic or cycloaliphatic. The hydrocarbyl groups can contain carbon atoms and hetero atoms. Hydrocarbyl groups can further include groups containing hetero-atoms such as the ones mentioned hereinabove. The hydrocarbyl groups

can be straight-chain or branched, and can contain saturated and/or non-saturated links.

Aromatic hydrocarbyl substituent groups can be aryl groups such as phenyl groups and alkyl phenyl groups.

Preferred hydrocarbyl substituent groups are alkyl groups, preferably having from 1 to 10 carbon atoms, more preferably from 1 to 4 carbon atoms. Linear, branched or cyclic alkyl groups can be used. Alkyl groups can be methyl, ethyl, propyl, iso-propyl, butyl and iso-butyl. More preferably methyl groups are used.

Most preferably the bivalent bridging group R is an ethylene group which is di-substituted, preferably with two alkyl groups, most preferably with two methyl groups.

X^1 and X^2 independently represent a substituted or non-substituted symmetrical phosphabicycloalkyl group. Of the three bridges present in such a phosphabicycloalkyl group, the bridge containing the phosphorus atom is preferably the shortest one. As explained above, the other two bridges have an equal length, i.e. contain an equal number of atoms in the bridge. By "a bridge" is meant a connection between both tertiary carbon atoms.

Preferred are symmetrical phosphabicycloalkyl groups with at least 7 ring atoms (of which one is, of course, a phosphorus atom) and preferably with from 7 to 11 ring atoms. More preferably X^1 and X^2 represent a substituted or non-substituted symmetrical phosphabicyclononyl group. Examples of symmetrical phosphabicycloalkyl groups therefore include substituted or non-substituted 2-phosphabicyclo[1.1.1]pentyl; 2-phosphabicyclo[2.1.1]-hexyl; 2-phosphabicyclo[3.1.1]heptyl; 3-phospha-bicyclo[3.1.1]heptyl; 7-phosphabicyclo[2.2.1]heptyl; 2-phosphabicyclo[2.2.2]octyl; 2-phosphabicyclo[5.1.1]-nonyl; 3-phosphabicyclo[5.1.1]nonyl; 4-phosphabicyclo-[5.1.1]nonyl; 2-phosphabicyclo[3.2.2]nonyl; 3-phospha-

bicyclo[3.2.2]nonyl; 9-phosphabicyclo[3.3.1]nonyl; 9-phosphabicyclo[3.3.2]decyl; 2-phosphabicyclo-[3.3.3]undecyl; 3-phosphabicyclo [3.3.3] undecyl. Of these, substituted or non-substituted 7-phospha-bicyclo[2.2.1]heptyl; 9-phosphabicyclo[3.3.1]nonyl; 9-phosphabicyclo[3.3.2] decyl are preferred. Particularly preferred are substituted or non-substituted 9-phospha-bicyclo[3.3.1]nonyl groups.

X^1 and X^2 can each represent a different symmetrical phosphabicycloalkyl or can both represent the same phosphabicycloalkyl. Preferably both X^1 and X^2 represent the same symmetrical phosphabicycloalkyl, preferably a symmetrical 9-phosphabicyclo[3.3.1]nonyl group.

One or both of the phosphabicycloalkyl rings can be substituted with one or more hydrocarbyl groups containing carbon atoms and/or hetero atoms. If a phosphabicycloalkyl ring is substituted, preferably one or both of the bridges not containing the phosphorus atom is substituted, preferably with one or more alkyl groups, preferably having from 1 to 10 carbon atoms, more preferably from 1 to 4 carbon atoms. Linear, branched or cyclic alkyl groups can be used. Preferred alkyl groups include methyl, ethyl, propyl, iso-propyl, butyl and iso-butyl. More preferably methyl groups are used. The substituted phosphabicycloalkyl ring can be mono- or poly-substituted and is preferably di-substituted. Most preferably the phosphabicycloalkyl ring is substituted with two methyl groups. Examples of substituted phospha-bicycloalkyl rings include 3,7 dimethyl,9-phospha-bicyclo[3.3.1]nonyl; 3,7 diethyl,9-phosphabicyclo[3.3.1]-nonyl; 2,6-dimethyl, 9-phosphabicyclo[3.3.1]nonyl.

Preferred bidentate diphosphines of formula II include 1,2-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)ethane; 1,3-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)propane;

1,2-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)propane; 2,3-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)butane; 2,3-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)pentane; 2,4-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)pentane; 1,2-P,P'bis(3,7-dimethyl, 9-phosphabicyclo[3.3.1]-nonyl)ethane; 1,3-P,P'bis(3,7-dimethyl, 9-phosphabicyclo[3.3.1]nonyl)propane; 1,2-P,P'bis(3,7-dimethyl, 9-phosphabicyclo[3.3.1]nonyl)propane; 2,3-P,P'bis(3,7-dimethyl, 9-phosphabicyclo[3.3.1]nonyl)butane; 2,3-P,P'bis(3,7-dimethyl, 9-phosphabicyclo[3.3.1]-nonyl)pentane; 2,4-P,P'bis(3,7-dimethyl, 9-phosphabicyclo[3.3.1]nonyl)pentane; 1,2-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)cyclopentane; 1,2-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)cyclohexane; and mixtures thereof.

These bidentate diphosphines can be prepared with methods as described in WO-A-00/02375 and/or non-pre-published WO-A-01/87899.

Especially preferred are 1,2-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)ethane; 1,2-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)propane; and 2,3-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)butane. Most preferred is 2,3-P,P'bis(9-phosphabicyclo[3.3.1]nonyl)butane.

Preferably more than 80% w/w and more preferably more than 85% w/w of the bidentate diphosphine present in the bidentate diphosphine composition of component (b) of the catalyst system has the general formula (II). Even more preferably in the range of from 90% w/w, more preferably of from 95% w/w to 100% w/w of the bidentate diphosphine present in the composition has the general formula (II). Most preferably in the range of from 99% w/w to 100% w/w of the bidentate diphosphine present in the composition has the general formula (II).

Examples of sources of Pt group metal cations of component (a) of the catalyst system are platinum or palladium compounds such as salts of palladium and nitric

acid, sulphuric acid or sulphonic acids, salts of platinum or palladium and carboxylic acids with up to 12 carbon atoms, palladium or platinum complexes, e.g. with carbon monoxide or acetylacetonate, or palladium combined with a solid material such as an ion exchanger. Palladium(II) acetate and platinum(II) acetylacetonate are examples of preferred metal sources.

Some of the catalyst systems which can be used in the process according to the present invention are novel.

Accordingly, the present invention provides a catalyst system including:

(a) a source of Pt group metal cations,

(b) a bidentate diphosphine composition

wherein more than 60% w/w of bidentate diphosphine present in the bidentate diphosphine composition has the general formula (II)

$$X^1\text{-}R\text{-}X^2 \qquad (II)$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms. Preferences for components (a) and (b) are as described hereinbefore.

Preferably the catalyst system also includes as an additional component (c) a source of anions. As anion source, any compound generating these anions can be used. Acids, or salts thereof, can be used as source of anions, for example any of the acids mentioned above, which can also participate in the salts of the metals of the platinum group.

