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Process for producing aldehydes

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The invention relates to a process for producing aldehydes by hydroformylation of olefins in the presence of water-soluble rhodium complex catalysts.

5 It is known to produce aldehydes and alcohols, which contain one carbon atom more than the starting olefin, by reacting olefins with carbon monoxide and hydrogen (hydroformylation). The reaction is catalyzed by hydrido-metal carbonyls, preferably those of the metals of group 10 VIII of the Periodic Table. Apart from cobalt, which is widely used industrially as a catalyst metal, rhodium has recently been gaining increasing importance. In contrast to cobalt, rhodium allows the reaction to be carried out at a low pressure; furthermore, preferably straight-chain 15 n-aldehydes are formed, with an only minor fraction of iso-aldehydes. Finally, the hydrogenation of the olefins to give saturated hydrocarbons in the presence of rhodium catalysts is also markedly less extensive than in the case of using cobalt catalysts.

20 In the processes accepted in industry, the rhodium catalyst is employed in the form of modified hydrido-rhodium carbonyls which contain additional ligands, especially tertiary organic phosphines or phosphites. In most cases, there is an excess of the ligands, so that 25 the catalyst system is composed of the complex compound and free ligand. The use of the rhodium catalysts described allows the hydroformylation reaction to be carried out at pressures below 30 MPa.

30 In this process, however, it proves to be difficult to separate off the reaction products and to recover the catalysts which are homogeneously dissolved in the reaction product. In general, the reaction product is distilled for this purpose out of the reaction mixture. In practice, however, because of the thermal sensitivity 35 of the aldehydes and alcohols formed, this approach is feasible only in the hydroformylation of lower olefins,

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5 i.e. olefins having up to about 8 carbon atoms in the molecule. In addition, it has been found that thermal stress on the distillation material also leads to considerable catalyst losses due to decomposition of the rhodium complex compounds.

10 The drawbacks described are avoided by the use of catalyst systems which are soluble in water. Such catalysts have been described, for example, in German Patent 2,627,354. The solubility of the rhodium complex compounds is here achieved by the use of sulfonated triarylphosphines as a complexing constituent. In this process variant, the catalyst is separated off from the reaction product after completion of the reaction, simply by separating the aqueous and organic phases, i.e. without
15 distillation and hence without additional thermal process steps. A further feature of this procedure is that n-aldehydes are formed with high selectivity from terminal olefins, with only very minor quantities of iso-aldehydes. Sulfonated triarylphosphines and in addition
20 also carboxylated triarylphosphines are preferably used as complexing constituents of water-soluble rhodium complex compounds.

25 The known two-phase processes have proven to be highly suitable on the industrial scale. Nevertheless, efforts are being made to perfect the process even further. Thus, it is attempted to increase the activity of the catalysts by modification of the complex ligands and to extend their activity with the object of further reducing the specific catalyst requirement - both rhodium and ligand -
30 and hence the production costs. Economic factors are also the reason for working towards a marked reduction in the phosphine/rhodium ratio. A further improvement in the hitherto achieved high selectivity with respect to the formation of non-branched aldehydes is also desired. It
35 must be remembered here that several million tonnes of hydroformylation products are manufactured per year, so that even a small increase in the selectivity has

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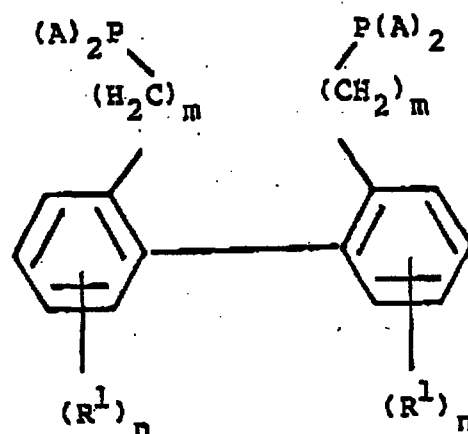
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economically significant consequences.

It is the object of the invention to improve the hydro-
formylation process as sketched above, i.e. to develop
catalysts which exceed the activity and selectivity of
5 known catalysts at the lowest possible ligand/rhodium
ratio.

The invention comprises a process for producing aldehydes
by reacting monoolefins, unconjugated polyolefins,
cycloolefins or derivatives of these classes of compounds
10 with carbon monoxide and hydrogen at temperatures from 20
to 150°C and pressures from 0.1 to 20 MPa in the presence
of water-soluble rhodium compounds, containing phosphines
in complex bonding, as catalysts. The process comprises
using, as the phosphines, diphosphines, derived from
15 biaryl compounds, of the general formula I



(I)

which are substituted by one or more sulfonic acid
groups, the A radicals in the formula I being identical
or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl
20 radicals, the R^1 radicals being identical or different and
being hydrogen, alkyl or alkoxy radicals having 1 to
14 carbon atoms, or also cycloalkyl, aryl or aryloxy
radicals having 6 to 14 carbon atoms, or a fused benzene

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ring, the m indices being identical or different and being integers from 0 to 5 and the n indices likewise being identical or different and being integers from 0 to 4.

- 5 The water-soluble rhodium/diphosphine complex compounds used as catalysts according to the novel process are distinguished by a remarkably high effectiveness, determined by the two criteria of "activity" A , namely

$$10 \quad A = \frac{\text{mol of aldehyde}}{\text{mol of Rh} \times \text{minute}}$$

and "productivity" P , namely

$$15 \quad P = \frac{\text{g of aldehyde}}{\text{ml of catalyst solution} \times \text{hour}}$$

- 20 The values of these two parameters, reached by the processes of the state of the art, are considerably exceeded by the procedure according to the invention. The formation of normal aldehydes increases further and the discharge of rare metal and phosphine with the reaction product is reduced. In addition, these results are achieved by the use of catalysts which have a markedly lower ligand/rhodium ratio than those used hitherto. These and other results, which are very valuable for
- 25 carrying out the process on an industrial scale, were neither derivable from theoretical considerations nor foreseeable from experience in practice.

