

Sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-
binaphthalenes, process for their preparation and their
use in a process for the hydroformylation of
olefinically unsaturated compounds

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5 The invention relates to novel sulfonated diphosphines and to their preparation. They form complex compounds with metals of group VIII of the periodic table of the elements and said compounds can be used as catalysts.

10 Complex compounds containing as the central atom a metal of group VIII of the periodic table of the elements and as ligands P(III) compounds such as phosphines or phosphites, and optionally also other groups capable of complexation, have recently become increasingly important as catalysts. Thus the reaction, extensively practiced in
 15 industry, of olefins with carbon monoxide and hydrogen to give aldehydes (hydroformylation) is carried out in the presence of catalyst systems composed of rhodium and triphenylphosphine. Catalysts based on complex compounds containing phosphines have also proved successful for the
 20 reaction of methanol with synthesis gas to give higher alcohols, especially ethanol and propanol (homologization). In said cases, the ligands are usually present in excess, so that the catalyst system is composed of complex compound and free ligand. In accordance with the
 25 solubility of these systems in organic media, the reaction is carried out in the homogeneous phase.

The reaction can also be carried out in the heterogeneous phase rather than in the homogeneous phase. This process variant is particularly convenient because it provides a
 30 way of separating the water-dissolved catalyst from the water-insoluble reaction product simply and under mild conditions. The hydroformylation process described in DE 26 27 354 C2, for example, works on this principle. The system rhodium/sodium triphenylphosphine trisulfonate
 35 is used as the catalyst.

In addition to monophosphines, diphosphines are also used

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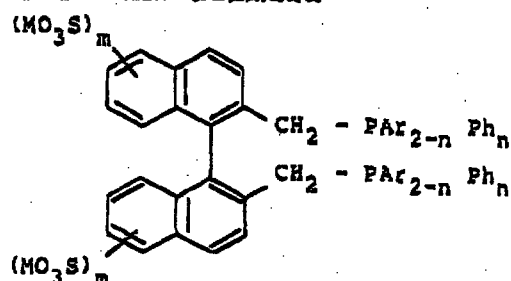
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as a constituent of catalyst systems in which the other component is a metal of group VIII of the periodic table. For example, DE-A 40 40 315 relates to the preparation of aldehydes by reaction of monoolefins, non-conjugated polyolefins, cycloolefins or derivatives of these classes of compounds with carbon monoxide and hydrogen in the presence of rhodium/diphosphine catalysts. Sulfonated 2,2'-bis(diphenylphosphinomethyl)biphenyls or 2-(diphenylphosphinomethyl)-1-[2-(diphenylphosphino-

5 methyl)phenyl]naphthalenes are used as diphosphines in this process. Together with the rhodium, they give catalysts which are distinguished from the known rhodium/monophosphine systems by a greater activity.

The assumption that the composition of the product formed under their influence, and the activity of rhodium complex catalysts, depend on the chemical characteristics of the ligands creates the task of developing novel ligands. They should open up the possibility of varying the course of the reaction so that particular products are formed preferentially or in some cases even exclusively. It is further required that the ligands and the complex compounds formed therefrom are soluble in water so as to benefit from the above-described advantages of hydroformylation in a two-phase system.

25 The invention provides such ligands. It relates to novel sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalenes of the formula



in which Ar is m-C₆H₄-SO₃M, M is hydrogen, ammonium, a monovalent metal or the equivalent of a polyvalent metal, Ph is the phenyl radical, m is identical or different and

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has the value 1 or 2 and n is identical or different and is 0, 1 or 2.

The parent substance used for the preparation of the novel compounds is 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene. This compound is obtained in a multistep synthesis by reductive dimerization of 1-bromo-2-methylnaphthalene with magnesium to give 2,2'-dimethyl-1,1'-binaphthalene, reaction of the binaphthalene with butyllithium to give the dilithium compound and reaction of the dilithium compound with chlorodiphenylphosphine. Instead of metalating 2,2'-dimethyl-1,1'-binaphthalene with butyllithium, it is also possible to convert it to 2,2'-bis(bromomethyl)-1,1'-binaphthalene with N-bromosuccinimide. Reaction of the dibromo compound with diphenyl phosphinate gives 2,2'-bis-(diphenylphosphinylmethyl)-1,1'-binaphthalene, which is reduced with trichlorosilane to give 2,2'-bis(diphosphinomethyl)-1,1'-binaphthalene. To introduce sulfonic acid groups into the binaphthyl radical and into the phenyl radicals, the diphosphine is treated with excess sulfur trioxide in the form of oleum as the sulfonating agent.

