

PROCESS FOR THE CARBONYLATION OF A CONJUGATED DIENE

The present invention provides a process for the carbonylation of a conjugated diene.

Carbonylation reactions of conjugated dienes are well known in the art. In this specification, the term carbonylation refers to a reaction of a conjugated diene under catalysis by a transition metal complex in the presence of carbon monoxide and a co-reactant. In this process, the carbon monoxide as well as the co-reactant add to the diene, as for instance described in WO-A-03/031457. WO-A-03/031457 discloses a process for the carbonylation of conjugated dienes, whereby the conjugated diene is reacted with carbon monoxide and a compound having an active hydrogen atom, for instance hydrogen, water, alcohols and amines in the presence of a catalyst system based on (a) a source of palladium cations, (b) a phosphorus-containing ligand of the formula (I)



wherein Q^1 is a divalent group which together with the phosphorus atom to which it is linked represents an unsubstituted or substituted 2-phospha-adamantane group or derivative thereof, wherein one or several of the carbon atoms are replaced by heteroatoms, Q^2 and Q^3 independently represent a monovalent group having 1-20 atoms or jointly divalent group having 2-20 atoms, and n is 4 or 5, and mixtures thereof.

Under the conditions usually employed for the carbonylation, conjugated dienes may also form dimers

and/or telomers, as for instance described in WO-A-03/040065. This side reaction is highly undesired, as it reduces the yield of the desired carbonylation products. The selectivity towards carbonylation products over telomerisation products is further referred to herein as chemoselectivity.

Other than the need to achieve an as high as possible chemoselectivity, there is also the desire to achieve a particularly high selectivity towards one of several possible isomeric carbonylation products, further referred to herein as regioselectivity. For the carbonylation of conjugated dienes, the regioselectivity towards a linear product, i.e. towards reaction at the primary carbon atom, is often desired, as the branched products usually have no industrial use, whereas the linear products are important intermediates, for instance in the synthesis of adipic acid derivatives for use in polyamides.

The catalysts disclosed in WO-A-03/031457 only provide limited chemoselectivity and yield, while requiring relatively large amounts of palladium and ligand to achieve at least satisfactory turnover numbers, and high temperatures. This makes the disclosed process costly to operate. Further, the product mixtures obtained need to undergo substantive purification and/or separation from byproducts due to the low selectivity, and ligand remainders due to low stability of the ligands employed, which is undesirable in an industrial process.

Accordingly, there remains the need to provide for a catalyst system that combines a higher chemoselectivity and a higher regioselectivity for the linear carbonylation products, while also giving a high turn over and yield employing a lower amount of palladium to

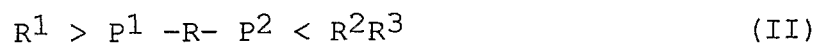
increase the overall efficiency of the process. Such a combination would also avoid having to subject the product mixture to a substantive purification to remove telomeric and polymeric by-products as well as the non-linear products.

It has now been found that the above identified process for the carbonylation of a conjugated diene with a coreactant having at least one active hydrogen atom can be very effectively performed in the presence of a novel catalytic system as set out below.

Summary of the invention

Accordingly, the subject invention provides a process for the carbonylation of a conjugated diene, comprising reacting the conjugated diene with carbon monoxide and a co-reactant having an active hydrogen atom in the presence of a catalyst system including:

- (a) a source of palladium; and
- (b) a bidentate diphosphine ligand of formula II,



wherein P^1 and P^2 represent phosphorus atoms;

R^1 represents an optionally substituted divalent organic group linked to the phosphorus atom by two tertiary carbon atoms; and R^2 and R^3 independently represent univalent groups of from 1 to 20 atoms containing a tertiary carbon atom through which each group is linked to the phosphorus atom, or R^2 and R^3 jointly form an optionally substituted divalent organic group containing at least 2 tertiary carbon atoms through which the group is linked to the phosphorus atom; and R represents a divalent bridging group comprising 3 atoms through which P^1 is linearly connected to P^2 ; and

- (c) a source of an anion.

In the process according to the invention, suitable sources for palladium of component (a) include palladium metal and complexes and compounds thereof such as palladium salts, for example the salts of palladium and halide acids, nitric acid, sulphuric acid or sulphonic acids; palladium complexes, e.g. with carbon monoxide or acetylacetonate, or palladium combined with a solid material such as an ion exchanger. Preferably, a salt of palladium and a carboxylic acid is used, suitably a carboxylic acid with up to 12 carbon atoms, such as salts of acetic acid, propionic acid and butanoic acid, or salts of substituted carboxylic acids such as trichloroacetic acid and trifluoroacetic acid. A very suitable source is palladium (II) acetate.

