

Bisphosphites having 2,4-dimethylphenyl units and use thereof as ligands in hydroformylation

5 The invention relates to bisphosphites having 2,4-dimethylphenyl units and a method for the preparation thereof. Furthermore, the invention relates to the use of the compounds as ligands in a ligand-metal complex. The compound, and also the complex, may be used as a catalytically active composition in hydroformylation reactions.

10 Phosphorus-containing compounds, as ligands, play a crucial role in a multitude of reactions. Said compounds include phosphite ligands, i.e., compounds comprising P-O bonds, used in hydrogenation, hydrocyanation and especially hydroformylation.

The reactions between olefin compounds, carbon monoxide and hydrogen in the presence of a catalyst to give the aldehydes comprising one additional carbon atom are known as hydroformylation or oxo synthesis. In these reactions, compounds of the transition metals of group VIII of the Periodic Table of the Elements are frequently employed as catalysts. Known ligands include, for example, compounds of the phosphine, phosphite and phosphonite classes each comprising trivalent phosphorus P^{III}. A good overview of the status of hydroformylation of olefins is found in R. Franke, D. Selent, A. Börner, "Applied Hydroformylation", Chem. Rev., 2012, DOI:10.1021/cr3001803.

The literature discloses the synthesis of symmetric bisphosphites, as disclosed in US 4,769,498 for example, and the use thereof in catalytically active transition metal-containing compositions for the hydroformylation of unsaturated compounds.

In US 4,769,498, and also in US 5,723,641, preferably symmetric bisphosphites are prepared and used as ligands for hydroformylation. The symmetric bisphosphite ligands used in the hydroformylation are prepared at low temperatures. Adherence to these low temperatures is absolutely necessary since according to these US documents higher temperatures would lead to rearrangements and ultimately to asymmetric bisphosphites.

One of the best catalysts at present for the hydroformylation of olefins is to use an asymmetrical bisphosphite as ligand. 4,8-di-tert-butyl-2,10-dimethoxy-6-((3,3',5,5'-tetramethyl-2'-((2,4,8,10-tetramethyldibenzo[d,f][1,3,2]dioxaphosphepin-6-yl)oxy)-[1,1'-biphenyl]-2-yl)oxy)dibenzo[d,f][1,3,2] dioxaphosphepine. This is characterized by a very good yield in combination with very good regioselectivity.

However, this ligand is very expensive to prepare due to its many synthetic stages. Since the price of ligands has an essential influence of the overall cost-effectiveness of a method, it is

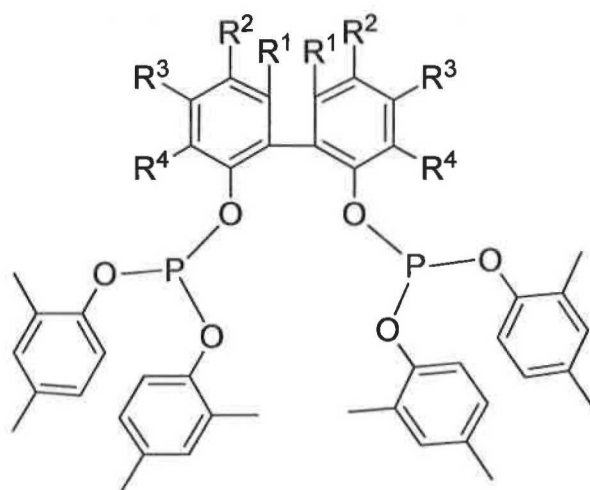
desirable to find alternative ligands with comparably good properties (yield and regioselectivity) but which are more cost-effective in terms of their preparation.

The technical object of the invention is the provision of a novel ligand which does not have the above-detailed disadvantages from the prior art in the hydroformylation of unsaturated compounds, but instead has the following properties:

- 1) a good activity/yield,
- 2) a high n-regioselectivity with respect to hydroformylation,
- 3) comparatively favourable preparation.

The object is achieved by a compound according to Claim 1.

Compound of the formula (I):



(I)

where

R^2 , R^3 , R^4 are selected from: -H, -(C₁-C₁₂)-alkyl, -O-(C₁-C₁₂)-alkyl,

wherein the alkyl groups mentioned may be substituted as follows:

substituted -(C₁-C₁₂)-alkyl groups and substituted -(C₁-C₁₂)-alkoxy groups, depending on their chain length, may have one or more substituents; the substituents are mutually independently selected from -(C₃-C₁₂)-cycloalkyl, -(C₃-C₁₂)-heterocycloalkyl, -(C₆-C₂₀)-aryl, fluorine, chlorine, cyano, formyl, acyl or alkoxycarbonyl.

In the context of the invention, the expression "-(C₁-C₁₂)-alkyl" encompasses straight-chain and branched alkyl groups. Preferably, these groups are unsubstituted straight-chain or branched -(C₁-C₈)-alkyl groups and most preferably -(C₁-C₆)-alkyl groups. Examples of -(C₁-C₁₂)-alkyl groups are especially methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, 2-pentyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 1,1-dimethylpropyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl, 2-hexyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-

dimethylbutyl, 2,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethylbutyl, 1-ethyl-2-methylpropyl, n-heptyl, 2-heptyl, 3-heptyl, 2-ethylpentyl, 1-propylbutyl, n-octyl, 2-ethylhexyl, 2-propylheptyl, nonyl, decyl.

