

Hydroformylation and catalysts containing phosphorus compounds as ligands which are suitable for this purpose

- 5 The invention relates to a process for the hydroformylation of alkenes using complexes of metals of transition group VIII of the Periodic Table of the Elements having ligands which contain a $\text{—}\overline{\text{P}}\text{=}$ (λ^3, σ^2)-group capable of complex formation, and also these novel complex catalysts.

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Every year about 7 million metric tons of products are produced worldwide by means of the hydroformylation of olefins (Weissermel, Arpe Industrielle Organische Chemie, 4th edition, 1994 VCH Weinheim). There is therefore great industrial interest

15 in operating the reaction with maximum selectivity and activity.

- Rhodium-containing phosphine-modified catalysts have achieved tremendous importance, particularly for the low-boiling olefins (e.g. Beller et al, Journal of Molecular Catalysis A: 104
- 20 (1995)17-85). Although α -olefins can be hydroformylated very well using rhodium-containing phosphine-modified catalysts (cf. J. Falbe, Ed.: New Syntheses With Carbon Monoxide, Springer, Berlin 1980, p. 55 ff), this catalyst system is not very suitable for internal and branched internal olefins nor for olefins having
- 25 more than 7 carbon atoms (cf. Falbe, p. 95 ff). Thus, internal carbon-carbon double bonds are hydroformylated only very slowly in the presence of such a catalyst.

- Rhodium-containing phosphite-modified catalysts have recently
- 30 been proposed for the hydroformylation of low-boiling olefins (see Beller et al Journal of Molecular Catalysis, loc cit). Both α -olefins and also short-chain internal olefins such as 2-butene or methyl 3-pentenoate can be hydroformylated very well using rhodium-containing chelating phosphite-modified catalysts.
- 35 Particularly high linearities are achieved with chelating ligands having a "bite" of about 120° . However, this system is not very suitable for long-chain internal olefins (having more than 7 carbon atoms) and branched internal olefins. For these olefins, monodentate, sterically hindered monophosphites have proven
- 40 useful.

- However, phosphites generally have the disadvantage of sensitivity to hydrolysis and the tendency to undergo degradation reactions, which hinders their industrial use.
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It is an object of the present invention to find novel ligands which are insensitive to hydrolysis and degradation reactions and are particularly suitable as coordinated cocatalysts for the hydroformylation of olefins catalyzed by transition metals of group VIII, in particular rhodium, and also a process for preparing aldehydes from α -olefins, from internal and/or branched olefins or from higher-boiling olefins (having more than 7 carbon atoms).

10 We have found that this object is achieved by means of a process for preparing aldehydes by hydroformylation of olefins with CO/H₂ in the presence of complexes of transition metals of group VIII of the Periodic Table of the Elements containing phosphorus compounds as ligands at from 20 to 200°C, preferably from 20 to 15 180°C, and pressures of up to 700 bar, preferably up to 300 bar, wherein the catalysts used have λ^3, σ^2 -phosphorus compounds capable of complex formation as ligands.

λ^3, σ^2 -Phosphorus compounds are ones in which the phosphorus atom 20 has a free electron pair as well as three bonds to two adjacent atoms.

The catalytically active complexes are carbonyl complexes which are formed by additional adding on of carbon monoxide.

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As carbonyl-free complexes of metals of transition group VIII having phosphabenzene as ligand, tetrakis(phosphobenzene)nickel is already known from Angew. Chem., 104 (1992), p. 1388 ff and chlorine-containing complexes including

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tris(phosphabenzene)rhodium chloride and bis(phosphabenzene)rhodium chloride dimer are already known from J. Heterocyclic Chem., Volume 9 (1972), p. 1457 ff, without use in catalytic chemistry, in particular in hydroformylation, having been described.

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Although many phosphorus-containing ligands are known for the rhodium-catalyzed low-pressure hydroformylation (including arylphosphines, alkylphosphines, chelating phosphines, monophosphites, chelating phosphites, phospholes), the use of

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phosphobenzenes has not previously been examined. In our experiments, we have found that these ligands are not only highly active and therefore very suitable as cocatalysts for the hydroformylation of α -olefins, but are also active for the hydroformylation of internal, branched olefins such as octene N,

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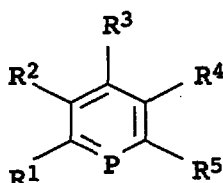
an isooctene mixture having a degree of branching of 1.3 which is obtained by the dimerization of butene by the IFP-dimersol process (cf. Weissermel, Arpe: Industrielle Organische Chemie,

p. 93, 4th edition, VCH Verlagsgesellschaft, Weinheim 1994). The degree of branching is defined as the arithmetic mean of the numbers of the side chains of all the types of molecule in an olefin mixture multiplied by their respective content in the
 5 olefin mixture in % by weight, divided by 100.

Suitable ligands for use according to the present invention are, for example, generally all open-chain or cyclic phosphorus compounds which have at least one group —P=C—

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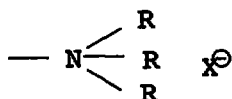
capable of complex formation. Apart from open-chain or cyclic phosphalkenes having at least 4, e.g. from 7 to 100, carbon atoms, these are in particular phosphaaromatics having at least 5, e.g. from 7 to 100, carbon atoms. Especially useful are
 15 unsubstituted or substituted phosphabenzenes of the formula I



I,

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where $R^1 - R^5$ are, independently of one another, hydrogen, alkyl, aralkyl or aryl radicals or heterocyclic radicals each having
 25 1-12 carbon atoms, or the radicals $\text{—COO}^\ominus\text{M}^\oplus$, $\text{—SO}_3^\ominus\text{M}^\oplus$,



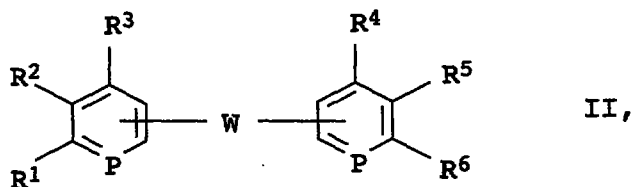
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—OR , —NR_2 , —COOR , —SR , $\text{—(CHRCH}_2\text{O)}_x\text{R}$ and $\text{(CH}_2\text{CH}_2\text{NR)}_x$, where R are identical or different radicals selected from the group consisting of hydrogen and aliphatic or aromatic radicals having from 1 to 18 carbon atoms, $\text{M}^\oplus$ is a cation, e.g. alkali metal or
 35 ammonium, and $\text{X}^\ominus$ is an anion, e.g. sulfate, and x is from 1 to 120, and the radicals $R^1 - R^5$ can be joined to form fused rings.

At least one of the substituents R^1 to R^5 , can have an additional phosphine or phosphite group and thus becomes a bidentate or
 40 multidentate ligand.

However, the bidentate or multidentate ligands which are preferably used according to the present invention have 2 or more phosphabenzene units which are connected by a bridge. Compounds
 45 of this type are those of the formula II

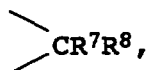
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where R^1 - R^6 are as defined above for R^1 - R^5 and W is a bridge in the form of a covalent bond or a chain comprising from 1 to 10, preferably 6, atoms which can be part of a cyclic or aromatic compound, and the phospharomatics are linked in the ortho or meta position relative to the phosphorus, with the ortho or meta positions not used for the bridge being substituted by radicals such as R^1 to R^5 in the formula I, and one or more of the substituents R^1 to R^6 can be a further phosphabenzene of the formula I bonded via a further bridge.