In the bidentate diphosphine ligand (b) according to formula (II), R^1 represents an optionally substituted divalent organic group linked to the phosphorus atom by two tertiary carbon atoms; R^2 and R^3 together or independently represent the same or a different optionally substituted organic group containing a tertiary carbon atom through which each group is linked to the phosphorus atom.

The groups R^1 , and R^2 and R^3 individually or jointly may further contain one or more heteroatoms such as oxygen, nitrogen, sulfur or phosphorus and/or be substituted by one or more functional groups comprising for example oxygen, nitrogen, sulfur and/or halogen, for example by fluorine, chlorine, bromine, iodine and/or a cyano group.

R^1 is in each case a branched cyclic, hetero-atom unsubstituted or substituted divalent alkyl group having from 4 to 10 atoms in the alkylene chain, in which the

CH₂- groups may also be replaced by hetero groups, for example -CO-, -O-, -SiR₂- or -NR- and in which one or more of the hydrogen atoms may be replaced by substituents, for example aryl groups.

5 Suitable monovalent groups R² and R³ are connected to each other only through the phosphorus atom P², and preferably have from 4 to 20 carbon atoms, and yet more preferably from 4 to 8 carbon atoms. The tertiary carbon atom through which each of the groups is connected to the
10 phosphorus atom can be substituted with aliphatic, cycloaliphatic, or aromatic substituents, or can form part of a substituted saturated or non-saturated aliphatic ring structure, all of which may contain hetroatoms. Preferably the tertiary carbon atom is
15 substituted with alkyl groups, thereby making the tertiary carbon atom part of a tertiary alkyl group, or with ether groups. Examples of particularly suitable organic groups R² and R³ are tert-butyl, 2-(2-methyl)-butyl, 2-(2-ethyl)butyl, 2-(2-phenyl)butyl, 2-(2-methyl)pentyl, 2-(2-ethyl)pentyl, 2-(2-methyl-4-phenyl)-
20 pentyl and 1-(1-methyl)cyclohexyl groups.

 Although the monovalent groups R² and R³ may be each individually different organic groups, due to the use of lower amount of different raw materials in the synthesis
25 the groups preferably represent the same group. Yet more preferably, R² and R³ represent tert-butyl groups due to the high steric hindrance induced by these groups and high selectivity achieved with such ligands.

 Although very good results have been obtained using
30 ligands wherein groups R² and R³ represent the same monovalent tertiary alkyl groups such as tert-butyl groups, such ligands can however be difficult to obtain

on an industrial scale due to the required use of metal organic compounds such as Grignard reactants.

Very good results were also obtained with diphosphine ligands, wherein R^1 , and R^2 and R^3 jointly represent the same or different divalent group that is directly attached to the phosphorus atom via two tertiary carbon atoms. This divalent group may have a monocyclic or a polycyclic structure.

R^2 together with R^3 may thus form an optionally substituted divalent organic group linked to the phosphorus atom by two tertiary carbon atoms as defined above for R^1 .

The tertiary carbon atom through which each of the groups is connected to the phosphorus atom can be substituted with aliphatic, cycloaliphatic, and forms part of a substituted saturated or non-saturated aliphatic ring structure, all of which may contain heteroatoms. Preferably the tertiary carbon atom is substituted with alkyl groups, thereby making the tertiary carbon atom part of a tertiary alkyl group, or by ether groups.

Suitable monocyclic diphosphine structures include those, wherein R^1 , and R^2 and R^3 together represent unsubstituted or substituted C_4 - C_{30} -alkylene groups in which CH_2 - groups may be replaced by hetero groups such as -O-, include 1,1,4,4-tetramethyl-buta-1,4-diyl-, 1,4-dimethyl-1,4-dimethoxy-buta-1,4-diyl-, 1,1,5,5-tetramethyl-penta-1,5-diyl-, 1,5-dimethyl-1,5-dimethoxy-penta-1,5-diyl-, 3-oxa-1,5-dimethoxy-penta-1,5-diyl-, 3-oxa-1,1,5,5-tetramethyl-penta-1,5-diyl-, 3-oxa-1,5-dimethyl-1,5-dimethoxy-penta-1,5-diyl- and similar

divalent radical structures bearing two tertiary carbon atoms connected to the phosphorus atom.