- 30 The sulfonated diphosphines characteristic as a catalyst constituent for the novel process can be prepared from biaryls, which are accessible by known syntheses, for example by coupling aryl-Grignard reagents with aryl halides. The introduction of the phosphorus-organic radical $-(H_2C)_nP(A)_2$ - into the biaryl molecule is also

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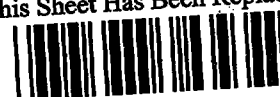


carried out by conventional methods, for example by reacting a phosphorus compound of the general formula $X-(H_2C)_mP(A)_2$, in which X is a halogen atom, with the biaryl in the presence of a reagent which eliminates protons, such as sodium amide or butyllithium. In the last reaction step, the diphosphine is sulfonated with oleum, i.e. with a solution of sulfur trioxide in sulfuric acid, at temperatures from 0 to 60°C. The sulfonation product is isolated from the acidic solution, diluted with water, in accordance with the state of the art, for example by extraction with the solution of a water-insoluble amine in a water-insoluble organic solvent.

Preferred sulfonated diphosphines in the procedure according to the invention are those which are derived from biaryls of the general formula I, in which the A radicals are identical or different and are a phenyl, tolyl or naphthyl radical, the R¹ radicals are likewise identical or different and are hydrogen or a methyl, isopropyl, isobutyl, t-butyl, phenyl or naphthyl radical or a fused benzene ring (so that a naphthyl structure is formed), m is 1 and n is 0 or 1.

Sulfonated diphosphines whose biaryl skeleton is substituted by radicals R¹ in the 6- and 6'-positions are also of great importance within the scope of the claimed process. The presence of these radicals hinders the rotation of the two substituted phenyl radicals. Rhodium complex compounds which contain such molecules as ligands can therefore be used as catalysts for enantioselective reactions.

Examples of diphosphines which are successfully used in the novel process are the products obtained by sulfonation of 2,2'-bis(diphenylphosphanomethyl)-biphenyl (called BISBIS below) and of 2-(diphenylphosphanomethyl)-1-[2-(diphenylphosphanomethyl)phenyl]-naphthalene (called PHENAPS below).



It is not necessary to use the disphosphines as single compounds. Mixtures of sulfonated disphosphines derived from biaryl compounds of different structure are equally suitable as mixtures of biaryls containing identical or different phosphine radicals and having different degrees of sulfonation. Finally, mixtures of sulfonated mono- and di-phosphines in combination with rhodium also give very active catalysts. Thus, for example, mixtures of BISBIS and Na triphenylphosphine-trisulfonate (called TPPTS below) have also proven suitable.

It has also been found to be advantageous to use rhodium and sulfonated diphosphine not in the stoichiometric ratio, i.e. corresponding to the chemical composition of the rhodium complex compound which forms in the course of the hydroformylation reaction, but to employ an excess of diphosphine. The rhodium/diphosphine ratio can here be varied within wide limits, and about 1 to 130 mol of diphosphine can be used per mol of rhodium. A rhodium/diphosphine ratio in the range from 1:2 to 1:25 and especially from 1:2 to 1:10 mol is preferred.

Rhodium is employed either as the metal or as a compound. In the metallic form, it is used either as finely dispersed particles or it is precipitated as a thin coating on a support such as activated carbon, calcium carbonate, aluminum silicate or alumina. Suitable rhodium compounds are substances which are water-soluble or become water-soluble under the reaction conditions. The various rhodium oxides, salts of inorganic hydrogen acids and oxygen acids and also salts of aliphatic monocarboxylic and polycarboxylic acids are suitable. Examples of rhodium salts are rhodium nitrate, rhodium sulfate, rhodium acetate, rhodium 2-ethylhexanoate and rhodium malonate. Rhodium halogen compounds are, however, less suitable because of the corrosive behavior of the halide ions. In addition, rhodium carbonyl compounds such as $\text{Rh}_3(\text{CO})_{12}$ or $\text{Rh}_3(\text{CO})_{16}$ or complex salts of rhodium, e.g. cyclooctadienyl-rhodium compounds, can be used. Rhodium



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oxide and especially rhodium acetate and rhodium 2-ethylhexanoate are preferred. It must be assumed that, in the presence of water gas, water-soluble rhodium complex compounds which contain carbon monoxide and diphosphine as ligands are formed under the conditions of the hydroformylation reaction. Together with the diphosphine dissolved in the water, they give the catalyst system.

The catalyst solution is prepared from the components either in the hydroformylation reactor or, beforehand, in separate equipment and then fed to the hydroformylation reactor.

The concentration of rhodium in the aqueous catalyst solution is 20 to 1000 ppm by weight (relative to the solution), preferably 100 to 600 ppm by weight and especially 200 to 400 ppm by weight.

The reaction of the olefin with carbon monoxide and hydrogen takes place under pressures from about 0.1 to about 30 MPa, preferably 1 to 12 MPa and especially 3 to 7 MPa. The composition of the synthesis gas, i.e. the volume ratio of carbon monoxide and hydrogen, can extend over wide ranges and be varied, for example, between 1:10 and 10:1. In general, gas mixtures are used in which the volume ratio of carbon monoxide and hydrogen is about 1:1 or deviates only slightly from this value in one direction or the other.

The reaction temperature is between about 20 and 150°C, and 80 to 140°C and especially 100 to 125°C are preferred.

The conversion of the reactants present in the liquid and gaseous phase takes place in conventional reactors. The progress of the reaction is decisively influenced by the fact that the aqueous catalyst solution must be saturated with the liquid or gaseous, hydrophobic olefin and with

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the synthesis gas. It is therefore necessary to produce the greatest possible contact area between the phases. It has proven suitable to stir the liquid reactor content - catalyst solution, if appropriate liquid olefin, and reaction product - intensively and to feed the gaseous reactants - synthesis gas and, if appropriate, olefin - to the liquid phase via distribution devices. It has been found to be very suitable to minimize the fraction of the organic phase in the reaction mixture. Surprisingly, the organic phase does not contribute to the solubility of the reactants in the aqueous phase, and undesired side reactions of the reaction product, which cannot be excluded in the case of increasing residence time of the product in the reactor, are avoided. Accordingly, the volume ratio of aqueous and organic phase is set to 1:1 to 100:1, preferably 10:1 to 100:1. For this purpose, a corresponding part of the reaction mixture can be discharged continuously from the reactor, the aqueous and organic phases can be separated from one another, and the aqueous phase can be recycled to the reactor. The reaction can be carried out batchwise or, preferably, continuously.