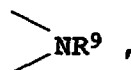
Such atoms of the bridge W can be, for example, methylene groups of the formula

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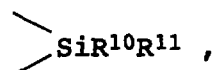
where R^7 and R^8 are identical or different and are each hydrogen, a C_1 - C_9 -alkyl group, in particular the methyl group, a C_6 - C_{12} -aryl group, in particular the phenyl group, or a C_7 - C_{15} -aralkyl group, in particular the benzyl group, the oxa group -O-, the amino group

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where R^9 is a C_1 - C_4 -alkyl group, in particular the methyl group, a C_6 - C_{12} -aryl group, in particular the phenyl group, or a C_7 - C_{15} -aralkyl group, in particular the benzyl group, or a silyl group of the formula

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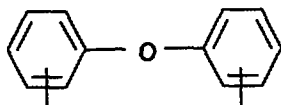
where the radicals R^{10} and R^{11} are identical or different and are each a C_1 - C_4 -alkyl group, in particular the methyl group, a C_6 - C_{12} -aryl group, in particular the phenyl group, a C_7 - C_{15} -aralkyl group, in particular the benzyl group.

As cyclic or aromatic compounds which, together with the covalent bond or the abovementioned bridge atoms, can be constituents of the bridge W, mention may be made of C_5 - C_{10} -cycloalkyldiyl groups, in particular the cyclopentanedyl group, the cyclohexyldiyl

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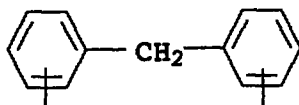
group or the decalindiyl group, C₆-C₁₂-aryldiyl groups such as the phenylenediyl, naphthylenediyl or 1,1'-biphenyldiyl group, the (diphenyl ether)-diyl group

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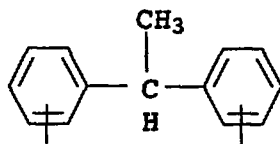


the diphenylmethane-diyl group

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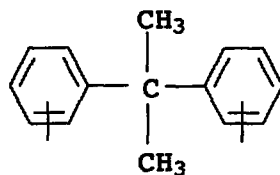


15 the diphenylethane-diyl group



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the diphenylpropane-diyl group



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or the ferrocenediyl group.

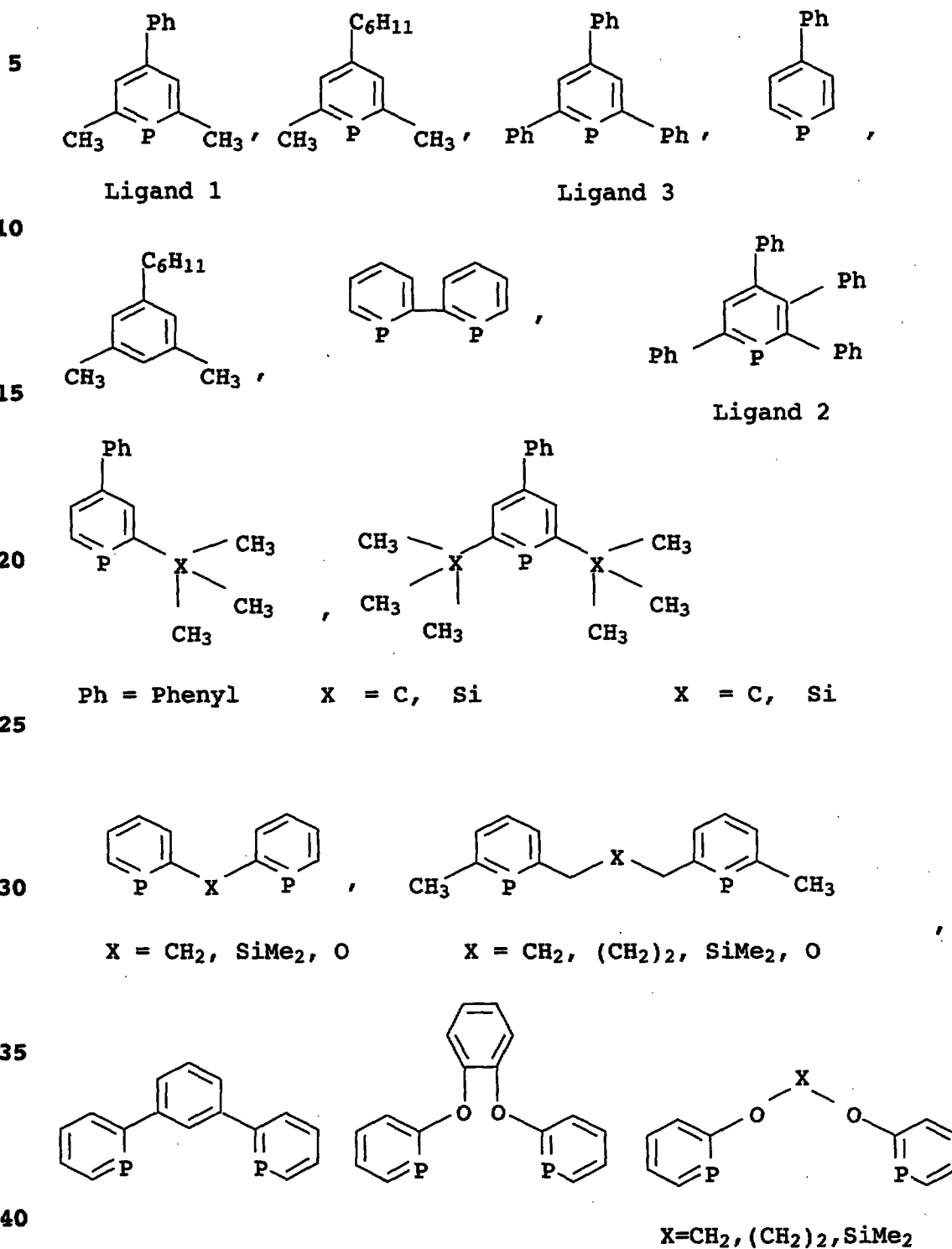
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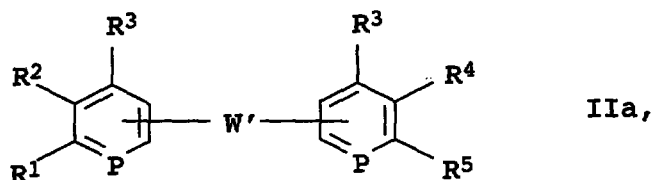
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Examples of phosphabenzenes are the following:



Bidentate ligands which are found to be particularly advantageous in the process of the present invention are the phosphabenzenes of the formula IIa

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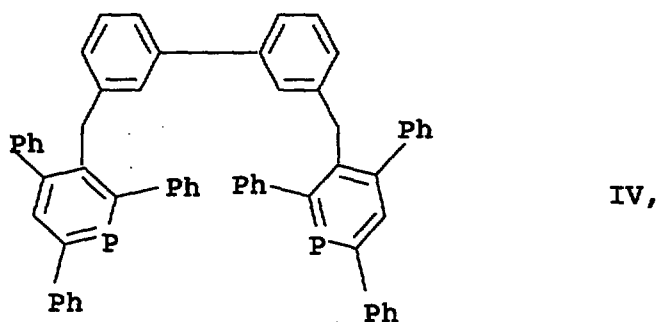


where the radicals R^1 to R^6 are identical or different and are as defined above for the radicals R^1 to R^5 and where W' is a 2,2'-, 10 4,4'- or 3,3'-biphenyldiyl group, a 2,2'-, 4,4'- or 3,3'-(diphenyl ether)-diyl group, a 2,2'-, 4,4'- or 3,3'-diphenylmethane-diyl group, a 2,2'-, 4,4'- or 3,3'-diphenylethane-diyl group or a 2,2'-, 4,4'- or 3,3'-diphenylpropane-diyl group which is in each case linked to 15 the two phosphabenzene groups in the ortho or meta position relative to the phosphorus atom via a covalent bond, an oxa group and/or a C_1 - C_4 -alkylene group, in particular a methylene group, where the biphenyl, diphenyl ether or C_1 - C_3 -diphenylalkane group is unsubstituted or substituted by from 1 to 4 identical or 20 different C_1 - C_4 -alkyl groups, and where the ortho or meta positions not used for the bridge are substituted by radicals such as R^1 to R^5 in the formula I. In the above, the biphenyl derivative groups concerned can be linked asymmetrically to the two phosphabenzene groups, i.e. via two different connecting 25 members.

