

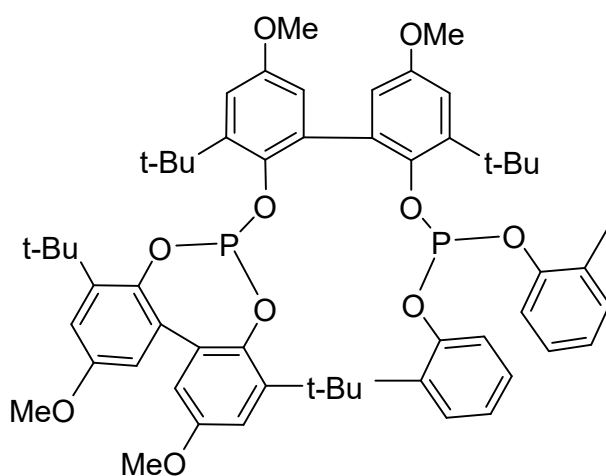
Diphosphites having an open, 2,4-methylated outer unit

The invention relates to diphosphites having an open, 2,4-methylated outer unit and use thereof
5 in hydroformylation.

Phosphorus-containing compounds play a crucial role as ligands in a multitude of reactions, e.g. in hydrogenation, in hydrocyanation and also in hydroformylation.

10 The reactions between olefin compounds, carbon monoxide and hydrogen in the presence of a catalyst to give the aldehydes with one carbon atom more are known as hydroformylation or the oxo process. 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 are, for example, compounds from the phosphine, phosphite and phosphonite classes, each containing trivalent
15 phosphorus P^{III}. A good overview of the situation on the hydroformylation of olefins can be found in R. Franke, D. Selent, A. Börner, "Applied Hydroformylation", Chem. Rev., 2012, DOI:10.1021/cr3001803.

The following compound is shown in EP 0213639 A2 on page 98 in example 10:



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(2).

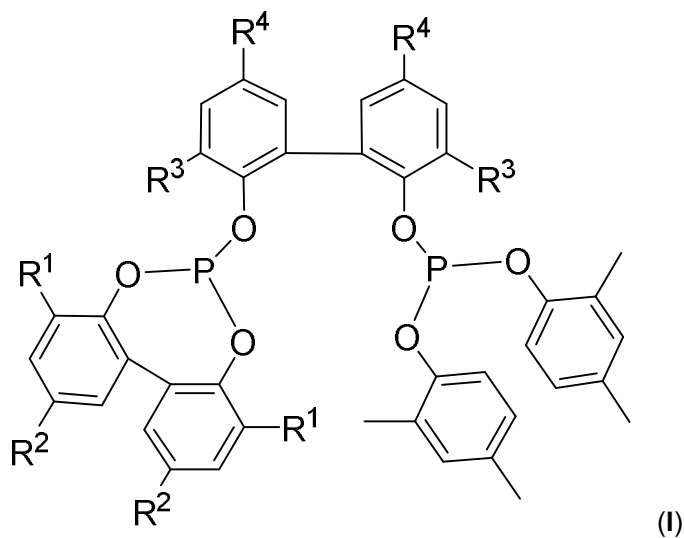
The compound (2) is used here as ligand in the hydroformylation of 1-butene.

The technical object of the invention is to provide novel ligands that exhibit increased n/iso
25 selectivity in the hydroformylation of olefins compared with the ligand known from the prior art.

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

Compound of the structure (I):

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where R^1 , R^2 , R^3 , R^4 are selected from: -H, $-(C_1-C_{12})$ -alkyl, $-O-(C_1-C_{12})$ -alkyl.

5 In one embodiment, R^1 , R^3 are selected from: -H, $-(C_1-C_{12})$ -alkyl.

In one embodiment, R^1 , R^3 are $-(C_1-C_{12})$ -alkyl.

In one embodiment, R^1 , R^3 are $-tBu$.

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In one embodiment, R^1 , R^3 are the same radical.

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

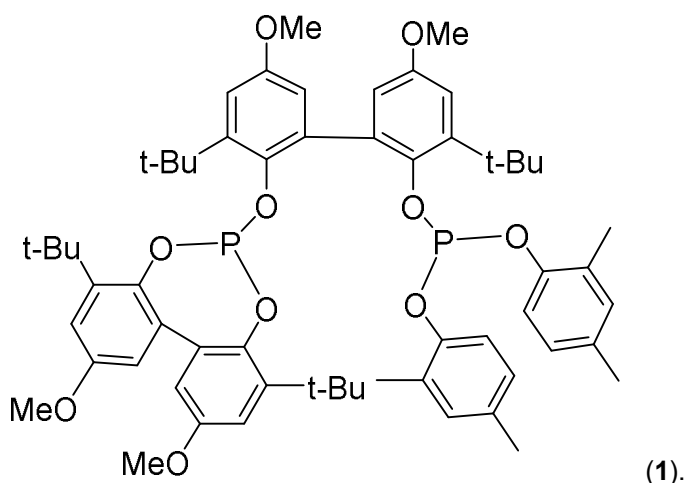
15 In one embodiment, R^2 , R^4 are $-O-(C_1-C_{12})$ -alkyl.