The process according to the invention is successfully applicable in the conversion of monoolefins, unconjugated polyolefins, cyclic olefins and derivatives of these unsaturated compounds. The olefins can be straight-chain or branched, and the double bonds can be terminal or within the chain. Examples of olefins which can be used in the novel process are ethylene, propylene, 1-butene, 2-butene, 1-pentene, 2-methyl-1-butene, 1-hexene, 2-hexene, 1-heptene, 1-octene, 3-octene, 3-ethyl-1-hexene, 1-decene, 3-undecene, 4,4-dimethyl-1-nonene, dicyclopentadiene, vinylcyclohexene, cyclooctadiene and styrene. Examples of derivatives of the said olefin types, which can be hydroformylated by the claimed procedure, are alcohols, aldehydes, carboxylic acids, esters, nitriles and halogen compounds, allyl alcohol, acrolein, methacrolein, crotonaldehyde, methyl acrylate, ethyl

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crotonate, diethyl fumarate, diethyl maleate and acrylonitrile. With particular success, the process is employed for the hydroformylation of olefins and olefin derivatives having 2 to 12 carbon atoms.

- 5 The examples which follow illustrate the invention, without restricting it to the embodiments described in more detail.

Examples

- 10 Propylene and a CO/H₂ mixture composed of equal parts by volume are fed to a 0.2 l stainless steel autoclave fitted with a stirrer at such a rate that 10 l(S.T.P.) of exit gas can be taken from the reactor per hour. At the same time, 300 ml of aqueous catalyst solution per hour are circulated through the reactor. The catalyst is
- 15 composed of 0.09 g of rhodium (as the acetate) and 5.89 mmol of P(III) (in the form of BISBIS), which have been dissolved in degassed and nitrogen-saturated water to give 300 ml of solution. The phosphorus/rhodium molar ratio is 6.7 : 1, corresponding to a ligand/rhodium ratio
- 20 of 3.4 : 1. The reaction of the reactants takes place at a temperature of 122°C and a pressure of 5 MPa.

- 25 In the table which follows, the results of the process according to the invention (Examples 1 to 3) are compared with those which are obtained by a procedure according to the state of the art (catalyst : rhodium/TPPTS) (Example 4). Examples 2 and 3 show very clearly that the novel procedure permits, in a completely surprising manner, a considerable increase in the propylene feed rate. Under such reaction conditions, the known processes
- 30 with Rh/TPPTS catalysts give only very low conversions or none at all.

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T a b l e
Experimental conditions Example 1 Example 2 Example 3 Example 4
(comparison)

Catalyst	Rh/BISBIS	Rh/BISBIS	Rh/BISBIS	Rh/TPPTS
Rhodium/ligand				
(mol/mol)	1:3.4	1:3.4	1:3.4	1:80
Temperature (°C)	122	123.5	122	122
Pressure (MPa)	5.0	5.0	5.0	5.0
Propylene feed rate (g/h)	39.0	91.6	110.6	37.6
<u>Experimental results</u>				
Conversion (%)	79.9	57.8	47.9	41.8
Activity mol of aldehyde mol of Rh x minute	30.25	60.5	90.4	15.8
Productivity g of aldehyde ml of catalyst solution x h	0.412	0.824	1.16	0.213
Aldehyde (g/h)	49.2	98.2	90.8	28.0
n/i ratio (parts by weight)	97/3	97/3	96/4	94/6
Alcohol (%)	8.45	1.34	2.07	0.73
Others (%)	1.5	0.16	0.24	0.57

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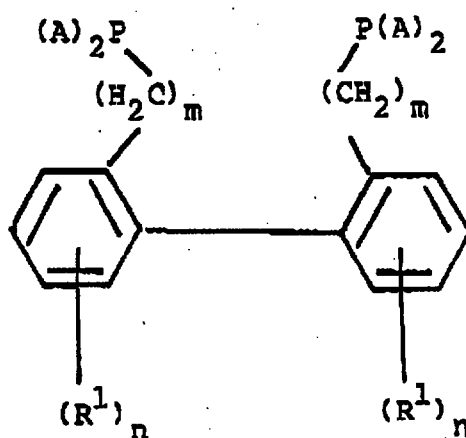
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Patent Claims

1. A process for producing aldehydes by reacting monoolefins, unconjugated polyolefins, cycloolefins or derivatives of these classes of compounds with carbon monoxide and hydrogen at temperatures from 20 to 150°C and pressures from 0.1 to 20 MPa in the presence of water-soluble rhodium compounds, containing phosphines in complex bonding, as catalysts, which comprises using, as the phosphines, diphosphines, derived from biaryl compounds, of the formula I



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which are substituted by one or more sulfonic acid groups, the A radicals in the formula I being identical or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, the R¹ radicals being identical or different and being hydrogen, alkyl or alkoxy radicals having 1 to 14 carbon atoms, or also cycloalkyl, aryl or aryloxy radicals having 6 to 14 carbon atoms, or a fused benzene ring, the m indices being identical or different and being integers from 0 to 5 and the n indices likewise being identical or different and being integers from 0 to 4.