A particularly advantageous ligand selected from the group consisting of phosphabenzenes of the formula IIa is the phosphabenzene IV, also designated in the examples as ligand 5,

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40 where Ph is the abbreviation for a phenyl group.

The ligands of the formula IIa, in particular the ligand of the formula IV, hydroformylate virtually only terminal double bonds and have a relatively high selectivity for the formation of 45 linear aldehydes, i.e. a relatively high n -selectivity.

The principle of preparing the phosphabenzenes is known. General information on the synthesis of phosphabenzenes may be found in Houben-Weyl, Phosphororganische Verbindungen, Editor M. Regitz, Volume 2, p. 72 ff. Compounds which have not yet been described individually are obtained in a similar manner.

The effective novel catalysts are those of the formula $M(L)_n(CO)_m$, where M is at least one central atom of an element of transition group VIII of the Periodic Table of the Elements, L is at least one ligand containing a $\overline{P} = (\lambda^3, \sigma^2)$ -group capable of complex formation, for example of the formula I, II or IIa, or the ligand of the formula IV, n and m are each at least 1 and, per equivalent of M, n and m are each, for example, from 1 to 3 and the sum $n+m$ is from 2 to 5, and further radicals such as hydrido or alkyl or acyl radicals can also be present as ligands.

The active carbonyl complex is generally formed in situ, i.e. in the hydroformylation reactor, from a salt or a compound of the metal M, the ligand and carbon monoxide; however, it can also be prepared separately and used as such.

The complex catalysts preferably comprise a central atom M selected from the group consisting of the transition metals cobalt, ruthenium, rhodium, palladium or platinum, but in particular cobalt and rhodium, complexed by carbonyl and also hydrido, alkyl or acyl radicals and also as ligands the monodentate or multidentate preferred phosphabenzenes to be used according to the present invention. If the complex catalysts are generated in situ, simple precursor complexes such as acetylacetonatodicarbonylrhodium or rhodium acetate in the presence of the corresponding ligands are exposed to the reaction conditions or precursor complexes are admixed with activating additives such as Brönsted or Lewis acids or Lewis bases.

For the in situ formation of the catalyst in the reaction mixture, the ligand (calculated as equivalents of phosphorus) is used in a molar ratio to rhodium of from 1:1 to 1000:1 and use is additionally made of an inert solvent. Particularly preferred solvents are the aldehydes which are formed by reaction of the respective olefin, and also the high boilers intrinsic to the synthesis which are formed by secondary reactions of the respective aldehyde in the hydroformylation process. In the case of ligands hydrophylyzed by suitable substituents, preference is given to using water, alcohols or other polar solvents.

The composition of the synthesis gas CO/H₂ used in the hydroformylation process of the present invention can be varied within wide limits. For example, synthesis gas having a CO/H₂ molar ratio of from 5:95 to 70:30 can be successfully used; 5 preference is given to using synthesis gas having a CO/H₂ ratio of from 40:60 to 60:40, particularly preferably about 1:1.

The hydroformylation reaction with the novel catalyst is preferably carried out at from 20 to 180°C, in particular from 50 10 to 150°C. However, for each catalyst system it is advantageous to determine an optimum temperature experimentally. The reaction pressure can, depending on the cocatalyst, i.e. ligand, and substrate, vary within a range from normal pressure, i.e. atmospheric pressure, to 700 bar, preferably up to 300 bar, with 15 reactions in a range up to about 30 bar normally being referred to as low-pressure reactions, those in a range up to about 100 bar being referred to as intermediate-pressure reactions and those above 100 bar being referred to as high-pressure reactions.

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The process is generally carried out with the catalyst, which is dissolved homogeneously in the reaction medium, being separated off from the product mixture from the hydroformylation reaction and being returned to the hydroformylation stage.

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The process generally gives virtually exclusively the corresponding aldehydes in excellent yields.

Suitable olefins to be hydroformylated according to the present 30 invention are α -olefins or internal olefins or branched internal olefins. The following olefins may be mentioned as examples: ethylene, propene, 1-butene, 1-octene, C₅₋₂₀ α -olefins, linear C₅₋₂₀ internal olefins, 2-butene; branched internal octene mixtures; branched internal nonene mixtures; branched internal 35 dodecene mixtures, cyclohexene, α -pinene, styrene, 4-isobutylstyrene, methyl 3-pentenoate, methyl 4-penteneoate, methyl oleate, 3-pentenitrile, 4-pentenitrile, octa-2-7-dien-1-ol, 7-octenal, methyl acrylate, methyl methacrylate, acrylonitrile, vinyl acetate, vinyl glycol 40 diacetate, vinyl methyl ether, polypropene, polyisobutylene, substrates which are likewise suitable are dienes or polyenes having isolated or conjugated double bonds. Examples are 1,3-butadiene, 1,5-hexadiene, vinyl cyclohexene, dicyclopentadiene, 1,5,9-cyclooctatriene, homopolymers and 45 copolymers of butadiene and polyisobutene.

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Otherwise, the hydroformulation reaction is carried out in a manner known per se. Details regarding the process procedure may be found in Beller and Falbe, loc cit, the contents of which are hereby incorporated by reference.

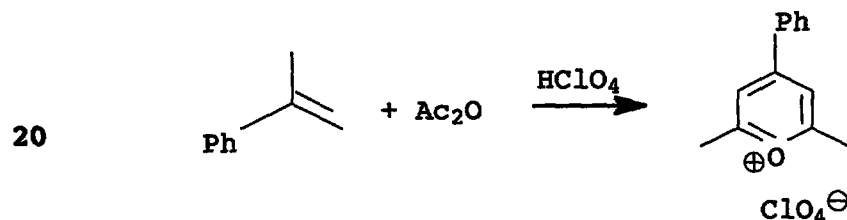
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Examples

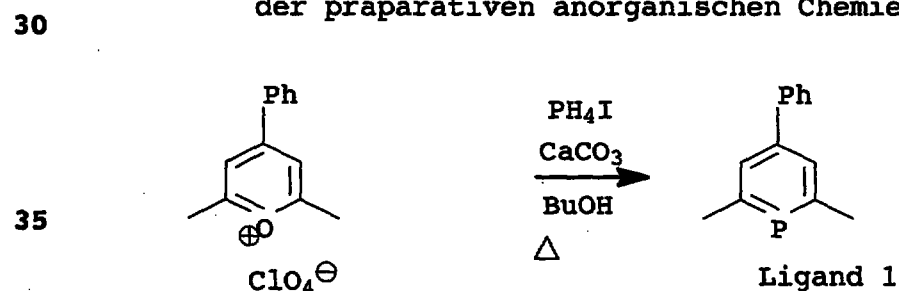
Ligand 1:

10 Catalyst precursor synthesis: 2,6-dimethyl-4-phenylphosphabenzene was prepared in two stages by literature methods:

15 1st stage: The synthesis of 2,6-dimethyl-4-phenylpyrylium perchlorate from methylstyrene and acetic anhydride was carried out as described in Houben-Weyl, volume 7b, p. 807 ff.



25 2nd stage: The 2,6-dimethyl-4-phenylpyrilium salt was subsequently converted by means of PH_4I and base into 2,6-dimethyl-4-phenylphosphabenzene as described in the thesis by F. Lieb, Universität Würzburg, 1969, p. 102 (PH_4I was prepared by the method of Brauer, "Handbuch der präparativen anorganischen Chemie", p. 475 ff).