In one embodiment, R^2 , R^4 are $-OMe$.

In one embodiment, R^2 , R^4 are the same radical.

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In one embodiment, R^1 , R^2 , R^3 , R^4 are not all simultaneously $-CH_3$.



As well as the compound per se, the use thereof for catalysis of a hydroformylation reaction is also claimed.

Use of a compound described above in a ligand-metal complex for catalysis of a hydroformylation reaction.

Additionally claimed is a process in which the above-described compound is used as a ligand.

Process comprising the process steps of:

- initially charging an olefin,
- adding an above-described compound and a substance containing a metal selected from: Rh, Ru, Co, Ir,
- supplying H₂ and CO,
- heating the reaction mixture from steps a) to c), with conversion of the olefin to an aldehyde.

In a preferred embodiment, the metal is Rh.

The ligands can also be used in excess here and it is not automatically the case that each ligand is present in bound form as a ligand-metal complex; it may instead be present in the reaction mixture as the free ligand.

The reaction is carried out under customary conditions.

Preference is given to a temperature of 80°C to 160°C and a pressure of 10 to 60 bar.

Particular preference is given to a temperature of 100°C to 140°C and a pressure of 20 to 50 bar.

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 more preferably 3 to 12 carbon

atoms, and 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 having different numbers of carbon atoms (preferably 2 to 4) produced by cooligomerization of olefins.

The process of the invention using the ligands of the invention can be used for the hydroformylation of α -olefins, terminally branched, internal and internally branched olefins.

The invention shall be illustrated in detail hereinbelow with reference to exemplary embodiments.

Work procedures

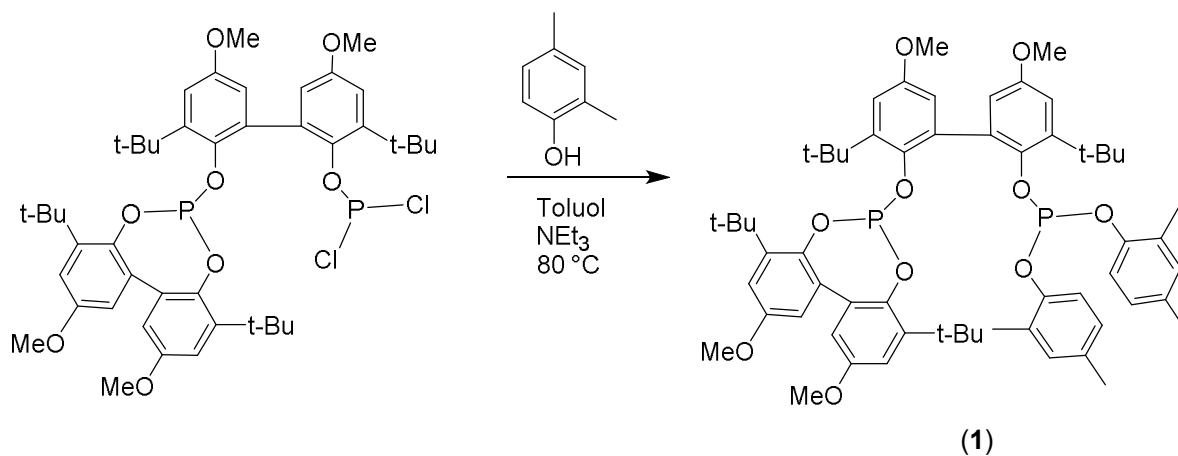
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General analysis

All the preparations that follow were carried out under inert gas using standard Schlenk techniques. The solvents were dried before use over suitable drying agents.

The products were characterized by NMR spectroscopy. Chemical shifts (δ) are reported in ppm.

25 The ³¹P NMR signals were referenced as follows: $SR^{31P} = SR^1H * (BF^{31P} / BF^1H) = SR^1H * 0.4048$.

Synthesis (1):