2. The process as claimed in claim 1, wherein A in the formula I is a phenyl, tolyl or naphthyl radical.

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3. The process as claimed in one or more of claims 1 and 2, wherein R^1 in the formula I is hydrogen, a methyl, isopropyl, isobutyl, t-butyl, phenyl or naphthyl radical or a fused benzene ring.
- 5 4. The process as claimed in one or more of claims 1 to 3, wherein, in the formula I, $m = 1$.
5. The process as claimed in one or more of claims 1 to 4, wherein $n = 0$ or 1.
- 10 6. The process as claimed in one or more of claims 1 to 5, wherein, in the formula I, the substituents R^1 (with the exception of a fused benzene ring) are located in the 6- and 6'-positions.
- 15 7. The process as claimed in one or more of claims 1 to 6, wherein 1 to 130, preferably 2 to 25 and especially 2 to 10 mol of diphosphine are employed per mol of rhodium.
- 20 8. The process as claimed in one or more of claims 1 to 7, wherein the rhodium concentration in the aqueous catalyst solution is 20 to 1000, preferably 100 to 600, and especially 200 to 400 ppm by weight (relative to the solution).
9. The process as claimed in one or more of claims 1 to 8, wherein the reaction takes place at 20 to 150°C, preferably 80 to 140°C and especially 100 to 125°C.
- 25 10. The process as claimed in one or more of claims 1 to 9, wherein the reaction takes place under pressures from 0.1 to 30, preferably from 1 to 12 and especially from 3 to 7 MPa.
- 30 11. The process as claimed in one or more of claims 1 to 10, wherein olefins or olefin derivatives having 2 to 12 carbon atoms are reacted.

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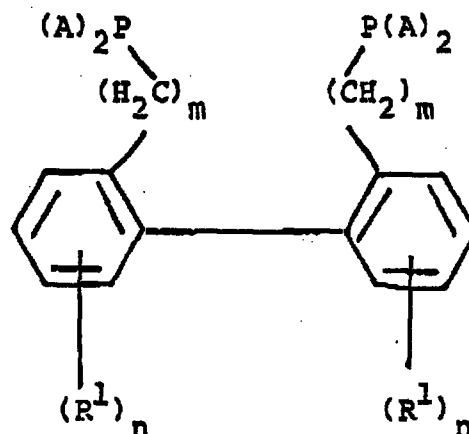


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12. A catalyst for the hydroformylation of monoolefins, unconjugated polyolefins, cycloolefins or derivatives of these classes of compounds, containing rhodium and a diphosphine in a molar ratio of 2:1 to 1:2, the diphosphine being obtained by sulfonation of biaryl compounds of the formula I



(I)

10

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in which the A radicals are alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, the R^1 radicals are identical or different and are hydrogen, alkyl or alkoxy radicals having 1 to 14 carbon atoms, or also cycloalkyl, aryl or aryloxy radicals having 6 to 14 carbon atoms, or a fused benzene ring, the m indices are identical or different and are integers from 0 to 5 and the n indices likewise are identical or different and are integers from 0 to 4.



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WERK RUHRCHEMIE FPR

Frankfurt, December 14, 1990

PAT/rcht-sei Hoe90/Y021

Hoechst Aktiengesellschaft, Frankfurt am Main 80Abstract of the disclosure

- 5 The invention relates to the hydroformylation of olefins and olefinically unsaturated compounds in the presence of a water-soluble rhodium complex compound which contains, as a ligand, at least one sulfonated diphosphine.

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Examples 5 - 14

The examples 5 to 14 relate to the hydroformylation of propylene in the apparatus used in examples 1 to 4. The test conditions are summarised below and the test results in table 2.

Test conditions

Catalyst

Rh/BISBIS

Rhodium concentration (ppm, related
to the catalyst solution)

306

Rhodium/ligand (mol/mol)

1 : 3.4

Temperature (°C)

125

Pressure (MPa)

5

Table 2

	Examples													
	5	6	7	8	9	10	11	12	13	14				
Propylene feed rate (g/h)	23.0	49.9	65.9	82.7	100.8	110.6	128.4	125.2	124.0	108.0				
Activity <u>mole of (n+i)-aldehyde</u> mole of Rh x min.	27.45	42.4	54.58	67.37	64.37	90.47	90.31	46.29	31.04	97.68				
Productivity <u>g of (n+i)-aldehyde</u> ml of cat. sol. x h	0.35	0.55	0.70	0.87	0.83	1.16	1.16	0.60	0.40	1.26				
n-Aldehyde (g/h)	83.48	84.59	85.46	87.58	89.73	87.64	88.0	89.35	89.00	87.37				
n/i Ratio (parts by wt)	95.61	97.05	96.12	95.81	95.89	95.72	92.26	96.45	95.51	96.86				
Alcohol (% by wt)	9.82	9.25	6.12	3.36	2.13	2.37	1.85	1.70	1.72	1.37				

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Examples 15 to 19

Examples 15 to 19 relate to the hydroformylation of hexene in the apparatus used in examples 1 to 4. The test conditions are summarised below and the test results in table 3.

Test conditions

Catalyst

Rh/BISBIS

Rhodium concentration (ppm, related
to the catalyst solution)

306

Rhodium/ligand (mol/mol)

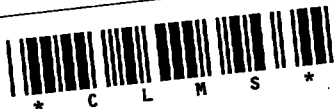
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Pressure (MPa)

5

Table 3

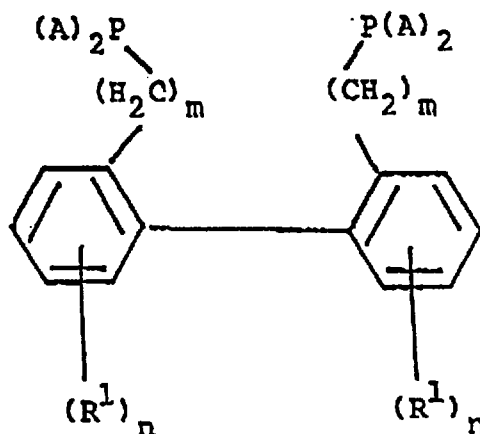
Examples					
	15	16	17	18	19
Hexene feed rate (g/h)	14.50	13.90	13.90	15.50	15.40
Activity	0.73	1.27	1.99	4.16	10.69
<u>mole of (n+1)-aldehyde</u>					
mole of Rh x min.					
Productivity g of <u>(n+1)-aldehyde</u>	0.007	0.011	0.023	0.058	
ml of cat. sol. x h					
n-Aldehyde (g/h)	4.60	8.90	13.80	26.10	30.30
n/i-Ratio (parts by wt)	97.12	96.23	96.00	95.38	94.56



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Patent Claims

1. A process for producing aldehydes by reacting monoolefins, unconjugated polyolefins, cycloolefins or derivatives of these classes of compounds with carbon monoxide and hydrogen at temperatures from 20 to 150°C and pressures from 0.1 to 20 MPa in the presence of water-soluble rhodium compounds, containing phosphines in complex bonding, as catalysts, which comprises using, as the phosphines, diphosphines, derived from biaryl compounds, of the formula I



which are substituted by one or more sulfonic acid groups, the A radicals in the formula I being identical or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, the R¹ radicals being identical or different and being hydrogen, alkyl or alkoxy radicals having 1 to 14 carbon atoms, or also cycloalkyl, aryl or aryloxy radicals having 6 to 14 carbon atoms, or a fused benzene ring, the m indices being identical or different and being integers from 0 to 5 and the n indices likewise being identical or different and being integers from 0 to 4.