- 5 The elucidations relating to the expression " $-(C_1-C_{12})$ -alkyl" also apply to the alkyl groups in $-O-(C_1-C_{12})$ -alkyl, i.e. in $-(C_1-C_{12})$ -alkoxy. Preferably, these groups are unsubstituted straight-chain or branched $-(C_1-C_6)$ -alkoxy groups.

- 10 Substituted $-(C_1-C_{12})$ -alkyl groups and substituted $-(C_1-C_{12})$ -alkoxy groups, depending on their chain length, may have one or more substituents; the substituents are mutually independently selected from $-(C_3-C_{12})$ -cycloalkyl, $-(C_3-C_{12})$ -heterocycloalkyl, $-(C_6-C_{20})$ -aryl, fluorine, chlorine, cyano, formyl, acyl or alkoxycarbonyl.

- 15 In one embodiment, R^2 , R^3 , R^4 are selected from: -H, -Me, -tBu, -OMe, -iPr.

In one embodiment, R^2 , R^4 are selected from: -Me, -tBu, -OMe, -iPr.

In one embodiment, R^2 , R^4 are selected from: -Me, -tBu, -OMe.

- 20 In one embodiment, R^2 is selected from: -Me, -tBu, -OMe.

In one embodiment, R^2 is selected from: -tBu, -OMe.

- 25 In one embodiment, R^2 is selected from: -Me, -OMe.

In one embodiment, R^2 is -OMe.

In one embodiment, R^3 is -H.

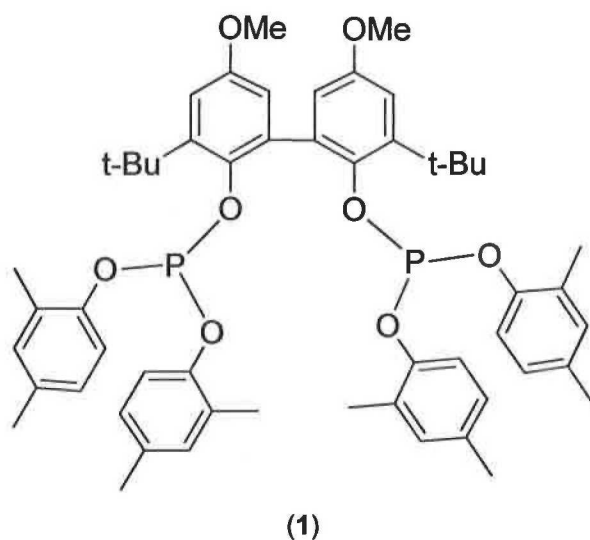
- 30 In one embodiment, R^4 is selected from: -Me, -tBu, -OMe.

In one embodiment, R^4 is selected from: -tBu, -OMe.

- 35 In one embodiment, R^4 is selected from: -Me, -tBu.

In one embodiment, R^4 is -tBu.

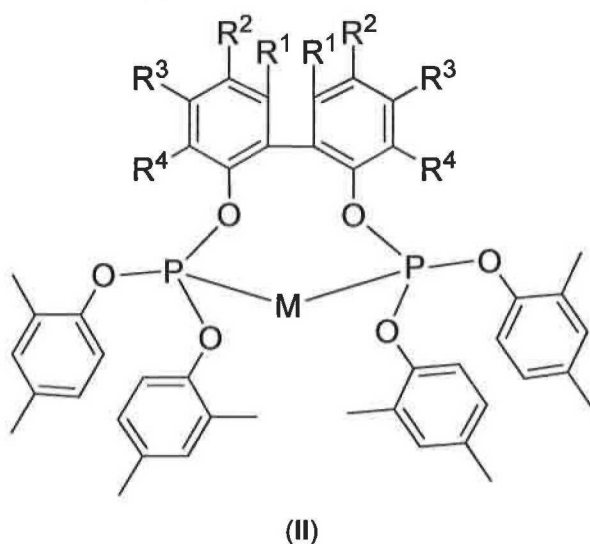
In one embodiment, the compound has the formula (1):



As well as the compounds, also claimed are complexes comprising the compound.

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Complex according to the formula (II):



10 where

R^2 , R^3 , R^4 are selected from: -H, -(C₁-C₁₂)-alkyl, -O-(C₁-C₁₂)-alkyl,

wherein the alkyl groups mentioned may be substituted as follows:

substituted -(C₁-C₁₂)-alkyl groups and substituted -(C₁-C₁₂)-alkoxy groups, depending on their chain length, may have one or more substituents; the substituents are mutually independently selected from -(C₃-C₁₂)-cycloalkyl, -(C₃-C₁₂)-heterocycloalkyl, -(C₆-C₂₀)-aryl, fluorine, chlorine, cyano, formyl, acyl or alkoxycarbonyl;

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and M is selected from: Rh, Ru, Co, Ir.

In a preferred embodiment, M = Rh.

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In one embodiment, R^2 , R^3 , R^4 are selected from: -H, -Me, -tBu, -OMe, -iPr.

In one embodiment, R^2 , R^4 are selected from: -Me, -tBu, -OMe, -iPr.

5 In one embodiment, R^2 , R^4 are selected from: -Me, -tBu, -OMe.

In one embodiment, R^2 is selected from: -Me, -tBu, -OMe.

In one embodiment, R^2 is selected from: -tBu, -OMe.

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In one embodiment, R^2 is selected from: -Me, -OMe.

In one embodiment, R^2 is -OMe.