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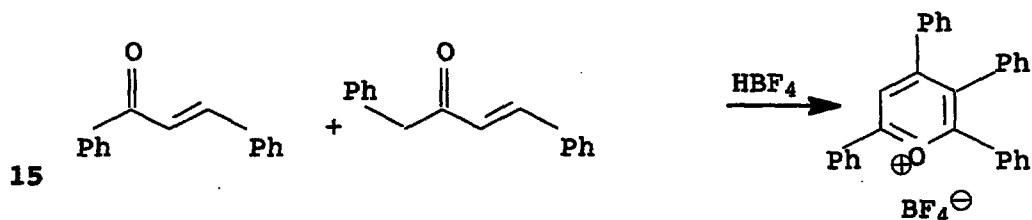
Ligand 2:

2,3,4,6-Tetraphenylphosphabenzene was prepared in two stages by literature methods:

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1st stage: The synthesis of 2,3,4,6-tetraphenylpyrylium tetrafluoroborate from 1,3-diphenyl-3-oxopropene (Chalkon) and deoxybenzoin was carried out as described in Houben-Weyl, Volume E7b, p. 856-7.

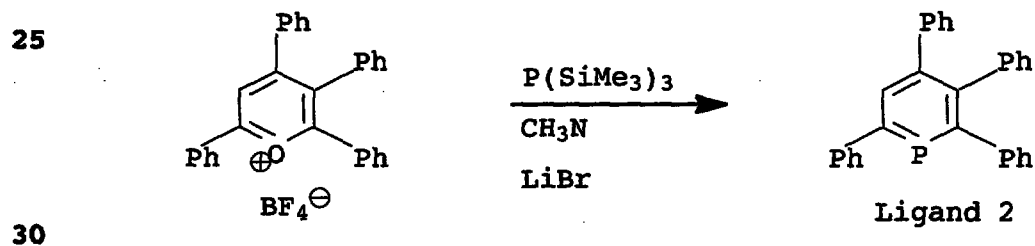
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2nd stage: The 2,3,4,6-tetraphenylpyrylium salt was subsequently converted by means of $\text{P}(\text{SiMe}_3)_3$ into 2,3,4,6-tetraphenylphosphabenzene (Angew. Chem., 79 (1967), p. 475 ff)

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Ligand 3:

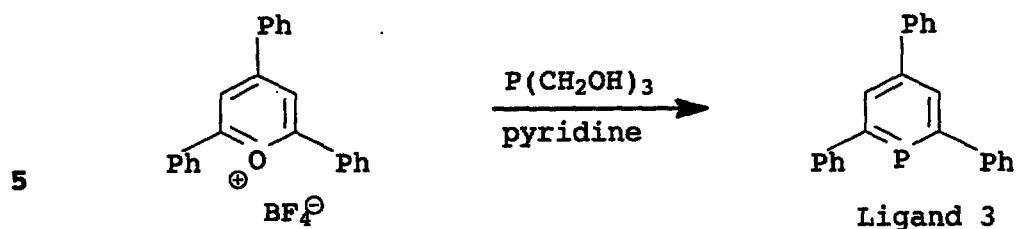
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Catalyst precursor synthesis: 2,4,6-triphenylphosphabenzene was prepared as described in DE-A 1618668 from the commercially available 2,4,6-triphenylpyrylium tetrafluoroborate (Aldrich) by means of $\text{P}(\text{CH}_2\text{OH})_3$. $\text{P}(\text{CH}_2\text{OH})_3$ was prepared from commercially available $[\text{P}(\text{CH}_2\text{OH})_4]\text{Cl}$ (Aldrich) using the method of Ellis et al.

40 Inorg. Chem. 1992, 31, 3026-33:

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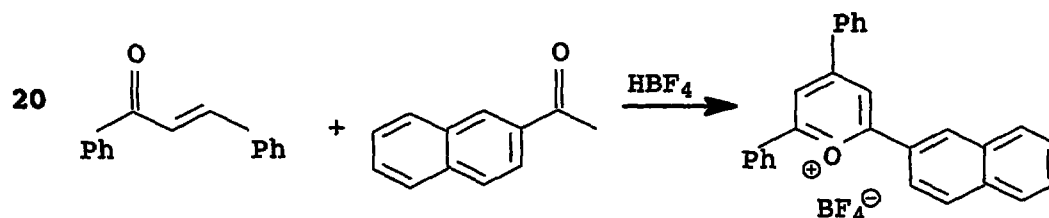
Ligand 4:

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Catalyst precursor synthesis: 2,4-diphenyl-6-(2-naphthyl)-phosphabenzene was prepared using a method similar to ligand 2, in two stages from 1,3-diphenyl-3-oxopropene (Chalcone) and 2'-acetonaphthone:

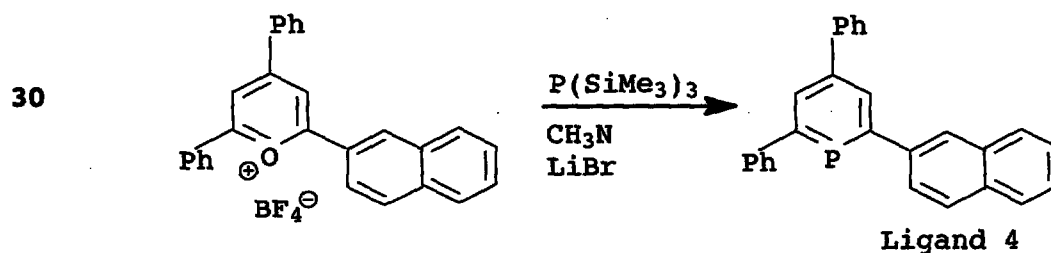
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1st stage:



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2nd stage:



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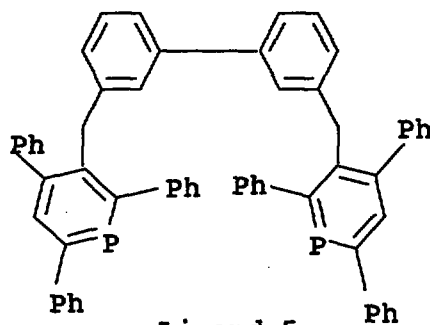
Ligand 5:

Catalyst precursor synthesis: ligand 5 was prepared in six stages:

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1st stage: preparation of 3,3'-bis(bromomethyl)biphenyl

Starting materials: 25 g = 0.137 mol of 3,3'-dimethylbiphenyl
 51 g = 0.287 mol of N-bromosuccinimide
 1 g = 4.13 mmol of dibenzoyl peroxide

Solvent: carbon tetrachloride

Experimental procedure:

The reaction mixture was refluxed for 5 hours and subsequently filtered hot in order to remove the succinimide. The product was crystallized from the filtrate.

2nd stage: preparation of 3,3'-bis(iodomethyl)biphenyl

Starting materials: 9 g = 26.5 mmol of 3,3'-bis(bromomethyl)-biphenyl
 7.94 g = 53 mmol of sodium iodide as a 1 molar solution in acetone

Solvent: acetone

Experimental procedure: the 3,3'-bis(bromomethyl)biphenyl was dissolved in acetone and the sodium iodide solution was slowly added to this solution. The reaction mixture was stirred until the reaction was complete and the precipitated sodium bromide was subsequently filtered off using reduced pressure. The 3,3'-bis(iodomethyl)biphenyl was crystallized from the filtrate. To crystallize further product, the mother liquor was admixed with small amounts of water.

3rd stage: preparation of 1,3,5-triphenylpent-2-ene-1,5-dione

Starting materials: 10 g = 25.3 mmol of 2,4,6-triphenylpyrylium tetrafluoroborate
 13.7 g = 101.2 mmol of sodium acetate

trihydrate

Solvent: 10 ml water/50 ml methanol/100 ml acetone

- 5 Experimental procedure: The sodium acetate together with the solvent mixture were heated to 60°C, the heating source was removed and the solid pyrylium salt was introduced a little at a time into this mixture. The reaction mixture immediately became orange. The reaction mixture was stirred for 4 hours without
10 further heating. Subsequently, diethyl ether was added to the reaction mixture and the aqueous phase was washed a number of times with diethyl ether. The combined ether extracts were dried over magnesium sulfate and part of the solvent was subsequently distilled off. The product 1,3,5-triphenylpent-2-ene-1,5-dione
15 crystallized from this concentrated solution (G.W. Fischer et al: J. Prakt. Chem. 326, 287 (1984), in particular p. 298).