2. The process as claimed in claim 1, wherein A in the formula I is a phenyl, tolyl or naphthyl radical.



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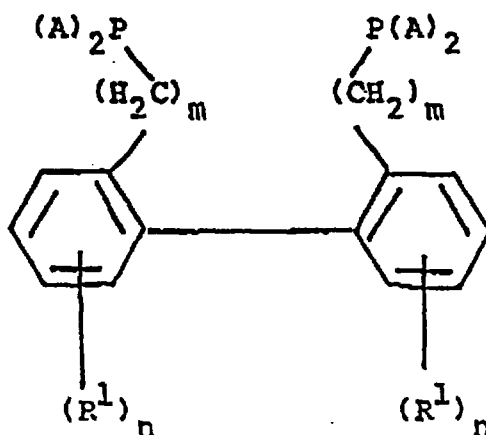
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3. The process as claimed in one or more of claims 1 and 2, wherein R^1 in the formula I is hydrogen, a methyl, isopropyl, isobutyl, t-butyl, phenyl or naphthyl radical or a fused benzene ring.
4. The process as claimed in one or more of claims 1 to 3, wherein, in the formula I, $m = 1$.
5. The process as claimed in one or more of claims 1 to 4, wherein $n = 0$ or 1.
6. The process as claimed in one or more of claims 1 to 5, wherein, in the formula I, the substituents R^1 (with the exception of a fused benzene ring) are located in the 6- and 6'-positions.
7. The process as claimed in one or more of claims 1 to 6, wherein 1 to 130, preferably 2 to 25 and especially 2 to 10 mol of diphosphine are employed per mol of rhodium.
8. The process as claimed in one or more of claims 1 to 7, wherein the rhodium concentration in the aqueous catalyst solution is 20 to 1000, preferably 100 to 600, and especially 200 to 400 ppm by weight (relative to the solution).
9. The process as claimed in one or more of claims 1 to 8, wherein the reaction takes place at 20 to 150°C, preferably 80 to 140°C and especially 100 to 125°C.
10. The process as claimed in one or more of claims 1 to 9, wherein the reaction takes place under pressures from 0.1 to 30, preferably from 1 to 12 and especially from 3 to 7 MPa.
11. The process as claimed in one or more of claims 1 to 10, wherein olefins or olefin derivatives having 2 to 12 carbon atoms are reacted.

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12. A catalyst for the hydroformylation of monoolefins, unconjugated polyolefins, cycloolefins or derivatives of these classes of compounds, containing rhodium and a diphosphine in a molar ratio of 2:1 to 1:2, the diphosphine being obtained by sulfonation of biaryl compounds of the formula I



(I)

in which the A radicals are alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, the R^1 radicals are identical or different and are hydrogen, alkyl or alkoxy radicals having 1 to 14 carbon atoms, or also cycloalkyl, aryl or aryloxy radicals having 6 to 14 carbon atoms, or a fused benzene ring, the m indices are identical or different and are integers from 0 to 5 and the n indices likewise are identical or different and are integers from 0 to 4.



23 AUG 1999

Process for producing aldehydes

Abstract of the disclosure

The invention relates to the hydroformylation of olefins and olefinically unsaturated compounds in the presence of a water-soluble rhodium complex compound which contains, as a ligand, at least one sulfonated diphosphine.

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Process for producing aldehydes

The invention relates to a process for producing aldehydes by hydroformylation of olefins in the presence of water-soluble rhodium complex catalysts.

It is known to produce aldehydes and alcohols, which contain one carbon atom more than the starting olefin, by reacting olefins with carbon monoxide and hydrogen (hydroformylation). The reaction is catalyzed by hydrido-metal carbonyls, preferably those of the metals of group VIII of the Periodic Table. Apart from cobalt, which is widely used industrially as a catalyst metal, rhodium has recently been gaining increasing importance. In contrast to cobalt, rhodium allows the reaction to be carried out at a low pressure; furthermore, preferably straight-chain n-aldehydes are formed, with an only minor fraction of iso-aldehydes. Finally, the hydrogenation of the olefins to give saturated hydrocarbons in the presence of rhodium catalysts is also markedly less extensive than in the case of using cobalt catalysts.

In the processes accepted in industry, the rhodium catalyst is employed in the form of modified hydrido-rhodium carbonyls which contain additional ligands, especially tertiary organic phosphines or phosphites. In most cases, there is an excess of the ligands, so that the catalyst system is composed of the complex compound and free ligand. The use of the rhodium catalysts described allows the hydroformylation reaction to be carried out at pressures below 30 MPa.

In this process, however, it proves to be difficult to separate off the reaction products and to recover the catalysts which are homogeneously dissolved in the reaction product. In general, the reaction product is distilled for this purpose out of the reaction mixture. In practice, however, because of the thermal sensitivity of the aldehydes and alcohols formed, this approach is feasible only in the hydroformylation of lower olefins,

i.e. olefins having up to about 8 carbon atoms in the molecule. In addition, it has been found that thermal stress on the distillation material also leads to considerable catalyst losses due to decomposition of the rhodium complex compounds.