Diphosphines containing such divalent groups have the advantage that they are accessible via a different synthetic route involving reacting phosphines at milder conditions, which makes them more accessible on an industrial scale. Accordingly, R^1 , and R^2 and R^3 together may also represent an optionally substituted divalent cycloaliphatic group, wherein the cycloaliphatic group is linked to the phosphorus atom via two tertiary carbon atoms. R^1 , and R^2 together with R^3 are in this case preferably a branched cyclic, hetero-atom unsubstituted or substituted divalent alkyl group having from 4 to 10 atoms in the alkylene chain, in which the CH_2 - groups may also be replaced by hetero groups, for example $-CO-$, $-O-$, $-SiR_2-$ or $-NR-$ and in which one or more of the hydrogen atoms may be replaced by substituents, for example aryl groups.

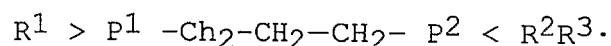
Of these, particularly preferred divalent monocyclic structures R^1 , and optionally R^2 and R^3 together are for instance 2,2,6,6-tetrasubstituted phosphinan-4-one or 2,2,6,6-tetrasubstituted phosphinan-4-thione structures, the ring atoms of which may be optionally substituted by heteroatom. Ligands comprising such structures may be conveniently obtained under mild conditions as described in WO 02/064249.

For instance, a bidentate diphosphine with identical organic groups R^1 , and jointly R^2 and R^3 may conveniently be obtained by reacting the compound $H^2P^1-R-P^2H_2$ (A) with a compound $(Z^1Z^2C)=(CZ^3)-(C=Y)-(CZ^4)=(CZ^5Z^6)$ (B), whereby Z^1 , Z^2 , Z^5 and Z^6 represent optionally heteroatom-

substituted organic groups, Z^3 and Z^4 represent optionally heteroatom-substituted organic groups or hydrogen groups, and whereby Y represents oxygen or sulfur.

5 An example for such a compound is 2,6-dimethyl-2,5-heptadien-4-one (also known as diisopropylidene acetone, or phorone). If more than a single compound (B) is employed, ligands with different groups comprising R^1 and R^2 , and comprising R^3 and R^4 are formed. The bidentate
10 ligands can be prepared in the meso- and rac-form. The meso-form is preferred for the purpose of the present invention.

 In the diphosphine ligand according to formula (II), R preferably represents divalent bridging group
15 comprising 3 atoms through which P^1 is linearly connected to P^2 . For the skilled person, the term "linearly connected" clearly and unambiguously has the meaning that the phosphorus atoms P^1 and P^2 are connected linearly and directly by the three-atom chain. For instance, if R was
20 a trimethylene group, the ligand would have the structure



 Suitable bridging groups R may be based on carbon atoms, such as in trimethylene (n-propane), which may optionally be substituted, and/or a derivative thereof,
25 wherein one or several of the carbon atoms are replaced by heteroatoms, such as for instance in oxydimethane, or in dimethylamine. Suitable heteroatoms include nitrogen, sulphur, silicon or oxygen atoms. The bridging group R can thus be substituted, for example with alkyl groups or
30 heteroatoms, or non-substituted. Suitable substituents for the bridging group include groups containing heteroatoms such as halides, sulphur, phosphorus, oxygen

and nitrogen. Examples of such groups include chloride, bromide, iodide and groups of the general formula -O-H, -O-X₂, -CO-X₂, -CO-O-X₂, -S-H, -S-X, -CO-S-X, -NH₂, -NHX, -NO₂, -CN, -CO-NH₂, -CO-NHX and -CO-NX₂, in which X independently represents alkyl groups having from 1 to 4 carbon atoms like methyl, ethyl, propyl, isopropyl and n-butyl. However, R preferably represents trimethylene (n-propane), since such ligands are readily accessible.

An especially preferred diphosphine ligand according to the subject invention is a compound according to formula (II), wherein R¹, and R² together with R³, together with the respective phosphorus atoms P¹ or P² form a 2,2,6,6-tetramethyl phosphinan-4-one, and wherein R represent a propylene (trimethylene) backbone structure.