In the process of the present invention, preferably acids are used as anion source having a pKa value of less than 6, more preferably less than 5, measured in aqueous solution at 18 °C.

Typical examples of anions which can be used are anions of phosphoric acid, sulphuric acid, sulphonic acids and halogenated carboxylic acids such as trifluoroacetic acid.

Sulphonic acids are in particular preferred, for example methanesulphonic acid, trifluoromethanesulphonic acid, tert-butane-sulphonic acid, p-toluenesulphonic acid and 2,4,6-trimethylbenzene-sulphonic acid.

Also, complex anions can be used, such as the anions generated by a combination of a Lewis acid such as BF_3, $AlCl_3$, SnF_2, $Sn(CF_3SO_3)_2$, $SnCl_2$ or $GeCl_2$, with a protic acid, such as a sulphonic acid, e.g. CF_3SO_3H or CH_3SO_3H or a hydrohalic acid such as HF of HCl, or a combination of a Lewis acid with an alcohol. Examples of such complex anions are BF_4-, $SnCl_3$-, $[SnCl_2.CF_3SO_3]$- and PF_6-.

The ethylenically unsaturated compound, used as starting material, is preferably an alkene having from 2 to 20 carbon atoms per molecule, or a mixture thereof. Preferred are alkenes having from 3 to 20 and more preferably from 3 to 14 carbon atoms, or mixtures thereof. They can comprise one or more double bonds per molecule but alkenes having 1 to 3 carbon-carbon double bonds per molecule are preferred. The alkene can be substituted or non-substituted. Preferred substituents include alkyl and aryl groups as well as groups containing hetero-atoms such as halides, sulphur, phosphorus, oxygen and nitrogen. Examples of substituents include chloride, bromide, iodide and hydroxy, alkoxy, carboxy, amino, amido, nitro, cyano, thiol or thioalkoxy groups. Examples of ethylenically unsaturated compounds include ethene, propene, 1-butene, 2-butene, isobutene, pentenes, hexenes, octenes and dodecenes, 1,5-cyclo-octadiene, cyclododecene, methyl pentenoates and pentene nitriles.

In the process of the present invention, these ethylenically unsaturated compounds can be converted by reaction with carbon monoxide and a coreactant with a high regioselectivity towards the linear product.

In the process of the present invention, the ethylenically unsaturated starting material and the formed product can act as reaction diluent. Hence, the use of a separate solvent is not necessary. Conveniently, however, the carbonylation reaction can be carried out in the additional presence of a solvent. As such, saturated hydrocarbons, e.g. paraffins and isoalkanes, are recommended and furthermore alcohols, the saturated hydrocarbons and alcohols preferably having from 4 to 10 carbon atoms per molecule, such as butanol, ethylhexanol-1, nonanol-1, or in general terms the alcohols formed as carbonylation product; ethers such as 2,5,8-trioxanonane (diglyme), diethylether and anisole, and ketones, such as methylbutylketone. Solvents, comprising or substantially consisting of sulphones are also preferred. Sulphones are in particular preferred, for example dialkylsulphones such as dimethylsulphone and diethylsulphone and cyclic sulphones, such as sulfolane (tetrahydrothiophene-2,2-dioxide), sulfolane, 2-methyl-sulfolane and 2-methyl-4-ethylsulfolane.

The quantity in which the catalyst system is used is not critical and can vary within wide limits. Usually amounts in the range of 10^{-8} to 10^{-1}, preferably in the range of 10^{-7} to 10^{-2} mole atom of platinum group metal per mole of ethylenically unsaturated compound are used.

The amounts of the participants in the catalyst system are conveniently selected such that per mole atom of platinum group metal from 0.5 to 10, preferably from 1 to 6 moles of bidentate diphosphine are used, from 0.5 to

15, preferably from 1 to 8 moles of anion source or a complex anion source.

Furthermore the presence of a small amount of catalyst promoter comprising a source of halide anions can have a significant favourable effect in that the conversion reaction proceeds at high rate, even at moderate temperatures, with very little formation of saturated hydrocarbons.

For hydroformylation the coreactant can be molecular hydrogen, or more generally a hydride source.
The carbon monoxide and hydrogen can be supplied in equimolar or non-equimolar ratios, e.g. in a ratio within the range of 5:1 to 1:5, preferably 3:1 to 1:3. More preferably they are supplied in a ratio within the range of 2:1 to 1:2.

The carbonylation can be carried out at moderate reaction conditions. Hence temperatures in the range of 50 to 200 °C are recommended, preferred temperatures being in the range of 70 to 160 °C. Reaction pressures in the range of 500 to 10000 kPa (5 to 100 bar) are preferred; lower or higher pressures can be selected, but are not considered particularly advantageous. Moreover, higher pressures require special equipment provisions.

The claimed catalyst system can also be useful in conversion reactions other than hydroformylation. In general the coreactant can be represented by NuH, wherein Nu represents the remnant nucleophilic moiety of the coreactant after removal of a hydrogen atom. The nature of the coreactant largely determines the type of product formed. The coreactant can be a nucleophilic compound having a mobile hydrogen atom, such as an alcohol, an acid, an amine or water. For an alcohol XOH (X being the carbon containing part), the XO moiety is represented by Nu and accordingly the product is an ester.

Similarly, the use of an acid XCOOH (Nu = XCOO) will introduce an anhydride group in the product of the mono-carbonylation reaction; the use of ammonia (Nu = NH_2) or an amine XNH_2 (Nu = XNH) or X_2NH (Nu = X_2N) will introduce an amide group; the use of a thiol XSH (Nu = XS) will introduce a thioester group; and the use of water (Nu = OH) will introduce a carboxy group.

Some of the bidentate diphosphine compositions which can be used in the process according to the present invention are novel.

Accordingly the present invention also provides a bidentate diphosphine composition wherein more than 60% w/w of bidentate diphosphine present has the general formula II

$$X^1\text{-}R\text{-}X^2 \qquad (II)$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms, with the proviso that the bidentate diphosphine is not 1,3-PP'bis(9-phosphabicyclo[3.3.1]nonyl)propane.

Preferably more than 80% w/w and more preferably more than 85% w/w of the bidentate diphosphine present in the bidentate diphosphine composition has the general formula (II). Even more preferably in the range of from 90% w/w, more preferably of from 95% w/w, to 100% w/w of the bidentate diphosphine present in the composition has the general formula (II). Most preferably in the range of from 99% w/w to 100% w/w of the bidentate diphosphine present in the composition has the general formula (II). Preferences for the bidentate diphosphine itself are as described above for the process.

Bidentate diphosphine compositions wherein a bidentate diphosphine is present having the general formula II are known in the art. For example, US-A-3527818 describes in example I a mixture of octamethylene-PP'-bis(9-phosphabicyclo[4.3.1]nonane), octamethylene-PP'-bis(9-phosphabicyclo[3.3.1]nonane)and octamethylene-P-(9-phosphabicyclo[4.2.1]nonane)P' (9-phosphabicyclo[3.3.1]nonane). To obtain a bidentate diphosphine composition which can be used in the process of the present invention, however, such compositions/ mixtures need to be purified to obtain a higher percentage of bidentate diphosphine having the general formula (II).