Of decisive importance for the degree of sulfonation which can be achieved are especially the SO_3 concentration in the oleum, the reaction temperature and the reaction time. Said parameters influence each other.

It has proved successful to use oleum containing 10 to 65% by weight or even more of sulfur trioxide. The sulfonating agent is to be used in excess, based on the diphosphine. It is convenient to use 25 to 80 and preferably 40 to 70 mol of SO_3 per mole of 2,2'-bis-(diphenylphosphinomethyl)-1,1'-binaphthalene. Oleum having a high concentration of free SO_3 , i.e. a proportion of about 40 to 65% by weight or more, gives products which contain at least four SO_3H groups and therefore have an excellent solubility in water. Concentrations of free



SO₂ in oleum which are lower than about 40% by weight give products with a smaller degree of sulfonation, i.e. diphosphines which have only a limited solubility in water.

5 The reaction temperature is 0 to 25°C, preferably 0 to 10°C. In principle, it is also possible to use higher temperatures, but these promote the oxidation of the diphosphines to phosphine oxides appreciably more than the sulfonation, so that the overall yield of sulfonated phosphines decreases. Therefore it is also not recommended to compensate for low concentrations of free SO₂ by raising the reaction temperature. On the other hand, it is possible to influence the degree of sulfonation of the diphosphine by means of the reaction time. Longer reaction times give compounds with a higher degree of sulfonation than shorter reaction times. In general, the reaction requires 10 to 60 and preferably 15 to 48 h in said temperature ranges. These times apply especially when using oleum which contains about 40% by weight or more of free oleum. Less concentrated oleum leads only to partially sulfonated compounds, even with long reaction times; furthermore, the increasing formation of oxidation products cannot be fully avoided. It is therefore convenient to carry out the sulfonation with more highly concentrated oleum and to control the degree of sulfonation by means of the reaction time.

Concentrated sulfuric acid has proved successful as a solvent for the starting compound to be sulfonated, namely 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene. This solution can be introduced into oleum in portions or oleum can be added thereto in portions. It is recommended to stir the reaction mixture vigorously and cool it thoroughly and to bring the reactants together slowly and in small portions so that the heat of reaction can be dissipated without difficulty. By this means, rather than the sulfonation proceeding in an uncontrolled

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manner, SO_3H groups are introduced successively into the binaphthyl radical and the phenyl radicals. Furthermore, oxidation of the phosphorus compound is effectively prevented. After all the sulfonating agent or diphosphine
5 has been added, the afterreaction can take place at room temperature, i.e. at about 20 to 25°C, and essentially without external cooling. It is convenient, however, to stir the reaction mixture at this stage as well, so that any heat of reaction still being produced is uniformly
10 distributed and can be dissipated without delay.

Following the sulfonation, the reaction solution is hydrolyzed. In this process step, care should be taken to ensure that the temperature does not exceed about 30°C; it is advantageous to maintain temperatures in the range
15 from 15 to 25°C. It is therefore recommended to add the reaction mixture carefully to ice or to carry out the hydrolysis with ice or ice-water and to make provision for intensive external cooling. The dilute solution, containing essentially 2,2'-bis(diphenylphosphinomethyl)-
20 1,1'-binaphthalene with different degrees of sulfonation and sulfuric acid, is worked up in a further process step.

To do this, the solution containing sulfuric acid is neutralized with an alkaline reagent such as an alkali
25 metal hydroxide or alkali metal carbonate, preferably sodium hydroxide. In order not to increase the volume of the reaction mixture unnecessarily and to precipitate a substantial part of the alkali metal sulfate formed, the neutralizing agent is used as a highly concentrated
30 solution or in undissolved solid form, e.g. flakes or pellets of caustic soda.

Because of its reduced solubility at lower temperatures, the bulk of the alkali metal sulfate can be removed from the solution by cooling. The appropriate temperatures
35 depend on the concentration of the sulfate in the



solution and the temperature profile of its solubility. The most favorable conditions therefore have to be determined by experiments in each individual case. The sulfate can be separated off in one step or else in
5 several steps; it has proved convenient to carry out the crystallization in two steps.