The ratio of moles of bidentate diphosphine, i.e. catalyst component (b), per mole atom of palladium, i.e. catalyst component (a), is not critical. Preferably it ranges from 0.1 to 100, more preferably from 0.5 to 10, yet more preferably from 1 to 5, yet more preferably in the range of 1 to 3, again more preferably in the range of 1 to 2, and yet more preferably in the range of 1 to 1.5. In the presence of oxygen, slightly higher than stoichiometric amounts are beneficial.

Quite surprisingly, similar ligands with tertiary butyl or cyclic substituents at the phosphorus atoms, wherein R is ethylene were found to have only a very limited activity compared to the ligands according to the process of the subject invention. Similarly, the ligands disclosed in WO-A-03/031457, wherein R¹ to R⁴ are as defined herein, but wherein R represents a bridging group having more than 3 atoms, in particular 4 or 5, are

significantly less active and require much higher amounts of palladium (of around 1:450 on the diene substrate) and higher temperatures in order to achieve a similar level of conversion, and only achieve a very limited
5 selectivity. Accordingly, in the subject process preferably the catalyst is present in an amount below 500 mole atom of palladium per mole of conjugated diene.

The subject process permits to react conjugated
dienes with carbon monoxide and a co-reactant. The
10 conjugated diene reactant has at least 4 carbon atoms. Preferably the diene has from 4 to 20 and more preferably from 4 to 14 carbon atoms. However, in a different preferred embodiment, the process may also be applied to molecules that contain conjugated double bonds within
15 their molecular structure, for instance within the chain of a polymer such as a synthetic rubber.

The conjugated diene can be substituted or non-substituted. Preferably the conjugated diene is a non-substituted diene. Examples of useful conjugated dienes
20 are the 1,3-butadienes, conjugated pentadienes, conjugated hexadienes, cyclopentadiene and cyclohexadiene, all of which may be substituted. Of particular commercial interest are 1,3-butadiene and 2-methyl-1,3-butadiene (isoprene).

25 The feed containing the diene reactant does not necessarily have to be free of admixture with alkenes, since the carbonylation reaction of the present invention is particularly selective for diene feeds. Even an admixture with up to 5 mol% of alkynes based on the diene
30 reactant, can be tolerated in the feed.

The ratio (v/v) of diene and co-reactant in the feed can vary between wide limits and suitably lies in the range of 1:0.1 to 1:500.

The co-reactant according to the present invention may be any compound having a mobile hydrogen atom, and capable of reacting as nucleophile with the diene under catalysis. The nature of the co-reactant largely
5 determines the type of product formed. A suitable co-reactant is water, a carboxylic acid, alcohol, ammonia or an amine, a thiol, or a combination thereof. Inasmuch as the co-reactant is water, the product obtained will be an ethylenically unsaturated carboxylic acid. Ethylenically
10 unsaturated anhydrides are obtained inasmuch as the co-reactant is a carboxylic acid. For an alcohol co-reactant, the product of the carbonylation is an ester. Similarly, the use of ammonia (NH_3) or a primary or secondary amine RNH_2 or $\text{R}'\text{R}''\text{NH}$ will produce an amide,
15 whereas and the use of a thiol RSH will produce a thioester. In the above-defined co-reactants, R , R' and/or R'' represent optionally heteroatom-substituted organic groups, preferably alkyl, alkenyl or aryl groups. When ammonia or amines are employed, a small portion of
20 these co-reactants will react with acids present under formation of an amide and water. Hence, in the case of ammonia or amine-co-reactants, there is always water present.

Preferably the carboxylic acid co-reactant has the
25 same number of carbon atoms as the diene reactant, plus one.

Preferred alcohol co-reactants are alkanols with 1 to 20, more preferably with 1 to 6 carbon atoms per molecule, and alkanediols with 2-20, more preferably 2 to
30 6 carbon atoms per molecule. The alkanols can be aliphatic, cycloaliphatic or aromatic. Suitable alkanols in the process of the invention include methanol,

ethanol, ethanediol, n-propanol, 1,3-propanediol, iso-propanol, 1-butanol, 2-butanol (sec butanol), 2-methyl-1-propanol (isobutanol), 2-methyl-2-propanol (tert-butanol), 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol (isoamyl alcohol), 2-methyl-2-butanol (tert-amyl alcohol), 1-hexanol, 2-hexanol, 4-methyl-2-pentanol, 3,3-dimethyl-2-butanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1,2-ethylene glycol and 1,3-propylene glycol, of which methanol is the most preferred due to the high turn over achievable and due to the particular usefulness of the obtained products.