The preparation of a purified bidentate diphosphine composition, that is a bidentate diphosphine composition wherein the percentage of bidentate diphosphine having the general formula (II) is as specified above, can be established by one or more of the following 3 ways:

I. Purification of the starting compound. That is, separation of the symmetrical phosphabicycloalkane from a composition of symmetrical and asymmetrical phosphabicycloalkanes to obtain a composition with a high percentage of symmetrical phosphabicycloalkane. Bidentate diphosphines are subsequently prepared from the composition having a high percentage of symmetrical phosphabicycloalkanes.

II. The use of specific reaction conditions during the preparation of bidentate diphosphines from a composition of phosphabicycloalkanes, such that reaction towards a bidentate diphosphine having general formula (II) is favoured.

III. Purification of a composition of bidentate diphosphines itself. That is, separation of the bidentate diphosphines with general formula (II) from a composition of bidentate diphosphines to obtain a composition with a

high percentage of bidentate diphosphines with general formula (II).

Preferably the presence of oxygen during all processes is avoided as much as possible in order to avoid the formation of oxides of the phosphabicycloalkanes and/or bidentate diphosphines. Most preferably processes are conducted under essentially oxygen-free conditions. Thus, preferably compounds used, such as for example solvents and solutions, are deoxygenated before use. In addition, the process is preferably conducted in an oxygen-free environment, for example by applying an atmosphere of nitrogen during all manipulations.

I. Purification of a starting compound.

Preferably the starting compound is purified to the extent that the resulting phosphabicycloalkane composition comprises more than 60% w/w, preferably more than 80% w/w, more preferably at least 90% w/w and even more preferably in the range of 95 to 100% w/w of symmetrical phosphabicycloalkane. Most preferably the resulting composition is essentially 100% w/w pure, that is it comprises in the range of from 99% w/w, most preferably of from 99.5% w/w to 100% w/w of symmetrical phosphabicycloalkane.

An example of the purification of a composition comprising symmetrical and asymmetrical phosphabicycloalkanes is given by J.H. Downing et al. in their article entitled "A simple procedure for the separation of the catalytically important phobane isomers", published in Chemical Communications, 1997, pages 1527-1528, which is described hereinbefore. A disadvantage of this method, however, is that it involves a number of chemical reactions, such as a reaction with formaldehyde. The use of chemical reactions slows down the process.

A novel method for the purification of a composition comprising symmetrical and asymmetrical phosphabi-

cycloalkanes which does not involve such chemical reactions has now been found. Surprisingly it was found that symmetrical and asymmetrical phosphabicycloalkanes can be separated by exploiting a difference found in basicity between the symmetrical and asymmetrical isomer of a phosphabicycloalkane.

The present invention therefore also provides a process for the separation of symmetrical phosphabicycloalkane from a composition containing symmetrical and asymmetrical phosphabicycloalkanes comprising the following steps:

a) adding means to protonate a phosphabicycloalkane to a composition containing symmetrical phosphabicycloalkane (SPBA) and asymmetrical phosphabicycloalkane (APBA), yielding a composition comprising protonated symmetrical phosphabicycloalkane (SPBA+) and non-protonated asymmetrical phosphabicycloalkane (APBA);

b) separating protonated symmetrical phosphabicycloalkane (SPBA+) and non-protonated asymmetrical phosphabicycloalkane (APBA), yielding separated protonated symmetrical phosphabicycloalkane (SPBA+) and separated non-protonated asymmetrical phosphabicycloalkane (APBA)

c) adding means to de-protonate the separated protonated symmetrical phosphabicycloalkane (SPBA+), yielding separated non-protonated symmetrical phosphabicycloalkane (SPBA).

The novel process is faster and more easy to conduct than the process described in the article of J. Downing et al. In addition the reversibility in protonating and deprotonating the phosphabicycloalkanes make it a "forgiving" process.

By "protonate a phosphabicycloalkane" is meant that a phosphabicycloalkane accepts a proton, i.e. a positively charged hydrogen atom (H+).

Preferred means to protonate a phosphabicycloalkane include a wide range of acids, such as hydrohalic acids, e.g. hydrogen chloride, hydrogen bromide, hydrogen iodide and hydrogen fluoride; halogen oxo acids, e.g. hypobromous acid, chlorous acid, hypochlorous acid, perchloric acid and periodic acid; mineral acids, e.g. sulphuric acids, nitric acids and phosphoric acids; some organic acids, such as acetylacetonic acids, sulphonic acids, carboxylic acids and halogenated carboxylic acids e.g. trichloroacetic acid and trifluoroacetic acid; complex acids such as HBF_4, $HSnCl_3$; and mixtures of those acids.

More preferred are inorganic acids such as the hydrohalic acids, halogen oxo acids and mineral acids mentioned. More preferred are hydrohalic acids of which HCl, HI, and HBr are most preferred.

Preferred means to de-protonate the separated protonated symmetrical phosphabicycloalkane (SPBA+) in step c) include a wide range of bases, such as ammonia and primary, secondary and tertiary amines; carbonates and hydrogencarbonates, such as for example Na_2CO_3, $NaHCO_3$, K_2CO_3, $MgCO_3$; and hydroxides such as $Ba(OH)_2$, Na(OH) and K(OH). More preferred are alkali metal hydroxides, such as potassium hydroxide and sodium hydroxide.

Preferably the separation in step b) is achieved by making use of a difference in solubility of SPBA+ and APBA. Preferably a composition containing SPBA and APBA is solved in a solvent which does not dissolve SPBA+.

Means to protonate a phosphabicycloalkane, such as for example a hydrohalogenic acid, can be added to the dissolved phosphabicycloalkanes as a gas, as a (dissolved) liquid or a solid, whichever is most suitable. For example a HCl gas or a 1 M aqueous solution

of HCl can be added to a diethylether solution of phosha-bicycloalkanes. The SPBA+ can subsequently be separated as a precipitated solid or as a solution in a second liquid phase. The precipitate can, however, be thick and sticky and difficult to handle in isolation and purification.

Preferably the separation in step b) is therefore achieved by phase separation. An especially preferred process for the separation of symmetrical phospha-bicycloalkane from a composition containing symmetrical and asymmetrical phosphabicycloalkanes accordingly comprises:

i] dissolving a composition containing SPBA and APBA in a suitable non-water miscible solvent, which does not dissolve SPBA+, yielding a non-aqueous phosphabicyclo-alkane (PBA) solution;

ii] combining the non-aqueous PBA solution with an aqueous solution of a suitable acid, yielding an aqueous phase containing protonated SPBA+ and a non-aqueous phase containing non-protonated APBA;

iii] separating the aqueous phase containing protonated SPBA+ and the non-aqueous phase containing non-protonated APBA, yielding an aqueous solution containing protonated SPBA+ and a non-aqueous solution containing non-protonated APBA;

iv] combining the aqueous solution containing protonated SPBA+ with a suitable non-water miscible solvent and an aqueous solution of a suitable base, yielding a non-aqueous solution containing non-protonated SPBA;

v] removing the solvent from the non-aqueous solution containing non-protonated SPBA, yielding separated SPBA.