After separation of the alkali metal sulfate, the solution is concentrated to dryness, preferably under an oil-pump vacuum, and the diphosphines with different
10 degrees of sulfonation are extracted from the crystal slurry in the form of the alkali metal salts. Suitable extractants are e.g. mixtures of lower alcohols, i.e. alcohols having up to 5 carbon atoms in the molecule, such as methanol, ethanol or propanol, with water. The
15 extraction is carried out by conventional methods in one or more steps, preferably two to four steps. The extracts are combined and concentrated to dryness.

It has also proved successful to react the solution containing sulfuric acid with a mixture of a water-insoluble amine and an organic solvent and to extract the
20 sulfonates as amine salts. Suitable amines are those having 10 to 60 and preferably 13 to 36 carbon atoms, e.g. methyldioctylamine, tri-n-octylamine, triisooctylamine, tri-2-ethylhexylamine and tridodecylamine, preferably triisooctylamine. Aliphatic and aromatic
25 hydrocarbons or hydrocarbon mixtures, e.g. toluene or kerosene-like mixtures, especially toluene, are successfully used as organic solvents.

0.5 to 1.5 mol, preferably 0.8 to 1.2 mol, of amine is
30 used per equivalent of sulfonic acid. After vigorous mixing of the solution containing sulfuric acid and the amine solution, the aqueous and organic phases are separated from one another. The organic phase, containing the amine salt, is reacted with an aqueous solution of a
35 base whose sulfonic acid salt is to be prepared. Examples

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of particularly suitable bases are sodium hydroxide and potassium hydroxide. This procedure gives an aqueous solution from which the desired sulfonic acid salt can be isolated.

- 5 Instead of the aqueous solution of the base being added all at once to the solution of the amine salt in the organic medium, it can also be added in portions. Such a gradual treatment of the amine solution, e.g. by adjusting the pH to certain values or ranges of values
10 with the aid of the base, enables substantial separation of phosphine oxides from the sulfonation mixture and partial decomposition of the latter into products with different degrees of sulfonation.

- The novel sulfonated diphosphines are colorless solids.
15 According to the sulfonation conditions, they contain up to six sulfonic acid groups. The alkali metal salts are soluble in water and the solubility increases with the degree of sulfonation.

- The free acids can be prepared by treating aqueous alkali
20 metal salt solutions of the sulfonated diphosphine with a cation exchanger in the H^+ form. Other salts of the novel sulfonated diphosphines can be obtained from the acids by reaction with hydroxides, carbonates, ammonia or amines.

- 25 The novel compounds have proved successful as components of catalyst systems containing metals of group VIII of the periodic table. In combination with rhodium, they are used especially as hydroformylation catalysts. Accordingly, the invention further relates to a process
30 for the preparation of aldehydes by reaction of mono-olefins, nonconjugated polyolefins, cycloolefins or derivatives of these classes of compounds with carbon monoxide and hydrogen at temperatures of 20 to 150°C and pressures of 0.1 to 20 MPa in the presence of catalysts



composed of water-soluble compounds of rhodium complexed with phosphines. The water-soluble phosphines used in said process are the above-described sulfonated 2,2'-bis-(diphenylphosphinomethyl)-1,1'-binaphthyls.

- 5 The water-soluble rhodium/diphosphine complex compounds used as catalyst in the novel process are distinguished by a remarkably high activity, determined by the two criteria "activity" A:

10
$$A = \frac{\text{mol of aldehyde}}{\text{mol of Rh} \cdot \text{min}}$$

and "productivity" P:

15
$$P = \frac{\text{g of aldehyde}}{\text{ml of catalyst solution} \cdot \text{h}}$$

The values of these two parameters achieved with the processes of the state of the art are far exceeded by the procedure according to the invention. The formation of normal aldehydes is greater and the amount of noble metal and phosphine discharged with the reaction product is smaller than in the known processes. Moreover, these results are obtained with a catalyst which has a distinctly smaller ligand/rhodium ratio than the catalysts used hitherto. These and other results of very great value for carrying out the process on the industrial scale could not be deduced from theoretical considerations nor predicted from practical experience.