15 In one embodiment, R^3 is -H.

In one embodiment, R^4 is selected from: -Me, -tBu, -OMe.

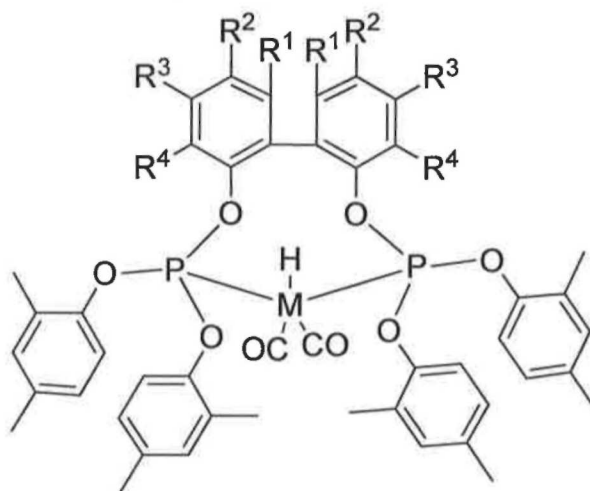
In one embodiment, R^4 is selected from: -tBu, -OMe.

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In one embodiment, R^4 is selected from: -Me, -tBu.

In one embodiment, R^4 is -tBu.

25 Complex according to the formula (III):



(III)

where

R^2 , R^3 , R^4 are selected from: -H, -(C₁-C₁₂)-alkyl, -O-(C₁-C₁₂)-alkyl,

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wherein the alkyl groups mentioned may be substituted as follows:

substituted $-(C_1-C_{12})$ -alkyl groups and substituted $-(C_1-C_{12})$ -alkoxy groups, depending on their chain length, may have one or more substituents; the substituents are mutually independently selected from $-(C_3-C_{12})$ -cycloalkyl, $-(C_3-C_{12})$ -heterocycloalkyl, $-(C_6-C_{20})$ -aryl, fluorine, chlorine, cyano, formyl, acyl or alkoxycarbonyl;

5 and M is selected from: Rh, Ru, Co, Ir.

In a preferred embodiment, M = Rh.

In one embodiment, R^2 , R^3 , R^4 are selected from: -H, -Me, -tBu, -OMe, -iPr.

10

In one embodiment, R^2 , R^4 are selected from: -Me, -tBu, -OMe, -iPr.

In one embodiment, R^2 , R^4 are selected from: -Me, -tBu, -OMe.

15 In one embodiment, R^2 is selected from: -Me, -tBu, -OMe.

In one embodiment, R^2 is selected from: -tBu, -OMe.

In one embodiment, R^2 is selected from: -Me, -OMe.

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In one embodiment, R^2 is -OMe.

In one embodiment, R^3 is -H.

25 In one embodiment, R^4 is selected from: -Me, -tBu, -OMe.

In one embodiment, R^4 is selected from: -tBu, -OMe.

In one embodiment, R^4 is selected from: -Me, -tBu.

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In one embodiment, R^4 is -tBu.

In addition to the compound and the complexes comprising the compound, the use of compound (I) and the complexes (II) or (III) for catalysis of a hydroformylation reaction is also claimed.

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Use of the compound (I) in a ligand-metal complex for catalysis of a hydroformylation reaction.

Use of the complex (II) for catalysis of a hydroformylation reaction.

40 Use of the complex (III) for catalysis of a hydroformylation reaction.

Furthermore, the hydroformylation process is also claimed in which the compound (I) or the complex (II) or (III) is used.

- 5 Process comprising the following process steps:
- a) initially charging an olefin,
 - b) adding an above-described complex,
 - or an above-described compound and a substance including a metal selected from: Rh, Ru, Co, Ir,
 - c) feeding in H₂ and CO,
 - 10 d) heating the reaction mixture, wherein the olefin is converted to an aldehyde.

Process steps a) to c) can be carried out here in any desired sequence.

The compound may be used as a ligand in a ligand-metal complex.

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An excess of ligands can also be used in this case and each ligand is not necessarily present bound in the form of a ligand-metal complex but is present as free ligand in the reaction mixture.

The reaction is conducted under customary conditions.

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Preference is given to a temperature of 80°C to 160°C and a pressure of 1 to 300 bar.

Particular preference is given to a temperature of 100°C to 160°C and a pressure of 15 to 250 bar.

In a preferred embodiment, the metal is Rh.

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The reactants for the hydroformylation in the process of the invention are olefins or mixtures of olefins, especially monoolefins having 2 to 24, preferably 3 to 16 and particularly preferably 3 to 12 carbon atoms, having terminal or internal C-C double bonds, for example 1-propene, 1-butene, 2-butene, 1- or 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1-, 2- or 3-hexene, the C₆ olefin mixture obtained in the dimerization of propene (dipropene), heptenes, 2- or 3-methyl-1-hexenes, octenes, 2-methylheptenes, 3-methylheptenes, 5-methyl-2-heptene, 6-methyl-2-heptene, 2-ethyl-1-hexene, the C₈ olefin mixture obtained in the dimerization of butenes (di-n-butene, diisobutene), nonenes, 2- or 3-methyloctenes, the C₉ olefin mixture obtained in the trimerization of propene (tripropene), decenes, 2-ethyl-1-octene, dodecenes, the C₁₂ olefin mixture obtained in the tetramerization of propene or the trimerization of butenes (tetrapropene or tributene), tetradecenes, hexadecenes, the C₁₆ olefin mixture obtained in the tetramerization of butenes (tetrabutene), and olefin mixtures prepared by cooligomerization of olefins having different numbers of carbon atoms (preferably 2 to 4).