Optionally an extra step vi] is added to the process comprising removing the solvent from the non-aqueous solution containing non-protonated APBA, yielding separated APBA.

By a non-water miscible solvent is meant a hydrophobic solvent. Such a solvent can be mixed with water but upon standing two phases will eventually separate.

A wide range of non-water miscible solvents are available in which SPBA and APBA can be solved and which do not dissolve SPBA+. By not dissolving SPBA+ is understood that this compound is essentially not dissolved, that is the molar ratio SPBA+ dissolved in the solvent to SPBA+ dissolved in an aqueous 6 M HCl solution lies in the range from 10:90 to 0:100 and more preferably in the range from 5:95 to 0:100.

Preferably the solvent is an aprotic solvent. Solvents which can be used include saturated and unsaturated hydrocarbons, e.g. paraffins and linear, branched and cyclic alkanes, alkenes and alkynes, such as hexane, hexene, pentene and pentane, aromatics such as toluene and benzene; ethers, such as for example dimethylether anisole (methyl phenyl ether), 2,5,8-trioxanonane (diglyme), diethylether, tetrahydrofuran, diphenylether, diisopropylether and the dimethylether of di-ethyleneglycol; esters, such as for example methylacetate, dimethyladipate, butyrolactone, propionates and pentenoates; ketones, such as methylbutylketone and diethylketone; and sulphones, for example dialkylsulphones such as dimethylsulphone and diethylsulphone and cyclic sulphones, such as sulfolane (tetrahydrothiophene-2,2-dioxide), 2-methylsulfolane and 2-methyl-4-ethylsulfolane.

Preferred are aprotic solvents having a dielectric constant that is below a value of 50, more preferably in the range of 1 to 8, at 298.15 °K and 100 kPa (1 bar). In the present context, the dielectric constant for a given solvent is used in its normal meaning of representing the

ratio of the capacity of a condenser with that substance as dielectric to the capacity of the same condenser with a vacuum for dielectric. Values for the dielectric constants of common organic liquids can be found in general reference books, such as the Handbook of Chemistry and Physics, 76th edition, edited by David R. Lide et al, and published by CRC press in 1995, and are usually quoted for a temperature of about 20 or 25 °C, i.e. about 293.15 or 298.15 °K, and atmospheric pressure, i.e. about 100 kPa (1 bar), or can readily be converted to that temperature and pressure using the conversion factors quoted. If no literature data for a particular compound is available, the dielectric constant can be readily measured using established physico-chemical methods.

For example, the dielectric constant of anisole is 4.3 (at 294.2 °K), of diethyl ether is 4.3 (at 293.2 °K), of sulfolane is 43.4 (at 303.2 °K), of diphenylether is 3.7 (at 283.2 °K), of dimethyladipate is 6.8 (at 293.2 °K), of tetrahydrofuran is 7.5 (at 295.2 °K), of methylnonanoate is 3.9 (at 293.2 °K), of toluene is 2.4 (at 296.4 °K), of pentane is 1.8 (at 293.2 °K).

Most preferred solvents are saturated alkanes and aromatics, such as hexane, pentane or toluene and ethers. Ethers are especially preferred because the use of ethers in this separation process results in a quick and efficient phase-separation. Examples of ethers which can be used include dimethylether, methylethylether, anisole, diethylether and diphenylether.

Another especially preferred solvent is toluene, since toluene is less volatile and less flamable than some of the other solvents and therefore easy to handle.

In addition a phosphabicycloalkane composition is conveniently supplied as a toluene solution.

The concentrations of the reactants can be varied over a wide range, but is preferably kept high so as to reduce the amounts of solvent to be used. Phosphabicycloalkanes are preferably dissolved in the non-water miscible solvent to give a concentration in the range of 0.01 to 10 molar, more preferably in the range from 0.1 to 5 molar.

Preferred acids in step ii] are as described above for means to protonate a phosphabicycloalkane. Preferably concentrations in the range from 2 to 20 molar are used, and more preferably concentrations in the range from 5 to 15 molar are used. Most preferred are concentrations in the range from 5 to 10 molar.

The aqueous solution of suitable acid in step ii] can be added as such to the non-aqueous PBA solution or can be prepared *in situ* by first adding water and subsequently adding acid in a more concentrated form.

Preferably a ratio of aqueous solution to non-aqueous solution in step ii] is used in the range from 1:10 to 10:1 v/v, more preferably in the range from 1:2 to 2:1 v/v.

After combining the non-aqueous PBA solution with a aqueous solution of suitable acid the system is preferably shaken or stirred, such to establish close contact between the acid and the phosphabicycloalkanes, whereafter the two phases are allowed to separate. The two phases are separated in step iii]. Preferably the aqueous solution containing protonated SPBA+ is extracted one or more, preferably in the range from 1 to 50, times with a non-water miscible solvent as described for step i] to remove residues of non-protonated phosphabicycloalkanes and protonated APBA+.

Similarly the non-aqueous solution containing non-protonated APBA is preferably extracted one or more, preferably in the range from 1 to 50, times with a aqueous solution of a suitable acid to remove residues of protonated SPBA+.

Subsequently the aqueous solution containing protonated SPBA+ is combined in step iv] with a non-water miscible solvent as described for step i] and an aqueous solution of a suitable base, yielding a non-aqueous solution containing non-protonated SPBA;

Preferred bases are as described above for means to de-protonate the protonated symmetrical phosphabicyclo-alkane. Preferably concentrations in the range from 2 to 20 molar are used, and more preferably concentrations in the range from 5 to 15 molar are used.

Optionally residues of water are removed from the non-aqueous solutions yielded in steps iii] and/or iv] in a way known to one skilled in the art. For example residues of water can be removed by washing with bases such as hydroxides and carbonates, such as Na_2CO_3, $NaHCO_3$, K_2CO_3, $MgCO_3$, $Ba(OH)_2$, Na (OH) and K(OH). Subsequently a non-aqueous solution can be dried over a drying agent such as for example K_2SO_4, Na_2SO_4 and $MgSO_4$.

Removal of the non-aqueous solvents in steps v] and vi] can be established in any way known to one skilled in the art to remove such solvents.

Further purification can be be established by sublimation of the isomers. Preferably pressures in the range from 0.0033 to 0.33 kPa (0.025 to 2.5 mm Hg), more preferably in the range from 0.027 to 0.27 kPa (0.2 to 2 mm Hg) are used. Depending on the pressure applied, the temperatures can vary widely. Preferably a temperature in the range of 40 °C and higher is used, more preferably a temperature in the range from 40 °C to 90 °C is used.