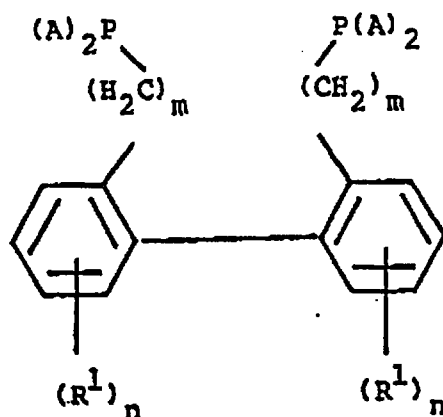
The drawbacks described are avoided by the use of catalyst systems which are soluble in water. Such catalysts have been described, for example, in German Patent 2,627,354. The solubility of the rhodium complex compounds is here achieved by the use of sulfonated triarylphosphines as a complexing constituent. In this process variant, the catalyst is separated off from the reaction product after completion of the reaction, simply by separating the aqueous and organic phases, i.e. without distillation and hence without additional thermal process steps. A further feature of this procedure is that n-aldehydes are formed with high selectivity from terminal olefins, with only very minor quantities of iso-aldehydes. Sulfonated triarylphosphines and in addition also carboxylated triarylphosphines are preferably used as complexing constituents of water-soluble rhodium complex compounds.

The known two-phase processes have proven to be highly suitable on the industrial scale. Nevertheless, efforts are being made to perfect the process even further. Thus, it is attempted to increase the activity of the catalysts by modification of the complex ligands and to extend their activity with the object of further reducing the specific catalyst requirement - both rhodium and ligand - and hence the production costs. Economic factors are also the reason for working towards a marked reduction in the phosphine/rhodium ratio. A further improvement in the hitherto achieved high selectivity with respect to the formation of non-branched aldehydes is also desired. It must be remembered here that several million tonnes of hydroformylation products are manufactured per year, so that even a small increase in the selectivity has

economically significant consequences.

It is the object of the invention to improve the hydroformylation process as sketched above, i.e. to develop catalysts which exceed the activity and selectivity of known catalysts at the lowest possible ligand/rhodium ratio.

The invention comprises a process for producing aldehydes by reacting monoolefins, unconjugated polyolefins, cycloolefins or derivatives of these classes of compounds with carbon monoxide and hydrogen at temperatures from 20 to 150°C and pressures from 0.1 to 20 MPa in the presence of water-soluble rhodium compounds, containing phosphines in complex bonding, as catalysts. The process comprises using, as the phosphines, diphosphines, derived from biaryl compounds, of the general formula I



(I)

which are substituted by one or more sulfonic acid groups, the A radicals in the formula I being identical or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, the R¹ radicals being identical or different and being hydrogen, alkyl or alkoxy radicals having 1 to 14 carbon atoms, or also cycloalkyl, aryl or aryloxy radicals having 6 to 14 carbon atoms, or a fused benzene

ring, the m indices being identical or different and being integers from 0 to 5 and the n indices likewise being identical or different and being integers from 0 to 4.

The water-soluble rhodium/diphosphine complex compounds used as catalysts according to the novel process are distinguished by a remarkably high effectiveness, determined by the two criteria of "activity" A , namely

$$A = \frac{\text{mol of aldehyde}}{\text{mol of Rh} \times \text{minute}}$$

and "productivity" P , namely

$$P = \frac{\text{g of aldehyde}}{\text{ml of catalyst solution} \times \text{hour}}$$

The values of these two parameters, reached by the processes of the state of the art, are considerably exceeded by the procedure according to the invention. The formation of normal aldehydes increases further and the discharge of rare metal and phosphine with the reaction product is reduced. In addition, these results are achieved by the use of catalysts which have a markedly lower ligand/rhodium ratio than those used hitherto. These and other results, which are very valuable for carrying out the process on an industrial scale, were neither derivable from theoretical considerations nor foreseeable from experience in practice.

The sulfonated diphosphines characteristic as a catalyst constituent for the novel process can be prepared from biaryls, which are accessible by known syntheses, for example by coupling aryl-Grignard reagents with aryl halides. The introduction of the phosphorus-organic radical $-(H_2C)_nP(A)_2-$ into the biaryl molecule is also

carried out by conventional methods, for example by reacting a phosphorus compound of the general formula $X-(H_2C)_mP(A)_2$, in which X is a halogen atom, with the biaryl in the presence of a reagent which eliminates protons, such as sodium amide or butyllithium. In the last reaction step, the diphosphine is sulfonated with oleum, i.e. with a solution of sulfur trioxide in sulfuric acid, at temperatures from 0 to 60°C. The sulfonation product is isolated from the acidic solution, diluted with water, in accordance with the state of the art, for example by extraction with the solution of a water-insoluble amine in a water-insoluble organic solvent.

Preferred sulfonated diphosphines in the procedure according to the invention are those which are derived from biaryls of the general formula I, in which the A radicals are identical or different and are a phenyl, tolyl or naphthyl radical, the R^1 radicals are likewise identical or different and are hydrogen or a methyl, isopropyl, isobutyl, t-butyl, phenyl or naphthyl radical or a fused benzene ring (so that a naphthyl structure is formed), m is 1 and n is 0 or 1.

Sulfonated diphosphines whose biaryl skeleton is substituted by radicals R^1 in the 6- and 6'-positions are also of great importance within the scope of the claimed process. The presence of these radicals hinders the rotation of the two substituted phenyl radicals. Rhodium complex compounds which contain such molecules as ligands can therefore be used as catalysts for enantioselective reactions.

Examples of diphosphines which are successfully used in the novel process are the products obtained by sulfonation of 2,2'-bis(diphenylphosphanomethyl)-biphenyl (called BISBIS below) and of 2-(diphenylphosphanomethyl)-1-[2-(diphenylphosphanomethyl)phenyl]-naphthalene (called PHENAPS below).

It is not necessary to use the diphosphines as single compounds. Mixtures of sulfonated diphosphines derived from biaryl compounds of different structure are equally suitable as mixtures of biaryls containing identical or different phosphine radicals and having different degrees of sulfonation. Finally, mixtures of sulfonated mono- and di-phosphines in combination with rhodium also give very active catalysts. Thus, for example, mixtures of BISBIS and Na triphenylphosphine-trisulfonate (called TPPTS below) have also proven suitable.