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The process according to the invention using the ligands according to the invention can be used to hydroformylate α -olefins, terminally branched, internal and internally branched olefins. The high yield of terminal hydroformylated olefins is notable in this case, even when only a low proportion of olefins having terminal double bonds was present in the reactant.

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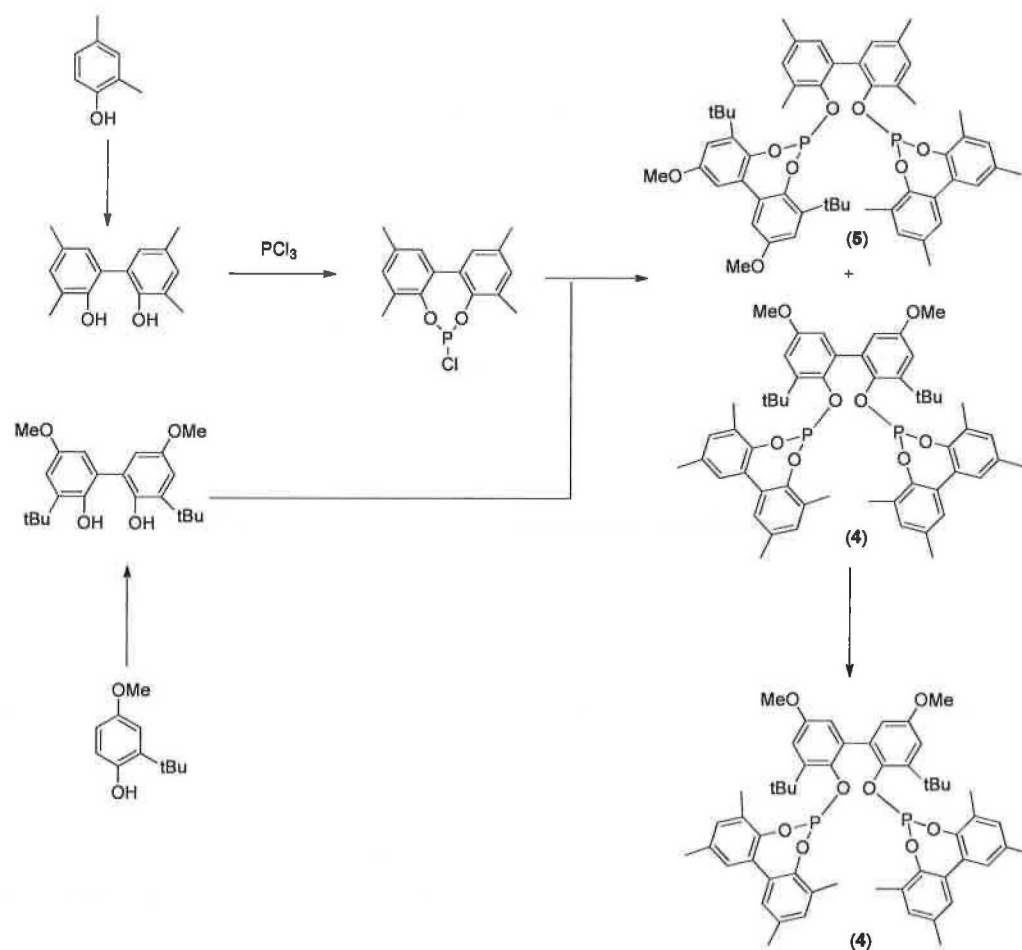
The invention is to be illustrated in greater detail hereinafter by working examples.