II. The use of specific reaction conditions during the preparation of bidentate diphosphines

A preferred method for the preparation of some bidentate diphosphine ligands comprises refluxing a phosphabicycloalkane hydride, viz. 9-phosphabicyclononane hydride, with a α,ω-dihaloalkane, such as 1,2-dibromoethane or 1,3-diiodopropane in a suitable solvent. After neutralisation with a suitable basic compound the bidentate diphosphine can be isolated.

It has now been surprisingly found that by the use of specific reaction conditions a similar preparation process can be used to prepare a bidentate diphosphine composition wherein more than 60% w/w of bidentate diphosphine present has the general formula II

$$X^1\text{-}R\text{-}X^2 \qquad \text{(II)}$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms.

The present invention therefore also relates to a process for the preparation of bidentate diphosphines having general formula (II) comprising:

A1) heating a composition of phosphabicycloalkane hydrides with a α,ω-dihaloalkane in a suitable solvent, in a molar ratio of phosphabicycloalkane to α,ω-dihaloalkane of more than 2, yielding a charged bidentate diphosphine dihydride;

A2) neutralisation of the charged bidentate diphosphine dihydride with a suitable basic compound, yielding a bidentate diphosphine composition wherein more than 60% w/w of bidentate diphosphine present has the general formula II.

Preferably the α,ω-dihaloalkane is a α,ω-dibromo-alkane, α,ω-dichloroalkane or α,ω-diiodoalkane.

The molar ratio of phosphabicycloalkane to α,ω-dihaloalkane is preferably more than 3, more preferably more than 4 and most preferably in the range more than 4 to 20.

The solvent used in step A1) can be any solvent found suitable for the process. Preferred solvents include saturated hydrocarbons, e.g. paraffins and linear, branched and cyclic alkanes, such as hexane and pentane, aromatics such as toluene and benzene; nitriles such as for example acetonitrile and alkanols such as for example ethanol, methanol and isopropanol and mixtures of two or more of those. Especially preferred solvents are acetonitrile, hexane, ethanol and toluene, and mixtures of two or more of those.

Preferably the basic compound in step A2) is ammonia or a primary, secondary and tertiary amine or a hydroxide such as $Ba(OH)_2$, Na(OH) or K(OH). More preferred are alkali metal hydroxides, such as potassium hydroxide and sodium hydroxide.

It is further found that the preparation of bidentate diphosphine having the general formula II is enhanced by the use of an alkanol as a solvent.

The present invention therefore also relates to a process for the preparation of bidentate diphosphines having general formula (II)

$$X^1\text{-}R\text{-}X^2 \qquad \text{(II)}$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms, comprising:

B1) heating a composition of phosphabicycloalkane hydrides with a α,ω-dihaloalkane in an alkanol, yielding a charged bidentate diphosphine dihydride;

B2) neutralisation of the charged bidentate diphosphine dihydride with a suitable basic compound, yielding a bidentate diphosphine composition wherein more than 60% w/w of bidentate diphosphine present has the general formula II.

Preferred alkanols in step B1) are methanol, ethanol and isopropanol. Most preferred is ethanol. Preferences for α,ω-dihaloalkane, the molar ratio of phosphabicycloalkane to α,ω-dihaloalkane, and the basic compound in step B2) are as described hereinabove for the steps A1) and A2).

III. Purification of a composition of bidentate diphosphines.

A further method for the preparation of a bidentate diphosphine composition wherein more than 60% w/w of the bidentate diphosphine present has the general formula (II), comprises purification of a bidentate diphosphine composition wherein 60% w/w or less of the bidentate diphosphine present has the general formula (II).

Now a very advantageous method has been found for purification of such a composition wherein 60% w/w or less of the bidentate diphosphine present has the general formula (II). Surprisingly it was found that a bidentate diphosphine with two symmetrical phosphabicycloalkyl groups (s,s BDP), i.e. a bidentate diphosphine with general formula (II), can be separated from a composition comprising a mixture of bidentate diphosphine with two symmetrical phosphabicycloalkyl groups (s,s BDP), bidentate diphosphine with two asymmetrical phosphabicycloalkyl groups (a,a BDP) and bidentate diphosphine

with a symmetrical and an asymmetrical phosphabicycloalkyl group (a,s BDP), by exploiting a difference found in solubility.

The present invention therefore also provides a process for separation of a bidentate diphosphine with two symmetrical phosphabicycloalkyl groups (s,s BDP) from a mixture of bidentate diphosphines with two symmetrical phosphabicycloalkyl groups (s,s BDP), bidentate diphosphines with two asymmetrical phosphabicycloalkyl groups (a,a BDP) and bidentate diphosphines with a symmetrical and a symmetrical phosphabicycloalkyl group (a,s BDP), comprising selective extraction and/or recrystallisation of the mixture in a suitable solvent.

Such a selective extraction and/or recrystallisation was not known before. By selective is meant that isomers of a bidentate diphosphine with two phosphabicycloalkyl groups are extracted and/or recrystallised to a different extent. Preferably the selective extraction and/or recrystallisation is carried out such that it yields a liquor containing a,a BDP and a,s BDP and a solid or suspension containing s,s BDP.

An advantage of the selective extraction and/or recrystallisation process is that the process is easy to perform. In addition, the process does not involve the handling of toxic, volatile phosphabicycloalkanes for purification but the more easily handled bidentate diphosphine itself. Furthermore the process enables the preparation of bidentate diphosphine compositions with very high percentages of bidentate diphosphine having general formula (II) by repeated recrystallisation steps.

Preferably a bidentate diphosphine composition is prepared wherein more than 80% w/w, more preferably more than 90% w/w, and even more preferably in the range of from 95 to 100% w/w of bidentate diphosphine present is s,s BDP. More preferably a bidentate diphosphine

composition is prepared wherein in the range of from 99% w/w, most preferably of from 99.5% w/w to 100% w/w of bidentate diphosphine present is s,s BDP.

Preferred solvents for recrystallisation include organic solvents such as saturated and unsaturated hydrocarbons, e.g. paraffins and linear, branched and cyclic alkanes and alkenes, such as hexane and pentane, cyclohexane, hexene, aromatics such as toluene and benzene; alkanols such as methanol, phenol, ethanol, propanol, isopropanol, butanol, iso-butanol; ethers, such as for example dimethylether anisole (methyl phenyl ether), 2,5,8-trioxanonane (diglyme), diethylether, tetrahydrofuran, diphenylether, diisopropylether and the dimethylether of di-ethyleneglycol; esters, such as for example methylacetate, dimethyladipate, butyrolactone, propionates and pentenoates; ketones, such as acetone, methylethylketone, methylbutylketone and diethylketone; and sulphones, for example dialkylsulphones such as dimethylsulphone and diethylsulphone and cyclic sulphones, such as sulfolane (tetrahydrothiophene-2,2-dioxide), 2-methylsulfolane and 2-methyl-4-ethylsulfolane and mixtures of one or more of those or mixtures thereof with water.

Preferred solvents are alkanols and ketones, preferably those comprising from 1 to 15 carbon atoms, and mixtures thereof with water. The use of alkanols or ketones or mixtures of those, optionally mixed with water, results in a high degree of separation and an attractive yield of s,s BDP.