4th stage: preparation of 1,3,5-triphenylpent-2-ene-1,5-dione sodium enolate

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Starting materials: 5 g = 15.38 mmol of 1,3,5-triphenylpent-2-ene-1,5-dione
0.89 g = 15.38 mmol of sodium methoxide
as 30% strength solution in methanol

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Solvents: benzene, diethyl ether

- Experimental procedure: The sodium methoxide solution was slowly added to a solution of the sodium enolate of 1,3,5-triphenylpent-
30 2-ene-1,5-dione in benzene. 200 ml of diethyl ether were then added to the reaction mixture and the mixture was stirred for 1 hour with exclusion of air. The precipitated, solid product was filtered off and dried under reduced pressure (G.W. Fischer: J. Prakt. Chem. 327, 983 (1985), in particular p. 987).

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5th stage: preparation of bis-3,3'-(3-(2,4,6-triphenyl)pyrylium-methyl)-1,1'-biphenyl diperchlorate

- Starting materials: 3.9 g = 11.21 mmol of 1,3,5-triphenylpent-
40 2-ene-1,5-dione sodium enolate
2.43 g = 5.6 mmol of 3,3'-bis(iodomethyl)-biphenyl

- Experimental procedure: 3,3'-Bis(iodomethyl)biphenyl was added at
45 room temperature to a solution of the enolate from the 4th stage and the mixture was stirred for one hour. The reaction solution was taken up in a diethyl ether/water mixture, the organic phase

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was washed a number of times with water, dried over sodium sulfate and evaporated under reduced pressure. The reaction product was subsequently mixed with ethanol, perchloric acid was added and the mixture was refluxed for 6 hours. After cooling this mixture, the precipitation of the pyrylium salt was completed by addition of diethyl ether, the pyrylium salt was filtered off and dried under reduced pressure (G.W. Fischer: J. Prakt. Chem. 327, 983 (1985), in particular p. 988).

10 6th stage: preparation of ligand 5

2.5 g of the pyrylium salts obtained in stage 5 were dissolved in ethanol and mixed with 0.5 g of a 30% strength by weight solution of hydrogen bromide in glacial acetic acid (Aldrich) and reacted with phosphine (PH_3) in a pressure vessel. For this purpose, phosphine was injected at room temperature into the pressure vessel until a pressure of 5 bar had been attained, and the charged pressure vessel was subsequently heated at 110°C for 4 hours while maintaining a pressure of 12.5 bar. After cooling and venting, the precipitated product was filtered off and recrystallized. Further product could be isolated from the solution.

25 General experimental procedure:

All experiments (batchwise) were carried out in a 100 ml autoclave (material HC). The reaction mixture was heated for 10 minutes at the reaction temperature and the solution was stirred vigorously with a gas-introducing stirrer. The desired pressure was set by means of CO/H_2 (1:1). During the reaction, the pressure in the reactor was maintained at the desired level by injection of further amounts via a pressure regulator. After the reaction time, the autoclave was cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an internal standard and correction factors.

Example 1: Low-pressure hydroformylation of 1-octene

3.1 mg of acetylacetonatodicarbonylrhodium (0.012 mmol), 23 mg of ligand 1 (0.12 mmol), 5.8 g of 1-octene (52 mmol) and 6.0 ml of Texanol® were heated to 100°C . The desired pressure of 10 bar was set by means of CO/H_2 (1:1). After 4 hours, the autoclave was cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an internal standard and correction factors. The conversion of 1-octene was 100%, the yield of nonanals was 92%, the selectivity to give nonanals was

92.5% (59.2% of n-isomer), the selectivity to give internal olefins was 2.7%.

Example 2: Intermediate-pressure hydroformylation of octene N

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The aldehydes in the reaction mixture from Example 1 were distilled off under reduced pressure at 100°C. This left a homogeneous solution comprising active catalyst, Texanol® and high boilers formed in the reaction. To this were added 18 g of
10 octene N (isooctene mixture, degree of branching: 1.3) with exclusion of air. The mixture was heated to 130°C and the desired pressure of 60 bar was set by means of CO/H₂ (1:1). After 4 hours, the autoclave was cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an
15 internal standard and correction factors. The octene conversion was 63%, the selectivity to give nonanal isomers was 100%.

Example 3: Intermediate-pressure hydroformylation of styrene

20 0.375 mol% of acetylacetonatodicarbonylrhodium, ligand 1 in a rhodium to ligand molar ratio of 1:5, styrene and toluene as solvent were reacted at 20°C with CO/H₂ (1:1) under a pressure of 50 bar in an autoclave. After 22 hours, the autoclave was vented and emptied. Analysis of the reaction mixture was carried out by
25 means of GC, using an internal standard and correction factors. The styrene conversion was 51%, the ratio of branched (2-phenylpropanal) to linear (3-phenylpropanal) product was 22.3:1.

30 Example 4: Intermediate-pressure hydroformylation of styrene

0.375 mol% of acetylacetonatodicarbonylrhodium, ligand 1 in a rhodium to ligand molar ratio of 1:2, styrene and toluene as solvent were reacted at 20°C with CO/H₂ (1:1) under a pressure of
35 50 bar in an autoclave. After 22 hours, the autoclave was vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an internal standard and correction factors. The styrene conversion was 80%, the ratio of branched (2-phenylpropanal) to linear (3-phenylpropanal) product was
40 26.6:1.

Example 5: Low-pressure hydroformylation of 1-octene

45 3.1 mg of acetylacetonatodicarbonylrhodium (0.012 mmol), 26 mg of ligand 2 (0.065 mmol), 5.6 g of 1-octene (50 mmol) and 6.0 ml of Texanol® were heated to 100°C. The desired pressure of 10 bar was set by means of CO/H₂ (1:1). After 4 hours, the autoclave was

cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an internal standard and correction factors. The conversion of 1-octene was 100%, the yield of nonanals was 88%, the selectivity to give nonanals was 5 88% (aldehyde composition: 15% of 2-propylhexanal, 19% of 2-ethylheptanal, 38% of methyloctanal, 28% of n-nonanal; 28% of n-isomer); the selectivity to give internal olefins was 12%.

Example 6: Intermediate-pressure hydroformylation of octene N
10

The aldehydes in the reaction mixture from Example 5 were distilled off under reduced pressure at 100°C. This left a homogeneous solution comprising active catalyst, Texanol® and high boilers formed in the reaction. To this were added 5.3 g of 15 octene N (isooctene mixture, degree of branching: 1.3) with exclusion of air. The mixture was heated to 130°C and the desired pressure of 60 bar was set by means of CO/H₂ (1:1). After 4 hours, the autoclave was cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an 20 internal standard and correction factors. The octene conversion was 56%, the selectivity to give nonanal isomers was 100 %.

Example 7: Intermediate-pressure hydroformylation of octene N

25 The aldehydes in the reaction mixture from Example 6 were distilled off under reduced pressure at 100°C. This left a homogeneous solution comprising active catalyst, Texanol® and high boilers formed in the reaction. To this were added 5.3 g of octene N (isooctene mixture, degree of branching: 1.3) with 30 exclusion of air. The mixture was heated to 130°C and the desired pressure of 60 bar was set by means of CO/H₂ (1:1). After 4 hours, the autoclave was cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an internal standard and correction factors. The octene conversion 35 was 55%, the selectivity to give nonanal isomers was 100 %.