It is not necessary to use the sulfonated diphosphines as pure compounds. It is also possible to use diphosphines with different degrees of sulfonation and/or sulfonate mixtures with different cations.

It has proved successful not to use rhodium and the diphosphines according to the invention in the stoichiometric ratio, i.e. in accordance with the chemical



composition of the rhodium complex compound which forms in the course of the hydroformylation reaction, but to use the diphosphines in excess. The ratio of rhodium to diphosphine can thereby be varied within wide limits and about 1 to 130 mol of diphosphine can be used per mole of rhodium. The preferred molar ratio of rhodium to diphosphine is in the range from 1:2 to 1:25 and especially 1:2 to 1:10.

Rhodium is used either as the metal or as a compound. As the metal, it is used in the form of finely divided particles or precipitated in a thin layer on a support such as activated charcoal, calcium carbonate, aluminum silicate or clay. Possible rhodium compounds are substances which are water-soluble or which become water-soluble under the reaction conditions. Suitable compounds are the various rhodium oxides, salts of inorganic hydracids or oxyacids and salts of aliphatic monocarboxylic or polycarboxylic acids. Examples of rhodium salts are rhodium nitrate, rhodium sulfate, rhodium acetate, rhodium 2-ethylhexanoate and rhodium malonate. Rhodium halide compounds, on the other hand, are less useful on account of the lower activity of the resulting complexes and the corrosive behavior of the halide ions. It is further possible to use rhodium carbonyl compounds such as $\text{Rh}_3(\text{CO})_{12}$ or $\text{Rh}_6(\text{CO})_{18}$, or complex salts of rhodium, e.g. cyclooctadienylrhodium compounds. Rhodium oxide and especially rhodium acetate and rhodium 2-ethylhexanoate are preferred. It can be assumed that water-soluble rhodium complex compounds containing carbon monoxide and diphosphine as ligands are formed in the presence of synthesis gas under the conditions of the hydroformylation reaction. Together with the excess diphosphine dissolved in the water, they make up the catalyst system.

The catalyst solution is prepared from the components either in the hydroformylation reactor or beforehand in

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a separate apparatus and then introduced into the hydroformylation reactor.

5 The concentration of rhodium in the aqueous catalyst solution is 10 to 500 ppm by weight (based on the solution), preferably 15 to 100 ppm by weight and especially 10 to 50 ppm by weight.

10 The reaction of the olefin with carbon monoxide and hydrogen takes place at pressures of 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 to hydrogen, can extend over a wide range and can be varied e.g. between 1:10 and 10:1. In general, gas mixtures are used in which the volume ratio of carbon monoxide to hydrogen is about 1:1 or only slightly different from this value in one or other direction.

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

20 The reaction of the reactants present in the liquid and gas phases takes place in conventional reactors. The course of the reaction is influenced decisively by the fact that the aqueous catalyst solution must be saturated with the liquid or gaseous hydrophobic olefin and the synthesis gas. It is therefore necessary to create the largest possible contact area between the phases. A procedure which has proved successful is vigorously to stir the liquid reactor contents - catalyst solution, optionally liquid olefin and reaction product - and introduce the gaseous reactants - synthesis gas and optionally olefin - into the liquid phase via distributing devices. A procedure which has proved very successful is to keep the proportion of organic phase in the reaction mixture small. Surprisingly, the organic phase does not contribute to the solubility of the

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reactants in the aqueous phase and the reaction product is prevented from undergoing undesirable secondary reactions which cannot be excluded when the residence time of the product in the reactor increases. Accordingly, the volume ratio of aqueous to organic phase is adjusted to 1:1 to 100:1, preferably 10:1 to 100:1. This can be done by continuously withdrawing an appropriate fraction of the reaction mixture from the reactor, separating the aqueous and organic phases from one another and recycling the aqueous phase into the reactor. The reaction can be carried out batchwise or, preferably, continuously.