More preferred solvents are alkanols, preferably those comprising from 1 to 10 carbon atoms and mixtures thereof with water. Most preferred are methanol, ethanol and isopropanol and mixtures thereof with water. Alkanols and mixtures of alkanols with water have the additional advantage that any bidentate diphosphine oxides present

dissolve readily and can be easily separated from the s,s BDP, which dissolves to a much lesser extent. This opens opportunities to use an aged, partly oxidised starting bidentate diphosphine composition.

The amount of solvent used depends on whether a selective extraction or recrystallisation or a combination of those is carried out. Extraction can be economically more attractive because less solvent can be used and/or less energy is required for heating.

By extraction preferably a,a BPA and a,s BPA are extracted from the bidentate diphosphine compositions by repeated washings with a suitable solvent.

The temperature of the solvent depends on the solvent used, the amount of solvent used, and on the extent to which one wishes to dissolve (parts of) the bidentate diphosphine composition. Low temperatures and low amounts of solvent are economically more attractive.

Selective extraction and/or recrystallisation can be carried out by refluxing the composition of bidentate diphosphine in the solvent. The reflux temperature depends on the solvent used. Preferably solvents are used resulting in a reflux temperature in range of 5 to 200 °C, more preferably in the range of 15 to 150 °C.

Preferably the pressure during refluxing is in the range from 100 to 500 kPa (1 to 5 bar). Higher pressures have the advantage that a larger part of the bidentate diphosphine can be dissolved. Atmospheric pressures are economically more advantageous.

Preferably, the bidentate diphosphine is refluxed in a suitable solvent for 0.01 to 10 hours, more preferably in the range from 0.01 to 5 hours.

Extraction can be performed intermittently or continuously. In an intermittent extraction the bidentate diphosphine composition is preferably extracted in the

range from 1 to 20 times, as much as is sufficient to obtain the desired extraction of unwanted isomers. If possible, a small number of extractions, i.e. in the range from 1 to 5 times, is preferred for economical reasons. Preferably continuous extraction can be performed with a Soxhlet configuration.

The present invention will be illustrated by the following non-limiting examples.

Example 1

The experiment was carried out in a 250 ml magnetically stirred Hastelloy C autoclave (Hastelloy is a trademark). The autoclave was charged with 10 ml of propene, 40 ml anisole and 10 ml sulfolane, 0.25 mmol of platinum(II) acetylacetonate, 0.3 mmol of 1,2-PP'bis(9-phosphabicyclo[3.3.1]nonyl)ethane with a purity of > 99%, 0.3 mmol $SnCl_2$ and 0.3 mmol HCl. After being flushed, the autoclave was pressurised with carbon monoxide and hydrogen to a partial pressure of 3000 kPa (30 bar) of each. Subsequently, the reactor was sealed and the contents were heated to 115 °C and maintained at that temperature for 1.5 hours. After cooling, a sample was taken from the contents of the reactor and analysed by Gas Liquid Chromatography. The selectivity towards the linear product n-butyraldehyde was 98.6%.

Example 2

The experiment was carried out in a 250 ml magnetically stirred Hastelloy C autoclave. The autoclave was charged with 10 ml of propene, 40 ml anisole and 10 ml sulfolane, 0.25 mmol of platinum(II) acetylacetonate, 0.3 mmol of 1,3-PP'bis(9-phosphabicyclo[3.3.1]nonyl)-propane with a purity of > 99%, 0.3 mmol $SnCl_2$ and 0.3 mmol HCl. After being flushed, the autoclave was pressurised with carbon monoxide and hydrogen to a partial pressure of 3000 kPa (30 bar) of each.

Subsequently, the reactor was sealed and the contents were heated to 115 °C and maintained at that temperature for 1.5 hours. After cooling, a sample was taken from the contents of the reactor and analysed by Gas Liquid Chromatography. The selectivity towards the linear product n-butyraldehyde was 90.8%.

Example 3

The example was carried out in a 250 ml magnetically stirred Hastelloy C autoclave. The autoclave was charged with 10 ml of propene, 40 ml anisole and 10 ml sulfolane, 0.25 mmol of platinum(II) acetylacetonate, 0.3 mmol of meso (R,S) 2,3-PP'bis(9-phosphabicyclo[3.3.1]nonyl)butane with a purity of > 99% by weight, 0.3 mmol $SnCl_2$ and 0.3 mmol HCl. After being flushed, the autoclave was pressurised with carbon monoxide and hydrogen to a partial pressure of 3000 kPa (30 bar) of each. Subsequently, the reactor was sealed and the contents were heated to 100 °C and maintained at that temperature until the reaction was substantially complete. Complete propene conversion occurred in 0.5 hr. After cooling, a sample was taken from the contents of the reactor and analysed by Gas Liquid Chromatography. The selectivity towards the linear product n-butyraldehyde was 99.0%.

Example 4 (separation of phosphabicyclononanes)

A mixture of symmetrical and asymmetrical phosphabicyclononanes (33.9 g, 239 mmol, 153 mmol symmetrical: 86 mmol asymmetrical isomer) was dissolved in diethyl ether (240 ml). Subsequently deoxygenated water (240 ml) was added. The biphasic mixture was stirred vigorously while deoxygenated concentrated HCl solution (240 ml, 6 molar) was added over 90 min. The two phases were then separated and the aqueous phase was extracted 20 times with diethyl ether (50 ml each). The organic phases were combined (to reduce the volume, some

of the solvent can be removed in vacuum before continuing the work-up) and washed with a concentrated HCl solution (2 ml), and subsequently washed with a saturated $NaHCO_3$ solution (30 ml). Hereafter the organic solution was dried over $MgSO_4$ and filtered over basic alumina. The solvent was removed in vacuum to give the asymmetrical isomer in a yield of 9.52 g (equivalent to 67.1 mmol, about 78% of amount of asymmetrical isomer started with) in a 100% purity as a colourless solid. To the vigorously stirred aqueous phase fresh diethyl ether (200 ml) was added, the mixture was cooled to 0 °C and a 14.4 M NaOH solution (200 ml) was added over 1.5 h. The phases were separated and the aqueous phase was washed four times with diethyl ether (50 ml each). The combined organic phases were dried over $MgSO_4$ and filtered over basic alumina. The solvent was removed in vacuum to give the symmetrical isomer in a yield of 19.79 g (equivalent to 139 mmol, about 91% of amount of asymmetrical isomer started with) in a 90% purity. Sublimation of the 90% pure symmetrical isomer at 0.27 kPa (2 mm Hg) and 60 °C gave a sample of 98% pure symmetrical isomer in 80% recovery (15.83 g, 111 mmol) as a colourless solid.

All reactions in Examples 5-13 were carried out in an inert atmosphere (nitrogen). Solely p.a. grade solvents were used which were obtained from Merck. 1,2-PP'bis (phosphabicyclononyl)ethane(BPE) compositions as specified for each example were analysed by ^{31}P-NMR to indicate the amount of:

BPE-S = 1,2-PP'bis (phosphabicyclo[3.3.1]nonyl)ethane.