Example 8: Intermediate-pressure hydroformylation of styrene

0.375 mol% of acetylacetonatodicarbonylrhodium, ligand 2 in a 40 rhodium to ligand molar ratio of 1:5, styrene (0.65 mol/l) and toluene as solvent were reacted at 20°C with CO/H₂ (1:1) under a pressure of 50 bar in an autoclave. After 22 hours, the autoclave was vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an internal standard and 45 correction factors. The styrene conversion was 98%, the ratio of

branched (2-phenylpropanal) to linear 3-phenylpropanal) product was 18:1.

Example 9: Intermediate-pressure hydroformylation of octene N

5

An experiment on the hydroformylation of octene N using ligand 3 (51 ppm of Rh, L/Rh molar ratio = 10.8) was carried out as described in Example 1. The pressure (60 bar), the temperature (130°C) and the reaction time (4 h) were set as in Example 2. The catalyst was separated off using a method similar to Example 2 and was reused four times. The following yields were achieved at approximately 100% selectivity to nonanals:

15	Experiment	Yield of nonanals %
	First use	63
	Recycle 1	56
	Recycle 2	53
20	Recycle 3	55
	Recycle 4	52

Example 10: Low-pressure hydroformylation of 1-octene

25

Experiments on the hydroformylation of 1-octene were carried out as described in Example 1 using ligand 3 at 90°C. As an additional change, the ligand to rhodium ratio was varied.

30	Rh content	L/Rh	1-Oct-ene conversion	Nonanal yield	Formation of internal olefins: Selectivity	Nonanal selectivity	n-Proportion	α -Proportion
35								
40	ppm	mol/mol	%	%	%	%	%	%
	51	21	99	64	35.6	64.4	40.8	79.6
	60	35	99	84	16.9	84.9	49.2	86.7
	60	89	98	90	8.5	92.1	65.2	99.6

n-proportion = (1-nonanal/total aldehydes) $\times$ 100

45 α -proportion = [(1-nonanal + 2-methyloctanal)/total aldehyde] $\times$ 100

Example 11: Low-pressure hydroformylation of 1-octene

Experiments on the hydroformylation of 1-octene were carried out as described in Example 1 using ligand 3 at a ligand to rhodium ratio of 11. In addition, the temperature was varied.

	Rh content	Temperature	1-Octene conversion	Nonanal yield	n-Proportion	Internal olefin selectivity	Nonanal selectivity
	ppm	°C	%	%	%	%	%
15	52	100	99	69	31.4	29.3	69.1
	58	90	98	12	50.7	81.7	11.9
	51	80	93	8	67.7	82.3	8.4

20 Example 12: Low-pressure hydroformylation of cyclohexene

0.375 mol% of acetylacetonatodicarbonylrhodium and ligand 3 in a rhodium to ligand molar ratio of 1:10, cyclohexene (0.68 mol/l; cyclohexene/Rh = 730 mol/mol) and toluene as solvent were reacted at 90°C with CO/H₂ (1:1) at a pressure of 20 bar in an autoclave. After 1 h, the autoclave was vented and emptied. Analysis of the reaction mixture was carried out by means of GC, using an internal standard and correction factors.

30 The yield of cyclohexane carbaldehyde was 29%, ie. the turnover frequency (TOF) was 214 h⁻¹. The TOF is calculated according to the formula:

$$\text{TOF} = \frac{\text{mol of product}}{\text{mol of catalyst} \cdot \text{h}}$$

Example 13: Hydroformylation of octene N

40 261 mg of octacarbonyldicobalt (0.763 mmol), 2.16 g of ligand 3 (6.9 mmol), 30 g of octene N (267.4 mmol) and 10 g of toluene were heated to 150°C under 30 bar of CO/H₂ (1:1). The pressure was set to 50 bar by the injection of further CO/H₂ (1:1). After 5 hours, the autoclave was cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC (using an internal standard and correction factors).

The conversion of octene N was 9.8%, the yield of C₉ aldehydes was 8.3%, the selectivity to aldehydes was 85% (n-proportion = 5.5%).

5 Example 14: Hydroformylation of 1-octene

90 mg of octacarbonyldicobalt (0.263 mmol), 0.41 g of ligand 3 (1.315 mmol), 30 g of 1-octene (267.4 mmol) and 10 g of toluene were heated to 130°C under 30 bar of CO/H₂ (1:1). The desired
10 pressure of 75 bar was set by injection of further CO/H₂ (1:1). After 9 hours, the autoclave was cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC (using an internal standard and correction factors).

15 The conversion of 1-octene was 98.9%, the yield of nonanals was 70.7%, the selectivity to nonanals was 71.5% (n-proportion = 45.3%), the selectivity to internal olefins was 11.1%.

Example 15: Hydroformylation of internal dodecenes

20

261 mg of octacarbonyldicobalt (0.763 mmol), 2.35 g of ligand 3 (7.5 mmol), 30 g of internal dodecenes (178.2 mmol) and 10 g of toluene were heated to 150°C under 30 bar of CO/H₂ (1:1). The pressure of 50 bar was set by injection of additional CO/H₂ (1:1).
25 After 5 hours, the autoclave was cooled, vented and emptied. Analysis of the reaction mixture was carried out by means of GC (using an internal standard and correction factors).

The conversion of dodecene was 26.2%, the yield of tridecanals
30 was 16.7%, the selectivity to tridecanals was 53.3% (n-proportion = 0.27%).

Example 16: Hydroformylation of isobutene

35 31.2 mg of acetylacetonatodicarbonylrhodium (0.12 mmol) and ligand 3 in a rhodium to ligand molar ratio of 1:15, 17.2 g of isobutene (0.31 mol) and 50 ml of Texanol[®] as solvent were reacted at 110°C with CO/H₂ (1:1) at a pressure of 50 bar in an autoclave. After 5 hours, the autoclave was vented and emptied. Analysis of
40 the reaction mixture was carried out by means of GC, using an internal standard and correction factors.

The isobutene conversion was 100%, the pentanal yield was 93.5%, the ratio of branched (pivalaldehyde) to linear
45 (isovaleraldehyde) product was 1:600.

Comparative Example 1: Hydroformylation of isobutene and rhodium/
triphenylphosphine

31.2 mg of acetylacetonatodicarbonylrhodium (0.12 mmol) and
5 triphenylphosphine in a rhodium to triphenylphosphine molar ratio
of 1:10, 14.5 g of isobutene (0.26 mol) and 50 ml of Texanol® as
solvent were reacted at 110°C with CO/H₂ (1:1) at a pressure of 50
bar in an autoclave. After 5 hours, the autoclave was vented and
emptied. Analysis of the reaction mixture was carried out by
10 means of GC, using an internal standard and correction factors.

The isobutene conversion was 82%, the pentanal yield was 69%, the
ratio of branched (pivalaldehyde) to linear (isovaleraldehyde)
product was 1:300.

15

Example 17: Hydroformylation of isoprenol

37 mg of acetylacetonatodicarbonylrhodium (0.14 mmol) and
ligand 3 in a rhodium to ligand molar ratio of 1:15 and 75 g of
20 isoprenol (0.87 mol) were reacted at 90°C with CO/H₂ (1:1) at a
pressure of 50 bar in an autoclave. After 5 hours, the autoclave
was vented and emptied. Analysis of the reaction mixture was
carried out by means of GC.

25 The isoprenol conversion was 100%, the product comprised 79.2% of
2-hydroxy-4-methyltetrahydropyran, 6.5% of 3-methylbutanol, 1.2%
of 3-methylbutanal, 3.2% of 4-methyl-3,6-dihydro-2H-pyran (main
components).