The process according to the invention can be successfully applied to the reaction of monoolefins, non-conjugated polyolefins, cyclic olefins and derivatives of these unsaturated compounds. The olefins used are not subject to any restrictions as far as molecular size is concerned; the procedure has proved successful with compounds having 2 to 20 carbon atoms. The olefinically unsaturated compounds can be linear or branched and the double bonds can be within or at the end of the chains. Examples of olefins which can be used in the novel process are ethylene, propylene, but-1-ene, but-2-ene, pent-1-ene, 2-methylbut-1-ene, hex-1-ene, hex-2-ene, hept-1-ene, oct-1-ene, oct-3-ene, 3-ethylhex-1-ene, dec-1-ene, undec-3-ene, 4,4-dimethyl non-1-ene, dicyclopentadiene, vinylcyclohexene, cyclooctadiene and styrene. Derivatives of said types of olefin which can be hydroformylated by the claimed procedure are e.g. alcohols, aldehydes, carboxylic acids, esters, nitriles and halogen compounds, such as allyl alcohol, acrolein, methacrolein, crotonaldehyde, methyl acrylate, ethyl crotonate, diethyl fumarate, diethyl maleate and acrylonitrile. The process is used with particular success for the hydroformylation of olefins and olefin derivatives having 2 to 20 and especially 2 to 8 carbon atoms.

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The following examples describe the preparation and properties of the novel compounds (Examples 1 to 10) and their use as constituents of catalysts for the hydroformylation of olefinically unsaturated compounds (Examples 12 to 17).

Example 1

10.11 g (15.54 mmol) of 2,2'-bis(diphenylphosphino-methyl)-1,1'-binaphthalene are dissolved in 25 ml of concentrated sulfuric acid at room temperature. The solution is cooled to 0°C and 50 ml of 65% oleum are added dropwise, the temperature being kept at a maximum of 10°C. The mixture is subsequently stirred for 48 h at room temperature and then added to ice and neutralized with sodium hydroxide solution (NaOH content: 50% by weight). Hydrolysis and neutralization are carried out under conditions such that the temperature does not exceed 25°C. The precipitated sodium sulfate is filtered off and the filtrate is stirred into methanol. The resulting white solid is separated off and the filtrate is concentrated to dryness. The residue is taken up in just the right amount of water required for complete dissolution and the aqueous solution is sprayed into twice the volume of methanol. The suspension obtained is filtered and the filtrate is concentrated to dryness. The combined filtrates are analyzed.

Characterization:

Solubility: 1300 g/l of water

Elemental

analysis: 13.8% by weight of sulfur; 4.42% by weight of phosphorus; 9.9% by weight of sodium, from which the following molar ratios are calculated:

P:S = 1:3; P:Na = 1:3; S:Na = 1:1,

corresponding to the introduction of six SO₃H groups into the 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene

molecule

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³¹P NMR: δ = -9.0Example 2

The sulfonation of 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene is carried out according to Example 1 and the progress of the reaction is followed by NMR spectroscopy of the solution containing sulfuric acid. The following measured values are obtained:

³¹P NMR: δ = -9.0 (hexasulfonated)
 δ = -9.89 (pentasulfonated)
 δ = -12.03 (tetrasulfonated)

Examples 3 - 10

The sulfonation of 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene is carried out according to Example 1, except that the reaction parameters temperature, time and SO₃ concentration are varied. The results are collated in the table below. Examples 5, 6 and 7 are comparative examples, in which higher reaction temperatures were used.

Example	SO ₃ content [% by weight] of the oleum	Reaction time [h]	Temperature [°C]	Oxide formation [%] ^{a)}
3	20	18	20	5
4	20	48	20	10
5	20	48	30	18
6	20	48	40	52
7	20	48	50	100
8	40	48	20	8
9	65	17	20	5
10	65	48	20	10

^{a)} previous standardization with completely oxidized, hexasulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene

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Example 11

- 60.7 g (93.2 mmol) of 2,2'-bis(diphenylphosphino-methyl)-1,1'-binaphthalene are dissolved in 300 g of concentrated sulfuric acid at 0 to 10°C, 601.7 g of 65% oleum are added with the temperature being kept at 0 to 10°C, and the mixture is then stirred for 48 h at room temperature. For hydrolysis, the sulfonation mixture is added dropwise to 3879.2 g of water over 30 min at temperatures below 10°C.
- 10 The sulfonation product is separated from the aqueous phase by extraction for 1 h at 40°C with a solution of 237.4 g of triisooctylamine in 948.8 g of toluene. The organic phase (1307.8 g) is then extracted at 40°C with 3% by weight sodium hydroxide solution.
- 15 Up to a pH of 3.5, the aqueous phase (357.6 g) contains 16.8 mmol of P(III) and 2.6 mmol of P(V), based in each case on one kilogram of solution, and 3.8% of sulfate. In the pH range 3.5 to 4.8, the P(III) content of the aqueous phase (463.0 g) is 163 mmol and the P(V) content
- 20 is 15.0 mmol, again based in each case on one kilogram of solution, and the sulfate content is 0.05%. In the range from pH 4.8 to pH 6.0, the useful product fraction (335.8 g) is separated off; it contains 212 mmol of P(III) and 1.0 mmol of P(V), based on one kilogram of
- 25 solution.