General procedure specifications

- 10 All the preparations which follow were carried out under protective gas using standard Schlenk techniques. The solvents were dried over suitable desiccants before use (Purification of Laboratory Chemicals, W. L. F. Armarego (Author), Christina Chai (Author), Butterworth Heinemann (Elsevier), 6th edition, Oxford 2009).
- 15 Phosphorus trichloride (Aldrich) was distilled under argon before use. All preparative operations were effected in baked-out vessels. The products were characterized by means of NMR spectroscopy. Chemical shifts (δ) are reported in ppm. The ^{31}P NMR signals were referenced as follows: $\text{SR}_{31\text{P}} = \text{SR}_{1\text{H}} * (\text{BF}_{31\text{P}} / \text{BF}_{1\text{H}}) = \text{SR}_{1\text{H}} * 0.4048$ (Robin K. Harris, Edwin D. Becker, Sonia M. Cabral de Menezes, Robin Goodfellow, and Pierre Granger, Pure Appl. Chem., 2001, 73, 1795-1818; Robin K. Harris, Edwin D. Becker, Sonia M. Cabral de Menezes, Pierre Granger, Roy E. Hoffman and Kurt W. Zilm, Pure Appl. Chem., 2008, 80, 59-84).
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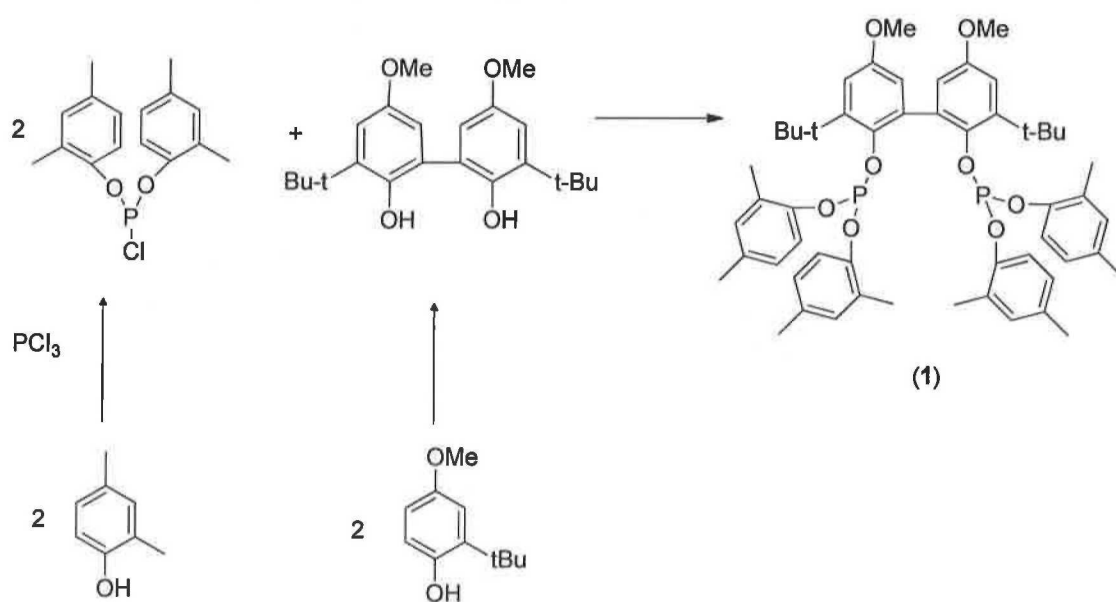
- The recording of nuclear resonance spectra was effected on Bruker Avance 300 or Bruker Avance 400, gas chromatography analysis on Agilent GC 7890A, elemental analysis on Leco TruSpec
- 25 CHNS and Varian ICP-OES 715, and ESI-TOF mass spectrometry on Thermo Electron Finnigan MAT 95-XP and Agilent 6890 N/5973 instruments.

General reaction equation (comparative ligands)



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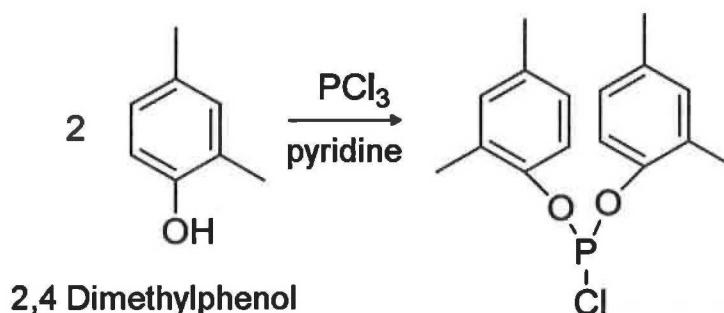
General reaction equation (inventive ligand)



As is clear by means of comparing the two reaction schemes, fewer synthetic stages are required for compound (1) than for compound (4) or (5). In the preparation of compound (1), the 2,4-dimethylphenol does not have to be first coupled to a biphenol, but can be reacted directly with PCl_3 to give the corresponding chlorophosphite.

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Preparation of bis(2,4-dimethylphenyl)chlorophosphite



- 10 50 g of PCl_3 (0.363 mol) and 86 g of pyridine (1.076 mol) in 380 ml of dry toluene were initially charged in a secured 1200 ml glass reactor provided with a dropping funnel. The milky yellow PCl_3 /pyridine solution was cooled down to -7°C with stirring. 86 ml of 2,4-dimethylphenol (0.720 mol) were then added to the dropping funnel and dissolved in 380 ml of dry toluene. To carry out the reaction, the phenol/toluene solution was added dropwise slowly and steadily to the
- 15 PCl_3 /pyridine solution. The reaction mixture was brought to room temperature overnight with stirring.

For workup, the hydrochloride formed was filtered off and rinsed with 60 ml of dry toluene and the resulting mother liquor was concentrated to dryness under reduced pressure.

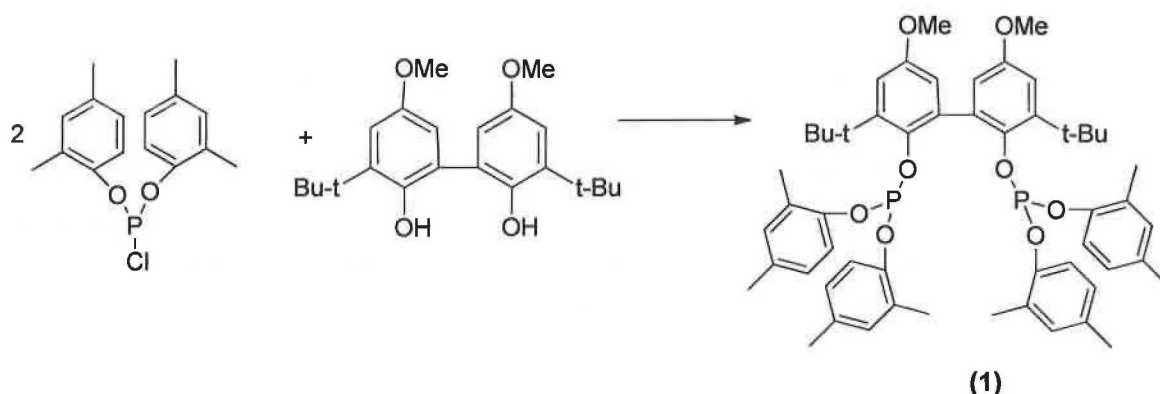
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- For further work-up, the crude solution was distilled. For this purpose, a pear-shaped flask was filled with the crude solution, on which flask a short distillation apparatus without cooling jacket was placed. The thermometer was placed at the upper opening, and at the other end a spider with four further pear-shaped flasks was attached. Subsequently, this apparatus was attached to
- 25 a cold trap and from there to the high vacuum pump. The pear-shaped flask with the crude ligand to be distilled was heated by means of an oil bath. Firstly, the forerun was removed at a top temperature of $25\text{--}30^\circ\text{C}$. The spider was then further rotated and the main run was removed at a top temperature of 140°C . When no more drops appeared in the main run, the distillation was stopped, the pump was shut down and the main run in the relevant pear-shaped flask was
- 30 removed, sealed and analysed.