30 Example 18: Hydroformylation of polyisobutene

20 mg acetylacetonatodicarbonylrhodium (0.077 mmol) and ligand 3
in a rhodium to ligand molar ratio of 1:15, 40 g of polyisobutene
having a mean molar mass (M_n) of 1000, 40 g of Mihagol as solvent
35 were reacted at 150°C with CO/H₂ (1:1) at a pressure of 50 bar in
an autoclave. After 5 hours, the autoclave was vented and
emptied. Analysis of the reaction product by means of ¹³C-NMR
spectroscopy indicated a polyisobutenaldehyde yield of 64%.

40 Example 19: Low-pressure hydroformylation of styrene

0.357 mol% of acetylacetonatodicarbonylrhodium, ligand 4 in a
rhodium to ligand molar ratio of 1:2, styrene (0.65 mol/l) and
toluene as solvent were reacted at 20°C with CO/H₂ (1:1) at a
45 pressure of 20 bar in an autoclave. After 22 hours, the autoclave
was vented and emptied. Analysis of the reaction mixture was

carried out by means of GC, using an internal standard and correction factors.

The aldehyde yield was 99%, the ratio of branched (2-phenyl-5 propanal) to linear (3-phenylpropanal) product was 26:1.

Example 20: Low-pressure hydroformylation of 1-octene

1.6 mg of acetylacetonatodicarbonylrhodium (0.006 mmol), 76 mg of
10 ligand 5 (0.09 mmol; L/Rh molar ratio = 15), 6.1 g of 1-octene
(54 mmol) and 6.0 ml of Texanol[®] were heated to 90°C. The pressure
was set to 10 bar by injection of additional CO/H₂ (1:1). After
4 hours, the autoclave was cooled, vented and emptied. Analysis
of the reaction mixture was carried out by means of GC, using an
15 internal standard and correction factors.

The conversion of 1-octene was 99%, the selectivity to nonanals
was 64%, the n-proportion was 71%, the α -proportion was 98.2% and
the selectivity to internal olefins was 32%; n-proportion =
20 $(1\text{-nonanal}/\text{total aldehydes}) \times 100$; α -proportion = $[(1\text{-nonanal} +$
 $2\text{-methyloctanal})/\text{total aldehyde}] \times 100$.

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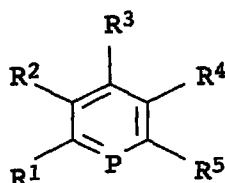
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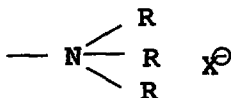
We claim:

1. A process for preparing aldehydes by hydroformylation of
olefins with CO/H₂ in the presence of complexes of transition
metals of group VIII of the Periodic Table of the Elements
containing phosphorus compounds as ligands at from 20 to
200°C and pressures of from atmospheric pressure to 700 bar,
wherein the catalysts used have λ³,σ²-phosphorus compounds
capable of complex formation as ligands.
2. A process as claimed in claim 1, wherein the ligands used are
open-chain or cyclic phosphorus compounds having at least one
group —P=C— capable of complex formation.
3. A process as claimed in claim 1, wherein the ligands used are
open-chain or cyclic phosphaaalkenes having at least 4 carbon
atoms.
4. A process as claimed in claim 1, wherein the ligands used are
phosphaaromatics having at least 5 carbon atoms.
5. A process as claimed in claim 1, wherein the ligands used are
unsubstituted or substituted phosphabenzene of the formula I,



I,

where R¹ - R⁵ are, independently of one another, hydrogen,
alkyl, aralkyl or aryl radicals or heterocyclic radicals each
having 1-12 carbon atoms, or radicals -COO[⊖]M[⊕], -SO₃[⊖]M[⊕],



-OR, -NR₂, -COOR, -SR, -(CHRCH₂O)_xR and (CH₂CH₂NR)_x, where R
are identical or different radicals selected from the group
consisting of hydrogen or aliphatic or aromatic radicals
having from 1 to 18 carbon atoms, M[⊕] is a cation and X[⊖] is an
anion and x is from 1 to 120, and the radicals R¹ - R⁵ can be
joined to form fused rings.

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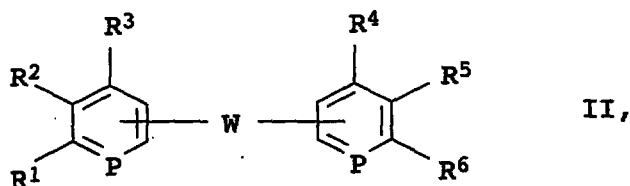
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6. A process as claimed in claim 5, wherein the ligands used are phosphabenzene of the formula I as set forth in claim 5 which has a phosphine or phosphite group in at least one side chain.

5

7. A process as claimed in claim 1, wherein the ligands used are a bidentate or multidentate compound of the formula II

10



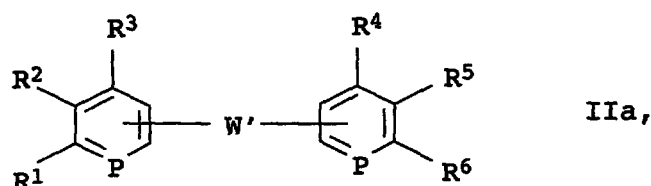
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where R^1 - R^6 are as defined for R^1 - R^5 in claim 5 and W is a bridge in the form of a covalent bond or a chain comprising from 1 to 10 atoms which can be part of a cyclic or aromatic compound, and the phosphaaromatics are linked in the ortho or meta position relative to the phosphorus, with the ortho or meta positions not used for the bridge being substituted by radicals R^1 to R^5 as in claim 5, and one or more of the substituents R^1 to R^6 can be a phosphabenzene of the formula I as set forth in claim 5 bonded via a further bridge W.

25

8. A bidentate phosphabenzene of the formula IIa

30



where the radicals R^1 to R^6 are identical or different and are as defined in claim 5 for the radicals R^1 to R^5 and where W' is a 2,2'-, 4,4'- or 3,3'-biphenyldiyl group, a 2,2'-, 4,4'- or 3,3'-(diphenyl ether)-diyl group, a 2,2'-, 4,4'- or 3,3'-diphenylmethane-diyl group, a 2,2'-, 4,4'- or 3,3'-diphenylethane-diyl group or a 2,2'-, 4,4'- or 3,3'-diphenylpropane-diyl group or a ferrocenediyl group which in each case is linked to the two phosphabenzene groups in the ortho or meta position relative to the phosphorus atom via a covalent bond, an oxa group and/or a C_1 - C_4 -alkylene group, in particular a methylene group, where the biphenyl, diphenyl ether or C_1 - C_3 -diphenylalkane group is unsubstituted or substituted by from 1 to 4 identical or different

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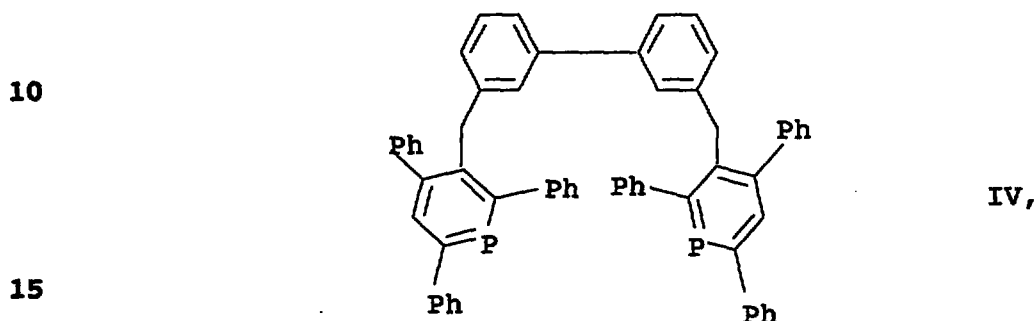


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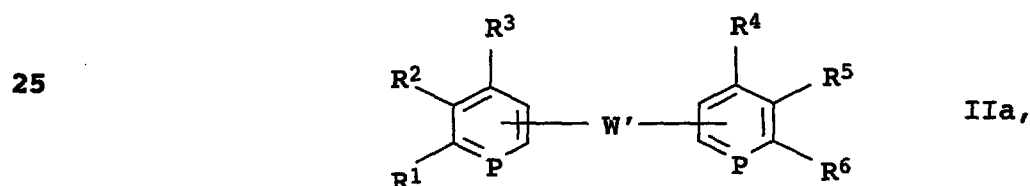
C₁-C₄-alkyl groups, and where the ortho or meta positions not used for the bridge are substituted by radicals R¹ to R⁵ as in claim 5.