Preferred amines have from 1 to 20, more preferably having 1 to 6 carbon atoms per molecule, and diamines having 2-20, more preferably 2 to 6 carbon atoms per molecule. The amines can be aliphatic, cycloaliphatic or aromatic. More preferred due to the high turnovers achieved are ammonia and primary amines. In the case that the anion (c) of the catalyst system is an acid, preferably the amount of ammonia or amine is less than then stoichiometric based on the amine functionality.

Inadvertently, when the coreactant is ammonia, and to a lesser extent a primary amine, a small amount of the acid present will react to an amide under liberation of water. Hence, there is also always a small amount of acid formed from the conjugated diene, carbon monoxide and the water, which in turn replaces acid converted to amide by the direct reaction as described above.

The thiol co-reactants can be aliphatic, cycloaliphatic or aromatic. Preferred thiol co-reactants are aliphatic thiols with 1 to 20, more preferably with 1 to 6 carbon atoms per molecule, and aliphatic dithiols

with 2-20, more preferably 2 to 6 carbon atoms per molecule.

The source of anions (c) preferably is an acid, more preferably a carboxylic acid, which can serve both as promoter component (c), as well as solvent for the reaction.

Again more preferably, the source of anions is an acid having a pK_a above 2.0 (measured in aqueous solution at 18 °C), and yet more preferably catalyst component (c) is an acid having a pK_a above 3.0, and yet more preferably a pK_a of above 3.6.

Examples of preferred acids include carboxylic acids, such as acetic acid, propionic acid, butyric acid, pentanoic acid, pentenoic acid and nonanoic acid, the latter three being highly preferred as their low polarity and high pK_a was found to increase the reactivity of the catalyst system. Very conveniently the acid corresponding to the desired product of the reaction can be used as the catalyst component (c).

Pentenoic acid is particularly preferred in case the conjugated diene is 1,3-butadiene. Catalyst component (c) can also be an ion exchanging resin containing carboxylic acid groups. This advantageously simplifies the purification of the product mixture.

The molar ratio of the source of anions, and palladium, i.e. catalyst components (c) and (b), is not critical. However, it suitably is between 2:1 and 10^7 :1 and more preferably between 10^2 :1 and 10^6 :1, yet more preferably between 10^2 :1 and 10^5 :1, and most preferably between 10^2 :1 and 10^4 :1 due to the enhanced activity of the catalyst system.

If a co-reactant should react with the acid serving as source of anions, then the amount of the acid to co-reactant should be chosen such that a suitable amount of free acid is present. Generally, a large surplus of acid over the co-reactant is preferred due to the enhanced reaction rates.

The quantity in which the complete catalyst system is used is not critical and may 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 palladium per mole of conjugated diene are used, preferably in the range of 10^{-5} to 10^{-2} gram atom per mole. The process may optionally be carried out in the presence of a solvent, however preferably the acid serving as component (c) is used as solvent and as promoter.

The carbonylation reaction according to the present invention is carried out at moderate temperatures and pressures. Suitable reaction temperatures are in the range of 0-250 °C, more preferably in the range of 50-200 °C, yet more preferably in the range of from 80-150 °C.

The reaction pressure is usually at least atmospheric. Suitable pressures are in the range of 0.1 to 15 MPa (1 to 150 bar), preferably in the range of 0.5 to 8,5 MPa (5 to 85 bar). Carbon monoxide partial pressures in the range of 0.1 to 8 MPa (1 to 80 bar) are preferred, the upper range of 4 to 8 MPa being more preferred. Higher pressures require special equipment provisions.

In the process according to the present invention, the carbon monoxide can be used in its pure form or diluted with an inert gas such as nitrogen, carbon

dioxide or noble gases such as argon, or co-reactant gases such as ammonia.

Furthermore, the addition of limited amounts of hydrogen, such as 3 to 20 mol% of the amount of carbon monoxide used, promotes the carbonylation reaction. The use of higher amounts of hydrogen, however, tends to cause the undesirable hydrogenation of the diene reactant and/or of the unsaturated carboxylic acid product.

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

Example 1 and Comparative Examples A-D - batch reactions for carbonylation of butadiene with methanol

A 250 ml magnetically stirred autoclave was successively charged with palladium acetate (0.1 mmol), 20 ml methanol, 40 ml pentenoic acid and 0.3 mmol of the respective ligands in Example 1 and Comparative Examples A and B, and 0.5 mmol of the ligands employed in Comparative Examples C and D.