Result:

Total mass: 56.7 g (46% yield)

5 Preparation of 3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyltetrakis(2,4-dimethylphenyl)bis(phosphite)



10 In a 1000 mL Schlenk flask, 260 ml of dry acetonitrile were added to 51.86 g (0.153 mol) of bis(2,4-dimethylphenyl)chlorophosphite at room temperature with stirring and the chlorophosphite was dissolved.

15 In a second 250 ml Schlenk flask, 12.4 ml (0.153 mol) of pyridine and 155 ml of dry acetonitrile were added to 20.1 g (0.056 mol) of 3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diol. The chlorophosphite solution in the Schlenk flask was then cooled to 0°C. The biphenol/pyridine solution was then slowly added dropwise with vigorous stirring. The reaction mixture was maintained at this temperature for ca. 3 h and then very slowly brought to room temperature overnight.

20 The suspension was then filtered off, washed thoroughly with 30 ml of acetonitrile and dried.

Result:

Mass: 44.01 g (yield: 85%)

25 **Reduction of chlorine level**

In order to decrease the chlorine content in this crude ligand, this ligand was purified.

The chlorine contents reported are meant as total chlorine contents.

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The total chlorine content is determined according to Wickbold: sample preparation according to DIN 51408 and analysis by ion chromatography according to DIN EN ISO 10304.

5.15 g of 3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyltetrakis(2,4-dimethylphenyl)bis(phosphite) in a first 250 ml Schlenk flask with 15 ml of degassed toluene and 5 ml of pyridine at 100°C were stirred until the 3,3'-di-tert-butyl-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyltetrakis(2,4-dimethylphenyl)bis(phosphate) had dissolved. After all had dissolved, the temperature was maintained for a further 15 min and then cooled to 90°C.

Meanwhile, 100 ml of heptane and 5 ml of pyridine were placed in a second 250 ml Schlenk flask and this solution was cooled down to 0°C. Subsequently, the solution from the first Schlenk flask was added via a frit to the second Schlenk flask with the cold heptane/pyridine solution and stirred at 0°C for 3 h. No precipitate was observed. By means of a vacuum pump, the solvent mixture was drawn off until the solid had precipitated and was dried. After that, 50 ml of acetonitrile was given onto the dried solid. This suspension has been stirred for two days at room temperature, fritted and dried by means of a vacuum pump.

Result:

Mass: 3.7 g

Chlorine determination: 20/20 ppm

Procedure for the catalysis experiments

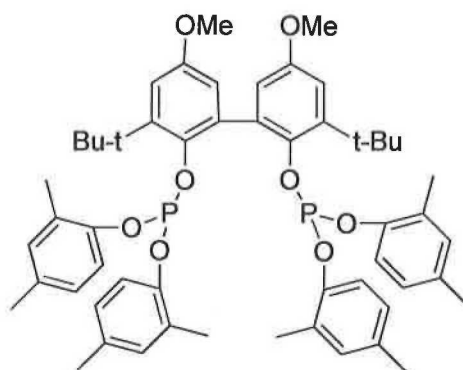
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Experimental description - general

In a 100 ml autoclave from Parr Instruments, cis-2-butene was hydroformylated with the aid of synthesis gas pressure ($\text{CO}/\text{H}_2 = 1:1$ (% by vol.)). As the precursor, $\text{Rh}(\text{acac})(\text{CO})_2$ was initially charged in toluene. The ligand was used in a molar excess of 4:1 relative to rhodium. Tinuvin 770DF was used as stabilizer in a molar ratio to the ligand of ca. 1:1. In addition, as GC standard, ca. 0.5 g of tetraisopropylbenzene (TIPB) was added. About 6 g of reactant were metered in after the reaction temperature envisaged had been attained.

During the reaction, the pressure was kept constant via synthesis gas regulation with a mass flow meter. The stirrer speed was 1200 min^{-1} . Samples were taken from the reaction mixture after 12 hours. The results of the experiments are summarized in Table 1.