Examples 12 to 17

- Propylene and a CO/H₂ mixture made up of equal parts by volume are introduced into a 0.2 l stainless steel autoclave, equipped with a stirrer, in an amount such
- 30 that 10 Nl/h of off-gas can be withdrawn from the reactor. 300 ml per hour of aqueous catalyst solution (261 mg of Rh as the acetate and 13.9 mmol of P(III) in the form of BINAS, dissolved in 1000 ml of degassed water

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saturated with nitrogen) are simultaneously circulated through the reactor. The molar ratio of phosphorus to rhodium is 5.5:1, corresponding to a ligand/rhodium ratio of 2.75:1. The reactants are reacted at a pressure of 5 MPa. The remaining reaction parameters can be found in the table.

10 In the table, the results obtained with the process according to the invention (Examples 12 to 16) are compared with the result obtained with a procedure according to the state of the art [catalyst: rhodium/
sodium triphenylphosphinetrisulfonate (TPPTS)] (Example 17). The experiments make it clear that in the novel process, with a surprisingly low Rh/P ratio, a high catalyst activity is achieved and the n/i ratio is
15 further increased. High conversions are obtained even when the olefin charge is considerably increased (Example 15).

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Table

Experimental conditions	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17 (Comparative)
<u>Catalyst</u>	<u>Rh/BINAS</u>	<u>Rh/BINAS</u>	<u>Rh/BINAS</u>	<u>Rh/BINAS</u>	<u>Rh/BINAS</u>	<u>Rh/TPPTS</u>
Rhodium/ligand (mol/mol)	1:2.75	1:2.75	1:2.75	1:2.75	1:2.75	1:100
Temperature (°C)	110	116	122	122	128	122
Pressure (MPa)	5.0	5.0	5.0	5.0	5.0	5.0
Propylene charge (g/h)	40.0	40.0	40.0	129.0	40.0	40.0
<u>Experimental results</u>						
Conversion (%)	44.7	40.4	50.8	47.9	57.8	39.0
Activity mol (n+i) of aldehyde mol of Rh · min	43.92	42.81	55.48	163.3	61.41	15.11
Productivity g (n+i) of aldehyde ml of cat. sol. · h	0.482	0.470	0.608	1.79	0.673	0.206
n/i ratio (parts by weight)	97/3	97/3	97/3	98/2	97/3	93/7

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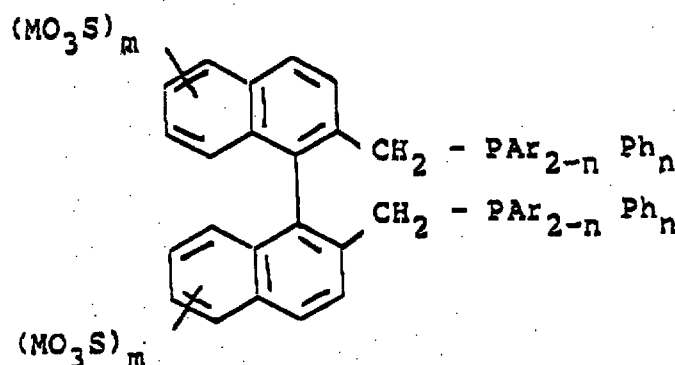
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WHAT IS CLAIMED IS:

1. A sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene of the formula



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in which Ar is m-C₆H₄SO₃M, M is hydrogen, ammonium, a monovalent metal or the equivalent of a polyvalent metal, Ph is the phenyl radical, m is identical or different and has the value 1 or 2 and n is identical or different and is 0, 1 or 2.

10

2. A process for the preparation of the compounds as claimed in claim 1, which comprises sulfonating 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalenes with oleum at temperatures of between 0 and 25°C, hydrolyzing the sulfonation mixture and isolating the sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalenes from the hydrolyzed sulfonation mixture.