The autoclave was then closed and evacuated and flushed with Nitrogen, and then 20 ml butadiene was pumped in. The autoclave was pressurized with CO to 6.0 MPa, sealed, heated to 135 °C and maintained at the temperature for 10 hours. Finally the autoclave was cooled and the reaction mixture was analysed with GLC.

The initial carbonylation rate (mol per mol Pd per hour) of this batch operation, as presented in Table I, is defined as the mean rate of CO consumption over the first two hours.

In Example 1, about 80% of the butadiene had been converted, with a selectivity for the methyl pentenoate of above 95%. In the comparative Examples A and B, about 30% of the butadiene had reacted to a mixture of

4-vinylcyclohexene and butadiene polymer. In Comparative Examples C and D, no CO conversion could be measured.

Table I

Example	Ligand	Initial carbonylation rate	Selectivity for pentenoate	Conversion of butadiene [%]	Byproducts
		mol/mol Pd/hr			
1	1,3-P,P'-bis(2,2,6,6-tetramethyl-phosphinan-4-on)-propane	500	>95	80	4-vinyl-cyclohexane (VCH)
A	1,3-bis(di-tert-butylphosphino)propane	80	<50	30	Polybutadiene and VCH
B	1,2-bis-(2,2,6,6-tetramethyl-phosphinan-4-on)ethane	35	<10	15	Polybutadiene and VCH
C	1,2-bis-(9-phosphabicyclo-[3.3.1]-nonylethane	-*	-*	30	Polybutadiene and VCH
D	1,4-(diphenylphosphino)-butane	-*	-*	30	Polybutadiene and VCH

* No CO conversion could be measured.

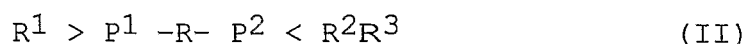
The results indicate that the subject process shows a surprisingly high conversion and selectivity for the catalyst system as claimed, whereas ligands not according to the present invention, however structurely closely related, show a much worse performance.

C L A I M S

1. A process for the carbonylation of a conjugated diene, comprising reacting the conjugated diene with carbon monoxide and a co-reactant having an active hydrogen atom in the presence of a catalyst system including:

(c) a source of palladium; and

(d) a bidentate diphosphine ligand of formula II,



wherein P^1 and P^2 represent phosphorus atoms;

R^1 represents an optionally substituted divalent organic group linked to the phosphorus atom by two tertiary carbon atoms; and R^2 and R^3 independently represent univalent groups of from 1 to 20 atoms containing a tertiary carbon atom through which each group is linked to the phosphorus atom, or R^2 and R^3 jointly form an optionally substituted divalent organic group containing at least 2 tertiary carbon atoms through which the group is linked to the phosphorus atom; and R represents a divalent bridging group comprising 3 atoms through which P^1 is linearly connected to P^2 ; and

(c) a source of an anion.

2. A process according to claim 1, wherein R is an optionally substituted trimethylene group.

3. A process according to claim 1 or claim 2, wherein

R^1 , and/or R^2 and R^3 together represent a 2,2,6,6-tetra-substituted phosphinan-4-one structure, or a 2,2,6,6-tetra-substituted phosphinan-4-thione structure.

4. A process according to any one of claims 1 to 3,
wherein the source of anions (c) is a carboxylic acid.

5. A process according to any one of claims 1 to 4,
wherein an amount of 3 to 20 mol%, related to the carbon
monoxide, of hydrogen is added.

6. A process according to any one of claims 1 to 5,
wherein the conjugated diene is 1,3-butadiene or 2-
methyl-1,3-butadiene.

7. A process according to any one of claims 1 to 6,
wherein the catalyst component(c) is present in a molar
ratio to catalyst component (a) in the range of $10^2:1$ and
 $10^4:1$.

8. A process as claimed in any one of claims 1 to 7,
wherein the reaction temperature is in the range of 50 to
250 °C, the reaction pressure is in the range of 0,1 to
15 MPa, and the carbon monoxide partial pressure is in
the range of 0,1 to 6,5 MPa.

9. A process according to any one of claims 1 to 8,
wherein the catalyst component is present in an amount
below 500 mole atom of palladium per mole of conjugated
diene.