- 5 9. A bidentate phosphabenzene as claimed in claim 8 having the formula IV



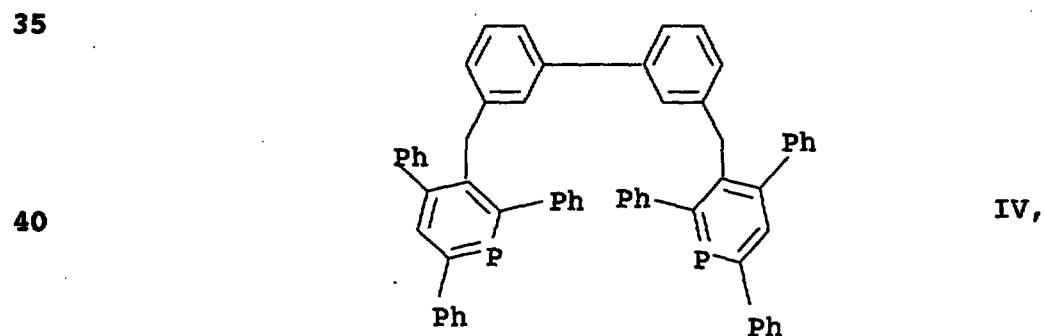
where Ph is the phenyl group.

- 20 10. A process as claimed in claim 1, wherein the ligands used are a bidentate phosphabenzene of the formula IIa



- 30 where R¹ to R⁶ and W' are as defined in claim 8.

11. A process as claimed in claim 1, wherein the ligand used is the bidentate phosphabenzene of the formula IV



- 45 12. A catalyst of the formula III

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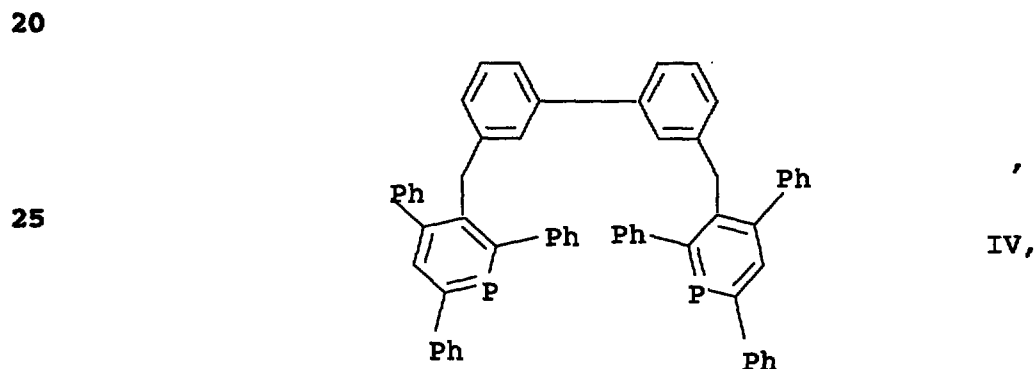
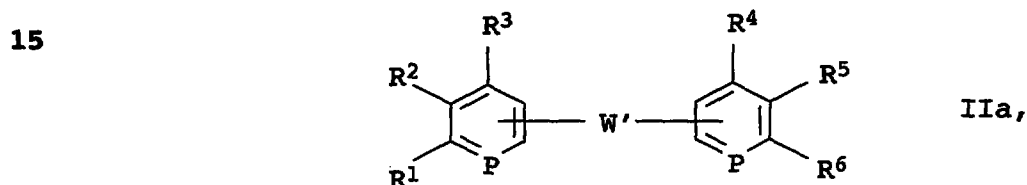
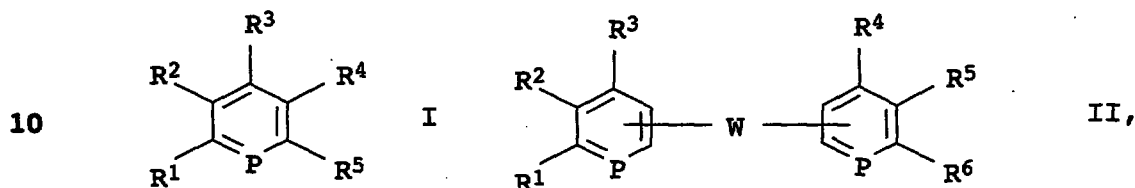




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M(L)_n(CO)_m III,THIS SHEET HAS BEEN
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- 5 where M is at least one central atom of an element of transition group VIII of the Periodic Table of the Elements, L is at least one ligand of the formula I or II or IIa or IV



- 25
- 30 where R¹-R⁶, W and W' are as defined in claims 5, 7 and 8, n and m are each at least 1 and where further radicals such as hydrido, alkyl or acyl radicals may be additionally present in the complex.

- 35
13. A catalyst as claimed in claim 12 which is prepared in situ in a hydroformylation or carbonylation reaction.
- 40 14. A process for preparing bis-3,3'-(3-(2,4,6-triphenyl)phosphabenzene)-1,1'-biphenyl of the formula IV

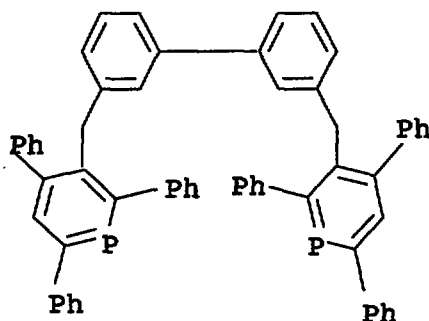
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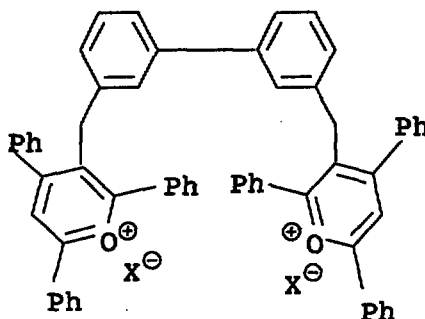


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IV,

which comprises reacting the pyrylium salt of the formula V



V,

where $X^{\ominus}$ is the equivalent of one anion, with phosphine in the temperature range from room temperature to 150°C in the presence of a catalytic amount of acid at elevated pressure in the presence or absence of a solvent in a pressure vessel.

15. A process as claimed in claim 14, wherein a phosphine partial pressure of from 0.5 to 50 bar is set in the reactor during the reaction.
16. A process as claimed in claim 14 or 15, wherein the phosphine is brought into contact with the pyrylium salt V at room temperature, this mixture is subsequently heated to above 100°C and after reaching this temperature the phosphine partial pressure in the pressure vessel is held essentially at from 0.5 to 50 bar during the reaction by passing in additional phosphine.
17. 2,4-Diphenyl-6-(2-naphthyl)phosphabenzene.
18. Bis-3,3'-(3-(2,4,6-triphenyl)phosphabenzene)-1,1'-biphenyl of the formula

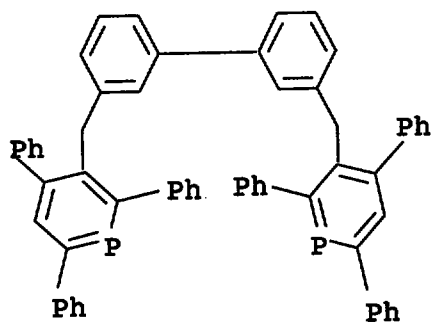
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