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3. The process as claimed in claim 2, wherein oleum containing 10 to 65 and especially 40 to 65% by weight of free sulfur trioxide is used for the sulfonation.
4. The process as claimed in claim 2 or 3, wherein 25 to 80 and preferably 40 to 70 mol of sulfur trioxide are used per mole of the 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalenes.



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5. The process as claimed in one or more of claims 2 to 4, wherein the sulfonation is carried out at temperatures of 0 to 25°C, preferably 0 to 10°C.
- 5 6. The process as claimed in one or more of claims 2 to 5, wherein the hydrolysis of the sulfonation mixture is carried out at temperatures of up to about 30°C, preferably of 15 to 25°C.
- 10 7. The process as claimed in one or more of claims 2 to 6, wherein the hydrolyzed sulfonation mixture is neutralized with alkali metal carbonate or alkali metal hydroxide, alkali metal sulfate is separated off, the aqueous solution is concentrated and the sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalenes are extracted from the residue with
- 15 a mixture of alcohols having up to 5 carbon atoms in the molecule and water.
8. The process as claimed in one or more of claims 2 to 6, wherein the hydrolyzed sulfonation mixture is reacted with a mixture of a water-insoluble amine and an organic solvent, especially a mixture of triisooctylamine and toluene, the sulfonates are extracted as amine salts and the aqueous solution of
- 20 a base, preferably sodium hydroxide or potassium hydroxide, is added to the solution of the amine salts, optionally in portions.
- 25 9. A process for the preparation of aldehydes by reaction of monoolefins, nonconjugated polyolefins, cycloolefins or derivatives of these classes of compounds with carbon monoxide and hydrogen at temperatures of 20 to 150°C and pressures of 0.1 to
- 30 20 MPa in the presence of catalysts composed of watersoluble compounds of rhodium complexed with diphosphines, wherein the diphosphines used are sulfonated 2,2'-bis(diphenylphosphinomethyl)-



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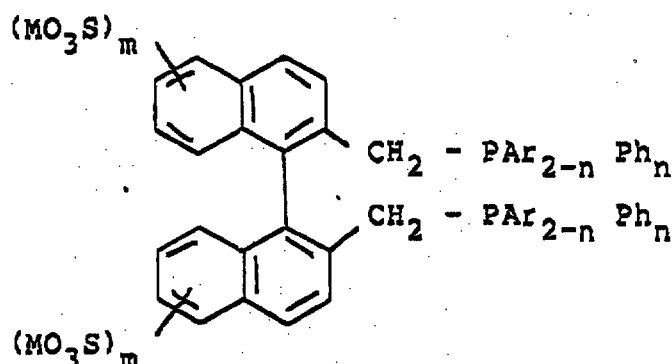
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1,1'-binaphthyls of the formula



in which Ar is m-C₆H₄SO₃M, M is hydrogen, ammonium, a monovalent metal or the equivalent of a polyvalent metal, Ph is the phenyl radical, m is identical or different and has the value 1 or 2 and n is identical or different and is 0, 1 or 2.

- 5
10. The process as claimed in claim 9, wherein 1 to 130, preferably 2 to 25 and especially 2 to 10 mol of sulfonated diphosphines are used per mole of rhodium.
- 10
11. The process as claimed in claim 9 or 10, 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 (based on the solution).
- 15
12. The process as claimed in one or more of claims 9 to 11, wherein the reaction is carried out at 20 to 150°C, preferably 80 to 140°C and especially 100 to 125°C.
- 20
13. The process as claimed in one or more of claims 9 to 12, wherein the reaction is carried out at pressures of 0.1 to 30, preferably 1 to 12 and especially 3 to 7 MPa.



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14. The process as claimed in one or more of claims 9 to 13, wherein olefins or olefin derivatives having 2 to 40, preferably 2 to 20 and especially 2 to 8 carbon atoms are reacted.
- 5 15. A rhodium/diphosphine catalyst for the hydro-
formylation of monoolefins, nonconjugated
polyolefins, cycloolefins or derivatives of these
classes of compounds, which contains 1 to 130,
preferably 1 to 25 and especially 1 to 10 mol of
10 sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-
binaphthyl per mole of rhodium.

This Sheet Has Been Replaced

* C L M S *