BPE-A = mixture of 1,2-PP'-bis(9-phosphabicyclo-[4.2.1]nonane) ethane, and 1-P-(9-phosphabicyclo-[4.2.1]nonane) 2-P'(9-phosphabicyclo[3.3.1]nonane) ethane.

BPE-O = mixture of oxides of 1,2-PP'bis(phosphabicyclononyl)ethane

Example 5: isopropanol as solvent

A suspension of 2.67 gram of BPE (containing 2.05 gram of BPE-S) in 25 ml of isopropanol was refluxed for 2 hrs. The now homogeneous solution was cooled to ambient temperature (about 20 °C) and stirred for 16 hours. A white precipitate was formed which was isolated by filtration under an atmosphere of nitrogen and the purified product was dried at 0.1 kPa (1 mbar) and 50 °C. Yield of BPE was 1.80 gram, containing 1.71 gram of BPE-S (84%). The liquid layer was evaporatedto dryness. Composition of precipitate and liquid layer was analysed by ^{31}P-NMR spectroscopy:

type BPE	precipitate	liquid layer
BPE-S	95.2	11.0
BPE-A	4.8	41.3
BPE-O	0.0	47.6

Example 6: methanol as solvent

2.33 gram of BPE (containing 1.74 gram of BPE-S) was suspended in 25 ml of methanol. The suspension was refluxed for 2 hours and subsequently stirred at ambient temperature (about 20 °C) for 16 hours. The white precipitate was isolated by filtration using Schlenk techniques and dried in vacuum. Yield of BPE was 1.92 gram, containing 1.64 gram of BPE-S (94%). The liquid layer was evaporated to dryness. The composition of precipitate and liquid layer were analysed by ^{31}P-NMR spectroscopy:

type BPE	Precipitate	liquid layer
BPE-S	85.4	11.8
BPE-A	14.6	57.0
BPE-O	0.0	31.1

Example 7: extractions with methanol

A suspension of 3.4 gram of BPE (containing 2.65 gram of BPE-S) in 25 ml of methanol was stirred for 4 hours at ambient temperature (about 20 °C). The white precipitate was isolated by filtration using Schlenk techniques and dried in vacuum (1st extraction). Yield of BPE was 2.88 gram, containing 2.52 gram of BPE-S (95%). The liquid layer was evaporated to dryness. This procedure was repeated twice (2nd and 3rd extraction). All fractions were weighted and analysed by ^{31}P-NMR spectroscopy.

	BPE starting material	precipitate 1st extraction	precipitate 2nd extraction	precipitate 3rd extraction
yield (gram)	3.4	2.8	2.3	1.8
overall BPE-S recovery (%)	-	92	85	70
BPE-S (%)	74.8	83.8	93.6	95.4
BPE-A (%)	21.8	11.8	6.4	4.6
BPE-O (%)	3.3	4.4	0.0	0.0

Example 8: Soxhlet extraction with methanol.

6.44 gram of BPE (containing 4.82 gram of BPE-S) was placed in a extraction filter and extracted with methanol for 2 hours in a Soxhlet configuration. The BPE material

was transferred to a round bottom flask and dried in vacuum. Yield of BPE was 4.4 gram, containing 3.92 gram of BPE-S (81%). The composition of precipitate and liquid layer were analysed by ^{31}P-NMR spectroscopy:

type BPE	precipitate	liquid layer
BPE-S	89.0	32.7
BPE-A	6.4	21.4
BPE-O	4.6	45.8

Example 9: Repetitive extraction with methanol/water (95/5 $^{v}/_{v}$)

A suspension of 3.18 gram of BPE (containing 2.64 gram of BPE-S) in 100 ml of methanol/water (95/5 $^{v}/_{v}$, degassed with N_2) was refluxed for 2 hours. After standing for 4 hours at ambient temperature (about 20 °C), the supernatant was decanted. The white precipitate was dried in vacuum (55 °C/0.1 kPa (1 mbar)). Yield of BPE was 2.50 gram, containing 2.37 gram of BPE-S (89%) (1st extraction). This procedure was repeated twice (2nd and 3rd extraction). All fractions were weighted and analysed by ^{31}P-NMR spectroscopy. The percentage BPE-O in the precipitate was < 0.5% and was therefore omitted for the calculations.

	BPE starting material	precipitate 1st extraction	precipitate 2nd extraction	precipitate 3rd extraction
yield (gram) overall BPE-S	3.18	2.5	2.2	1.78
recovery (%)	-	89	81	73
BPE-S (%)	83.6	94.9	96.9	97.7
BPE-A (%)	16.3	5.1	3.1	2.3

Example 10: Extraction of BPE material using 100 ml portions methanol/water (90/10 $^{v}/_{v}$):

A suspension of 4.98 gram of BPE starting material (containing 3.47 gram of BPE-S) in 100 ml of methanol/-water (90/10 $^{v}/_{v}$, degassed with N_2) was refluxed for 4 hours. After standing for 4 hours at ambient temperature (about 20 °C), the supernatant was decanted. The white precipitate was dried in vacuum (55 °C/0.1 kPa (1 mbar)). Yield of BPE was 3.72 gram, containing 3.34 gram of BPE-S (96%) (1st extraction). This procedure was repeated (2nd extraction). All fractions were weighted and analysed by ^{31}P-NMR spectroscopy.

	BPE starting material	precipitate 1st extraction	precipitate 2de extraction
yield (gram)	4.98	3.34	3.47
overall BPE-S recovery (%)	-	96	94
BPE-S (%)	69.7	89.9	92.0
BPE-A (%)	16.5	8.4	5.6
BPE-O (%)	13.8	1.8	2.4

Example 11: Extraction of BPE material using 200 ml portions methanol/water (90/10 $^{v}/_{v}$):

A suspension of 5.00 gram of BPE material (containing 3.48 gram of BPE-S) in 200 ml of methanol/water (90/10 $^{v}/_{v}$, degassed with N_2) was refluxed for 19 hours. After standing for 1 hour at ambient temperature (about 20 °C), the supernatant was decanted. The white precipitate and supernatant were dried in vacuum (55 °C/0.1 kPa (1 mbar)). Yield of BPE was 2.98 gram, containing 2.74 gram of BPE-S (79%). Both fractions were weighted and analysed by ^{31}P-NMR spectroscopy.