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(1)

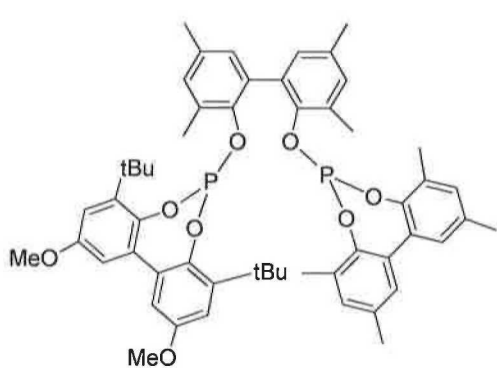
5 Experimental description - specific

In a 100 ml autoclave from Parr Instruments, 5.6 g of cis-2-butene were hydroformylated at 120°C and 20 bar synthesis gas pressure. As the precursor, 0.0056 g of Rh(acac)(CO)₂ was initially charged in 48.8 g of toluene. As the ligand, 0.0779 g of ligand was used in the catalyst mixture solution. 0.0416 g of Tinuvin 770DF was added as the organic amine, and a GC standard. The reactant was metered in after attainment of the reaction temperature envisaged.

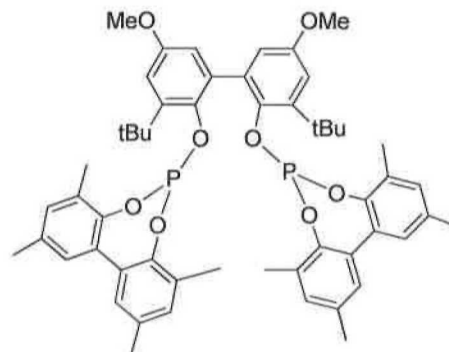
During the reaction, the pressure was kept constant via synthesis gas regulation with a mass flow meter. Samples were taken from the reaction mixture after 12 hours.

Furthermore, compound (5), its symmetrical isomer compound (4) and compound (6) were tested under corresponding conditions. These compounds were prepared according to WO 2014/056733 A1, EP 2 907 819 A1 and WO 2007/109005A2 respectively.

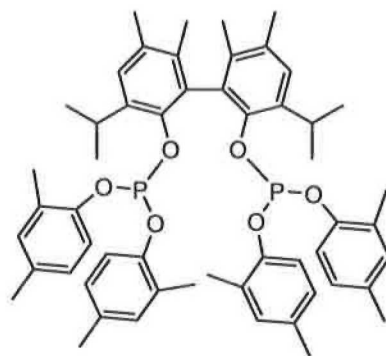
In Table 1 the hydroformylation results of cis-2-butene at 20 bar synthesis gas pressure are shown.



(5)



(4)



(6)

5 Table 1:

Entry	Ligand	Aldehyde yield in [%]	Regioselectivity n-pentanal in %
1	5	95	94
2	4	66	90
3	1*	95	98
4	6	79	98

* inventive compound

10 Definition of the selectivity:

in hydroformylation, there is the n/iso selectivity (n/iso = the ratio of linear aldehyde (= n) to branched (= iso) aldehyde). In this case, the n-pentanal regioselectivity signifies that this amount of linear product was formed. The remaining percentages then correspond to the branched isomer. Rate of selectivity was estimated by gas chromatography.

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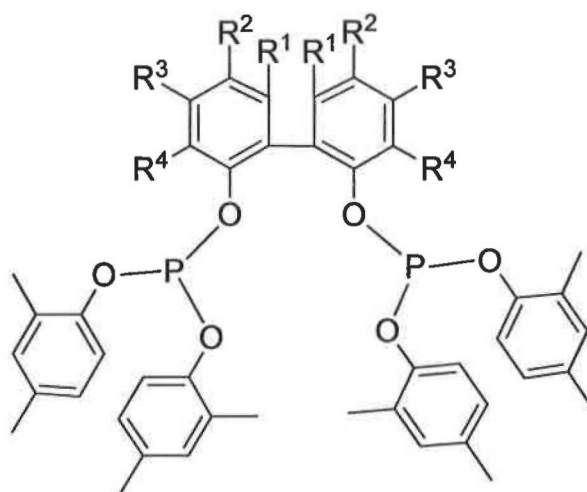
Ligands (**5**) (entry 1) and (**6**) (entry 4) have a very good n-pentanal regioselectivity and achieve good or at least moderate yields of aldehydes. Isomer (**4**) (entry 2) has a lower n-pentanal selectivity of only 90% and distinctly lower activities, i.e. yields. The best selectivity of 98% is achieved with the ligand (**1**) according to the invention. Beyond that, ligand (**1**) has an excellent

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yield of 95 %. The experiments carried out demonstrate that the objects presented are achieved by the compound (**1**) according to the invention.

Claims

1. Compound of the formula (I):



(I)

where

R^2 , R^3 , R^4 are selected from: -H, $-(C_1-C_{12})$ -alkyl, $-O-(C_1-C_{12})$ -alkyl,

wherein the alkyl groups mentioned may be substituted as follows:

substituted $-(C_1-C_{12})$ -alkyl groups and substituted $-(C_1-C_{12})$ -alkoxy groups, depending on their chain length, may have one or more substituents; the substituents are mutually independently selected from $-(C_3-C_{12})$ -cycloalkyl, $-(C_3-C_{12})$ -heterocycloalkyl, $-(C_6-C_{20})$ -aryl, fluorine, chlorine, cyano, formyl, acyl or alkoxycarbonyl.