It has also been found to be advantageous to use rhodium and sulfonated diphosphine not in the stoichiometric ratio, i.e. corresponding to the chemical composition of the rhodium complex compound which forms in the course of the hydroformylation reaction, but to employ an excess of diphosphine. The rhodium/diphosphine ratio can here be varied within wide limits, and about 1 to 130 mol of diphosphine can be used per mol of rhodium. A rhodium/diphosphine ratio in the range from 1:2 to 1:25 and especially from 1:2 to 1:10 mol is preferred.

Rhodium is employed either as the metal or as a compound. In the metallic form, it is used either as finely dispersed particles or it is precipitated as a thin coating on a support such as activated carbon, calcium carbonate, aluminum silicate or alumina. Suitable rhodium compounds are substances which are water-soluble or become water-soluble under the reaction conditions. The various rhodium oxides, salts of inorganic hydrogen acids and oxygen acids and also salts of aliphatic monocarboxylic and polycarboxylic acids are suitable. Examples of rhodium salts are rhodium nitrate, rhodium sulfate, rhodium acetate, rhodium 2-ethylhexanoate and rhodium malonate. Rhodium halogen compounds are, however, less suitable because of the corrosive behavior of the halide ions. In addition, rhodium carbonyl compounds such as $\text{Rh}_3(\text{CO})_{12}$ or $\text{Rh}_6(\text{CO})_{16}$ or complex salts of rhodium, e.g. cyclooctadienyl-rhodium compounds, can be used. Rhodium

oxide and especially rhodium acetate and rhodium 2-ethylhexanoate are preferred. It must be assumed that, in the presence of water gas, water-soluble rhodium complex compounds which contain carbon monoxide and diphosphine as ligands are formed under the conditions of the hydroformylation reaction. Together with the diphosphine dissolved in the water, they give the catalyst system.

The catalyst solution is prepared from the components either in the hydroformylation reactor or, beforehand, in separate equipment and then fed to the hydroformylation reactor.

The concentration of rhodium in the aqueous catalyst solution is 20 to 1000 ppm by weight (relative to the solution), preferably 100 to 600 ppm by weight and especially 200 to 400 ppm by weight.

The reaction of the olefin with carbon monoxide and hydrogen takes place under pressures from about 0.1 to about 30 MPa, preferably 1 to 12 MPa and especially 3 to 7 MPa. The composition of the synthesis gas, i.e. the volume ratio of carbon monoxide and hydrogen, can extend over wide ranges and be varied, for example, between 1:10 and 10:1. In general, gas mixtures are used in which the volume ratio of carbon monoxide and hydrogen is about 1:1 or deviates only slightly from this value in one direction or the other.

The reaction temperature is between about 20 and 150°C, and 80 to 140°C and especially 100 to 125°C are preferred.

The conversion of the reactants present in the liquid and gaseous phase takes place in conventional reactors. The progress of the reaction is decisively influenced by the fact that the aqueous catalyst solution must be saturated with the liquid or gaseous, hydrophobic olefin and with

the synthesis gas. It is therefore necessary to produce the greatest possible contact area between the phases. It has proven suitable to stir the liquid reactor content - catalyst solution, if appropriate liquid olefin, and reaction product - intensively and to feed the gaseous reactants - synthesis gas and, if appropriate, olefin - to the liquid phase via distribution devices. It has been found to be very suitable to minimize the fraction of the organic phase in the reaction mixture. Surprisingly, the organic phase does not contribute to the solubility of the reactants in the aqueous phase, and undesired side reactions of the reaction product, which cannot be excluded in the case of increasing residence time of the product in the reactor, are avoided. Accordingly, the volume ratio of aqueous and organic phase is set to 1:1 to 100:1, preferably 10:1 to 100:1. For this purpose, a corresponding part of the reaction mixture can be discharged continuously from the reactor, the aqueous and organic phases can be separated from one another, and the aqueous phase can be recycled to the reactor. The reaction can be carried out batchwise or, preferably, continuously.

The process according to the invention is successfully applicable in the conversion of monoolefins, unconjugated polyolefins, cyclic olefins and derivatives of these unsaturated compounds. The olefins can be straight-chain or branched, and the double bonds can be terminal or within the chain. Examples of olefins which can be used in the novel process are ethylene, propylene, 1-butene, 2-butene, 1-pentene, 2-methyl-1-butene, 1-hexene, 2-hexene, 1-heptene, 1-octene, 3-octene, 3-ethyl-1-hexene, 1-decene, 3-undecene, 4,4-dimethyl-1-nonene, dicyclopentadiene, vinylcyclohexene, cyclooctadiene and styrene. Examples of derivatives of the said olefin types, which can be hydroformylated by the claimed procedure, are alcohols, aldehydes, carboxylic acids, esters, nitriles and halogen compounds, allyl alcohol, acrolein, methacrolein, crotonaldehyde, methyl acrylate, ethyl

crotonate, diethyl fumarate, diethyl maleate and acrylonitrile. With particular success, the process is employed for the hydroformylation of olefins and olefin derivatives having 2 to 12 carbon atoms.

The examples which follow illustrate the invention, without restricting it to the embodiments described in more detail.

Examples

Propylene and a CO/H₂ mixture composed of equal parts by volume are fed to a 0.2 l stainless steel autoclave fitted with a stirrer at such a rate that 10 l(S.T.P.) of exit gas can be taken from the reactor per hour. At the same time, 300 ml of aqueous catalyst solution per hour are circulated through the reactor. The catalyst is composed of 0.09 g of rhodium (as the acetate) and 5.89 mmol of P(III) (in the form of BISBIS), which have been dissolved in degassed and nitrogen-saturated water to give 300 ml of solution. The phosphorus/rhodium molar ratio is 6.7 : 1, corresponding to a ligand/rhodium ratio of 3.4 : 1. The reaction of the reactants takes place at a temperature of 122°C and a pressure of 5 MPa.