	BPE starting material	precipitate	liquid layer
yield (gram)	5.00	2.98	1.50
BPE-S recovery (%)	-	79	-
BPE-S (%)	69.7	92.1	9.3
BPE-A (%)	16.5	5.6	51.7
BPE-O (%)	13.8	2.3	39.0

Example 12: Extraction of BPE material with isopropanol/water (98/2 $^{v}/_{v}$)

A suspension of 5.30 gram of BPE material (containing 3.69 gram of BPE-S) in 40 ml of isopropanol and 0.8 ml of H_2O was refluxed for 6 hrs. The now homogeneous solution was cooled to ambient temperature (about 20 °C) and stirred for 16 hours. A white precipitate was formed which was isolated by filtration under an atmosphere of nitrogen and the purified product was dried (0.1 kPa (1 mbar)/60 °C). Yield of BPE was 3.50 gram, containing 3.30 gram of BPE-S (89%). The liquid layer was evaporated to dryness. Composition of precipitate and liquid layer was analysed by ^{31}P-NMR spectroscopy:

	BPE starting material	precipitate	filtrate
yield (gram)	5.30	3.50	1.60
BPE-S recovery %)	-	89	-
BPE-S (%)	69.7	94.4	13.3
BPE-A (%)	16.5	3.4	44.4
BPE-O (%)	13.8	2.3	42.3

Example 13: Repetitive extraction of BPE material with methanol/water (95/5 $^{v}/_{v}$)

A suspension of 3.18 gram of BPE material (containing 2.64 gram of BPE-S) in 100 ml of methanol/water (95/5 $^{v}/_{v}$, degassed with N_2) was refluxed for 2 hours. After standing for 4 hours at ambient

temperature (about 20 °C), the supernatant was decanted. The white precipitate was dried in vacuum (55 °C/0.1 kPa(1 mbar)). Yield of BPE was 2.50 gram, containing 2.37 gram of BPE-S (89%) (1st extraction). This procedure was repeated twice (2nd and 3rd extraction). All fractions were weighted and analysed by ^{31}P-NMR spectroscopy. The percentage BPE oxides in the precipitate was < 0.5% and were therefore omitted for the calculations.

	BPE starting material	precipitate 1st extraction	precipitate 2nd extraction	precipitate 3rd extraction
yield (gram)	3.18	2.5	2.2	1.78
overall SS recovery (%)	-	89	81	73
BPE-S (%)	83.6	94.9	96.9	97.7
BPE-A (%)	16.3	5.1	3.1	2.3

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REVISED CLAIMS

1. A process for the carbonylation of optionally substituted ethylenically unsaturated compounds by reaction with carbon monoxide and a coreactant in the presence of a catalyst system including:

(a) a source of Pt group metal cations,

(b) a bidentate diphosphine composition

wherein from 95% w/w to 100% w/w of bidentate diphosphine present in the bidentate diphosphine composition has the general formula II

$$X^1\text{-}R\text{-}X^2 \qquad \text{(II)}$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms.

2. Catalyst system including:

(a) a source of Pt group metal cations,

(b) a bidentate diphosphine composition

wherein from 95% w/w to 100% w/w of bidentate diphosphine present in the bidentate diphosphine composition has the general formula (II)

$$X^1\text{-}R\text{-}X^2 \qquad \text{(II)}$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms.

3. Catalyst system as claimed in claim 2, wherein as an additional component (c) a source of anions is included.

4. Bidentate diphosphine composition wherein from 95% w/w to 100% w/w of bidentate diphosphine present has the general formula II

$$X^1\text{-}R\text{-}X^2 \qquad \text{(II)}$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms, with the proviso that the bidentate diphosphine is not 1,3-PP'bis(9-phosphabicyclo[3.3.1]nonyl)propane.

5. A process for the separation of symmetrical phosphabicycloalkane from a composition containing symmetrical and asymmetrical phosphabicycloalkanes comprising the following steps:

a) adding means to protonate a phosphabicycloalkane to a composition containing symmetrical phosphabicycloalkane (SPBA) and asymmetrical phosphabicycloalkane (APBA), yielding a composition comprising protonated symmetrical phosphabicycloalkane (SPBA+) and non-protonated asymmetrical phosphabicycloalkane (APBA);

b) separating protonated symmetrical phosphabicycloalkane (SPBA+) and non-protonated asymmetrical phosphabicycloalkane (APBA), yielding separated protonated symmetrical phosphabicycloalkane (SPBA+) and separated non-protonated asymmetrical phosphabicycloalkane (APBA)

c) adding means to de-protonate the separated protonated symmetrical phosphabicycloalkane (SPBA+), yielding separated non-protonated symmetrical phosphabicycloalkane (SPBA).

6. A process for the separation of symmetrical phosphabicycloalkane from a composition containing symmetrical and asymmetrical phosphabicycloalkanes comprising:

i] dissolving a composition containing symmetrical phosphabicycloalkane (SPBA) and asymmetrical phosphabicycloalkane (APBA) in a suitable non-water miscible solvent, which does not dissolve protonated symmetrical phosphabicycloalkane (SPBA+), yielding a non-aqueous phosphabicycloalkane (PBA) solution;

ii] combining the non-aqueous PBA solution with an aqueous solution of a suitable acid, yielding an aqueous phase containing protonated SPBA+ and a non-aqueous phase containing non-protonated APBA;

iii] separating the aqueous phase containing protonated SPBA+ and the non-aqueous phase containing non-protonated APBA, yielding an aqueous solution containing protonated SPBA+ and a non-aqueous solution containing non-protonated APBA;

iv] combining the aqueous solution containing protonated SPBA+ with a suitable non-water miscible solvent and an aqueous solution of a suitable base, yielding a non-aqueous solution containing non-protonated SPBA;

v] removing the solvent from the non-aqueous solution containing non-protonated SPBA, yielding separated SPBA.

7. Process as claimed in claim 6, wherein an extra step vi] is added to the process comprising removing the solvent from the non-aqueous solution containing non-protonated APBA, yielding separated APBA.

8. Process for the preparation of bidentate diphosphines having general formula (II)

$$X^1\text{-}R\text{-}X^2 \qquad \text{(II)}$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms, comprising

A1) heating a composition of phosphabicycloalkane hydrides with a α,ω-dihaloalkane in a suitable solvent, in a molar ratio of phosphabicycloalkane to α,ω-dihaloalkane of more than 2, yielding a charged bidentate diphosphine dihydride;

A2) neutralisation of the charged bidentate diphosphine dihydride with a suitable basic compound, yielding a bidentate diphosphine composition wherein more than 60% w/w of bidentate diphosphine present has the general formula II.

9. Process for the preparation of bidentate diphosphines having general formula (II)

$$X^1\text{-}R\text{-}X^2 \qquad \text{(II)}$$

wherein X^1 and X^2 independently represent an optionally substituted symmetrical phosphabicycloalkyl group, having at least 5 ring atoms; and R represents a bivalent organic bridging group, connecting both phosphorus atoms, comprising

B1) heating a composition of phosphabicycloalkane hydrides with a α,ω-dihaloalkane in an alkanol, yielding a charged bidentate diphosphine dihydride;

B2) neutralisation of the charged bidentate diphosphine dihydride with a suitable basic compound, yielding a bidentate diphosphine composition wherein more than 60% w/w of bidentate diphosphine present has the general formula II.

10. Process for separation of a bidentate diphosphine with two symmetrical phosphabicycloalkyl groups (s,s BDP) from a mixture of bidentate diphosphines with two symmetrical phosphabicycloalkyl groups (s,s BDP), bidentate diphosphines with two asymmetrical phosphabicycloalkyl groups (a,a BDP) and bidentate diphosphines with a symmetrical and a symmetrical

phosphabicycloalkyl group (a,s BDP), comprising selective extraction and/or recrystallisation of the mixture in a suitable solvent.