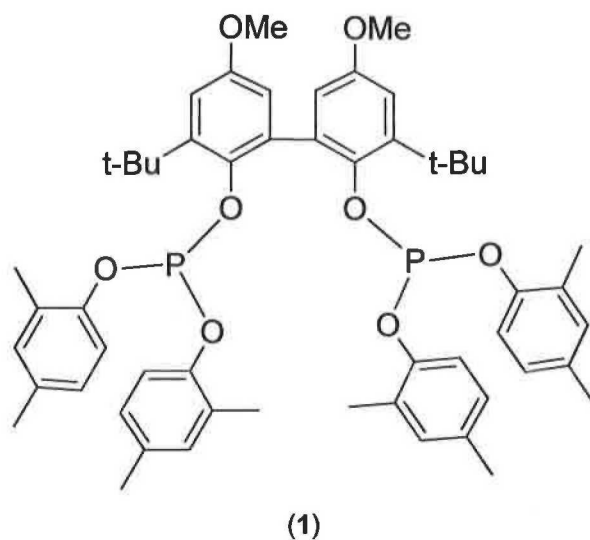
2. Compound according to Claim 1,
where R^2 is selected from: -Me, -tBu, -OMe.

3. Compound according to either of Claims 1 and 2,
where R^2 is -OMe.

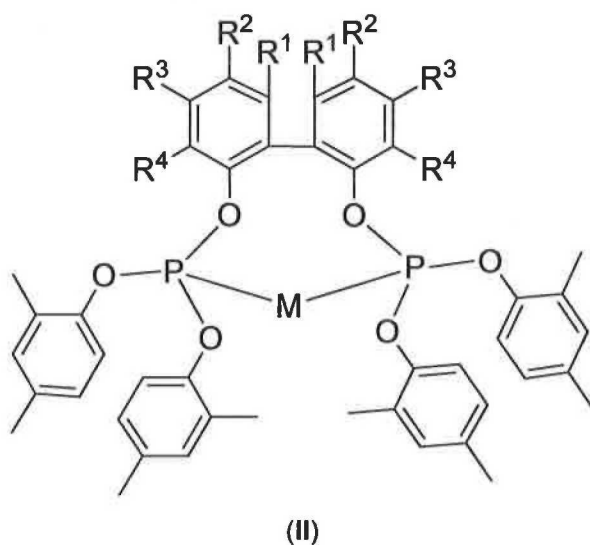
4. Compound according to any of Claims 1 to 3,
where R^4 is selected from: -Me, -tBu, -OMe.

5. Compound according to any of Claims 1 to 4,
where R^4 is -tBu.

6. Compound according to any of Claims 1 to 5,
according to the formula (1):



7. Complex according to the formula (II):



where

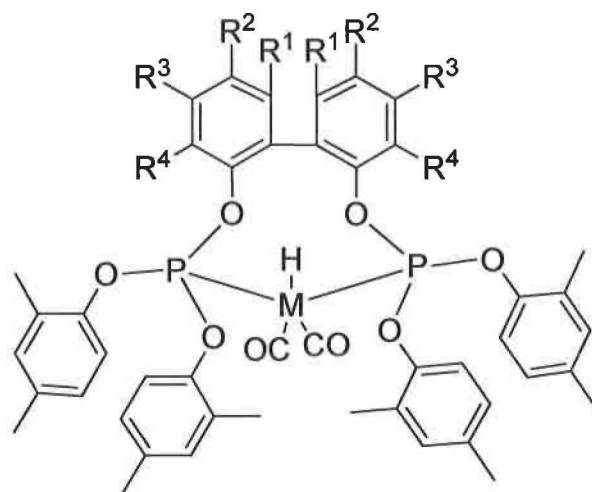
R^2 , R^3 , R^4 are selected from: -H, $-(C_1-C_{12})$ -alkyl, $-O-(C_1-C_{12})$ -alkyl,

10 wherein the alkyl groups mentioned may be substituted as follows:

substituted $-(C_1-C_{12})$ -alkyl groups and substituted $-(C_1-C_{12})$ -alkoxy groups, depending on their chain length, may have one or more substituents; the substituents are mutually independently selected from $-(C_3-C_{12})$ -cycloalkyl, $-(C_3-C_{12})$ -heterocycloalkyl, $-(C_6-C_{20})$ -aryl, fluorine, chlorine, cyano, formyl, acyl or alkoxycarbonyl;

15 and M is selected from: Rh, Ru, Co, Ir.

8. Complex according to the formula (III):



(III)

where

R^2 , R^3 , R^4 are selected from: -H, -(C₁-C₁₂)-alkyl, -O-(C₁-C₁₂)-alkyl,

5 wherein the alkyl groups mentioned may be substituted as follows:

substituted -(C₁-C₁₂)-alkyl groups and substituted -(C₁-C₁₂)-alkoxy groups, depending on their chain length, may have one or more substituents; the substituents are mutually independently selected from -(C₃-C₁₂)-cycloalkyl, -(C₃-C₁₂)-heterocycloalkyl, -(C₆-C₂₀)-aryl, fluorine, chlorine, cyano, formyl, acyl or alkoxycarbonyl;

10 and M is selected from: Rh, Ru, Co, Ir.

9. Complex according to Claim 7 or 8,

where M = Rh.

15 10. Use of a compound according to Claims 1 to 6,

in a ligand-metal complex for catalysis of a hydroformylation reaction.

11. Process comprising the following process steps:

a) initially charging an olefin,

20 b) adding a complex according to any of Claims 7 to 9,

or a compound according to any of Claims 1 to 6 and a substance including a metal selected from: Rh, Ru, Co, Ir,

c) feeding in H₂ and CO,

d) heating the reaction mixture, wherein the olefin is converted to an aldehyde.