In the table which follows, the results of the process according to the invention (Examples 1 to 3) are compared with those which are obtained by a procedure according to the state of the art (catalyst : rhodium/TPPTS) (Example 4). Examples 2 and 3 show very clearly that the novel procedure permits, in a completely surprising manner, a considerable increase in the propylene feed rate. Under such reaction conditions, the known processes with Rh/TPPTS catalysts give only very low conversions or none at all.

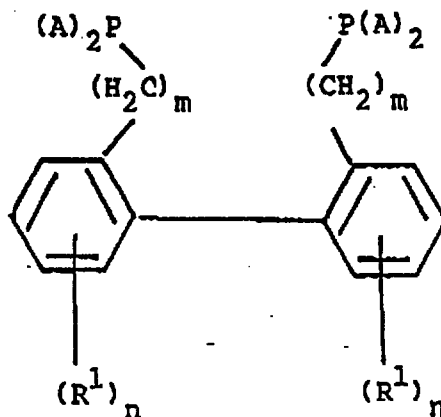
Table

Experimental conditions Example 1 Example 2 Example 3 Example 4
(comparison)

Catalyst	Rh/BISBIS	Rh/BISBIS	Rh/BISBIS	Rh/TPPTS
Rhodium/ligand (mol/mol)	1:3.4	1:3.4	1:3.4	1:80
Temperature (°C)	122	123.5	122	122
Pressure (MPa)	5.0	5.0	5.0	5.0
Propylene feed rate (g/h)	39.0	91.6	110.6	37.6
<u>Experimental results</u>				
Conversion (%)	79.9	57.8	47.9	41.8
Activity $\frac{\text{mol of aldehyde}}{\text{mol of Rh} \times \text{minute}}$	30.25	60.5	90.4	15.8
Productivity $\frac{\text{g of aldehyde}}{\text{ml of catalyst solution} \times \text{h}}$	0.412	0.824	1.16	0.213
Aldehyde (g/h)	49.2	98.2	90.8	28.0
n/i ratio (parts by weight)	97/3	97/3	96/4	94/6
Alcohol (%)	8.45	1.34	2.07	0.73
Others (%)	1.5	0.16	0.24	0.57

Patent Claims

1. A process for producing aldehydes by reacting monoolefins, unconjugated polyolefins, cycloolefins or derivatives of these classes of compounds with carbon monoxide and hydrogen at temperatures from 20 to 150°C and pressures from 0.1 to 20 MPa in the presence of water-soluble rhodium compounds, containing phosphines in complex bonding, as catalysts, which comprises using, as the phosphines, diphosphines, derived from biaryl compounds, of the formula I



(I)

which are substituted by one or more sulfonic acid groups, the A radicals in the formula I being identical or different alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, the R¹ radicals being identical or different and being hydrogen, alkyl or alkoxy radicals having 1 to 14 carbon atoms, or also cycloalkyl, aryl or aryloxy radicals having 6 to 14 carbon atoms, or a fused benzene ring, the m indices being identical or different and being integers from 0 to 5 and the n indices likewise being identical or different and being integers from 0 to 4.

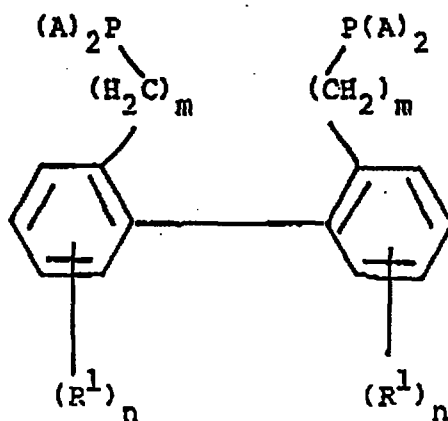
2. The process as claimed in claim 1, wherein A in the formula I is a phenyl, tolyl or naphthyl radical.



3. The process as claimed in one or more of claims 1 and 2, wherein R^1 in the formula I is hydrogen, a methyl, isopropyl, isobutyl, t-butyl, phenyl or naphthyl radical or a fused benzene ring.
4. The process as claimed in one or more of claims 1 to 3, wherein, in the formula I, $m = 1$.
5. The process as claimed in one or more of claims 1 to 4, wherein $n = 0$ or 1.
6. The process as claimed in one or more of claims 1 to 5, wherein, in the formula I, the substituents R^1 (with the exception of a fused benzene ring) are located in the 6- and 6'-positions.
7. The process as claimed in one or more of claims 1 to 6, wherein 1 to 130, preferably 2 to 25 and especially 2 to 10 mol of diphosphine are employed per mol of rhodium.
8. The process as claimed in one or more of claims 1 to 7, wherein the rhodium concentration in the aqueous catalyst solution is 20 to 1000, preferably 100 to 600, and especially 200 to 400 ppm by weight (relative to the solution).
9. The process as claimed in one or more of claims 1 to 8, wherein the reaction takes place at 20 to 150°C, preferably 80 to 140°C and especially 100 to 125°C.
10. The process as claimed in one or more of claims 1 to 9, wherein the reaction takes place under pressures from 0.1 to 30, preferably from 1 to 12 and especially from 3 to 7 MPa.
11. The process as claimed in one or more of claims 1 to 10, wherein olefins or olefin derivatives having 2 to 12 carbon atoms are reacted.



12. A catalyst for the hydroformylation of monoolefins, unconjugated polyolefins, cycloolefins or derivatives of these classes of compounds, containing rhodium and a diphosphine in a molar ratio of 2:1 to 1:2, the diphosphine being obtained by sulfonation of biaryl compounds of the formula I



(I)

in which the A radicals are alkyl, cycloalkyl, phenyl, tolyl or naphthyl radicals, the R¹ radicals are identical or different and are hydrogen, alkyl or alkoxy radicals having 1 to 14 carbon atoms, or also cycloalkyl, aryl or aryloxy radicals having 6 to 14 carbon atoms, or a fused benzene ring, the m indices are identical or different and are integers from 0 to 5 and the n indices likewise are identical or different and are integers from 0 to 4.



Process for producing aldehydes

Abstract of the disclosure

The invention relates to the hydroformylation of olefins and olefinically unsaturated compounds in the presence of a water-soluble rhodium complex compound which contains, as a ligand, at least one sulfonated diphosphine.