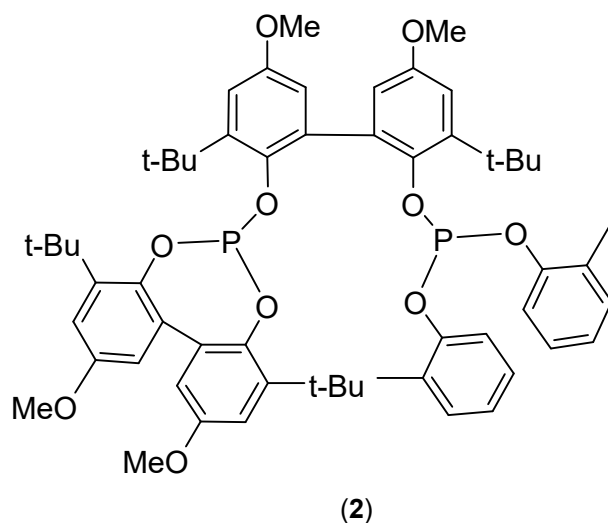
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In a glovebox, 9 g (0.01 mol) of diorganophosphite dichlorophosphite were weighed into a secured 250 ml Schlenk flask, then evacuated and dissolved in 75 mL of dried toluene. In a second secured 250 ml Schlenk flask, 2.5 g (0.02 mol) of 2,4-dimethylphenol and 3 mL (0.022 mol) of degassed triethylamine were dissolved in 50 mL of toluene. The chlorophosphite solution was added slowly and constantly at room temperature to the phenol-triethylamine solution over 1.5 h. The reaction mixture was stirred at room temperature overnight. The reaction mixture was heated to 80°C. After 18 hours, the reaction mixture was passed through a frit and the filtrate was concentrated at 40°C under oil pump vacuum. Subsequently, the solid was dried for 18 hours on an oil vacuum pump. The solid was then crashed and stirred in 50 mL of dried ACN. The precipitated white solid was then removed by frit.

Purity 96%, yield 48%.

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Synthesis (2) (comparative ligand)

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In a glovebox, 9 g (0.01 mol) of diorganophosphite dichlorophosphite were weighed into a secured 250 mL Schlenk flask, then evacuated and dissolved in 75 mL of dried toluene. In a second secured 250 mL Schlenk flask, 2.2 g (2.1 mL 0.02 mol) of 2-methylphenol were weighed out and dried at room temperature for 12 hours by means of an oil vacuum pump. 50 mL of dried toluene and 3 mL = 2.2 g (0.022 mol) of degassed triethylamine were added with stirring and dissolved. The dichlorophosphite was added at room temperature to the phenol-triethylamine solution over 1.5 hours. The reaction mixture was stirred at room temperature for 2 hours and then heated to 80°C. The reaction mixture was stirred at this temperature for 15 hours and then 3 times 1.5 mL (0.011 mol) of triethylamine were metered in and left to stir for a further 15 hours. The ammonium hydrochloride was removed by frit, washed with 1 x 10 mL of dried toluene and concentrated to dryness. The solid was dried at room temperature for 15 hours and stirred with 40 mL of degassed acetonitrile. The precipitated white solid was removed by frit, the Schlenk flask was post-rinsed with 2 times 10 mL of ACN and after drying introduced into a glove box. Yield 90%, purity: 95%.

15 Catalysis experiments

The hydroformylation was carried out in a 16 ml autoclave from HEL Group, Hertfordshire, United Kingdom, equipped with a pressure-retaining valve, gas flowmeter and sparging stirrer. The n-octene used as substrate (Oxeno GmbH, mixture of octene isomers of 1-octene: 3%; cis+trans-2-octene: 49%; cis+trans-3-octene: 29%; cis+trans-4-octene: 16%; structurally isomeric octenes: 3%) was heated under reflux for several hours over sodium and distilled under argon.

The reaction solutions for the experiments were prepared beforehand under an argon atmosphere. For this, 0.0021 g of $\text{Rh}(\text{acac})(\text{CO})_2$ and the corresponding amount of phosphite compound were weighed out and filled with 8.0 ml of toluene. The mass of toluene introduced in each case was determined for the GC analysis. 1.80 g of n-octene (16 mmol) was then added. The prepared solutions were then introduced into the autoclave, which was flushed three times with argon and three times with syngas (Linde; H_2 (99.999%): CO (99.997%) = 1:1). The autoclave was then heated to the desired temperature at an overall pressure of 10 bar with stirring (900 rpm). On reaching the reaction temperature, the syngas pressure was increased to 20 bar and the reaction carried out at constant pressure for 4 h. At the end of the reaction time, the autoclave was cooled to room temperature, depressurized while stirring and flushed with argon. 0.5 ml of each reaction mixture was removed at the end of the reaction, diluted with 4 ml of pentane and analysed by gas chromatography: HP 5890 Series II plus, PONA, 50 m x 0.2 mm x 0.5 μm . Residual olefin and aldehyde were quantitatively determined against the solvent toluene as internal standard.

Results of the catalysis experiments

Reaction conditions:

- 5 [Rh]: 120 ppm, L:Rh = 1:2, p: 20 bar, T: 120°C; t: 4 h

Table 1: Hydroformylation of n-octenes

Ligand	n/iso selectivity in %
1*	72
2	56

* inventive compound

- 10 Definition of selectivity:

In the hydroformylation there is n/iso selectivity, which is the ratio of linear aldehyde (= n) to branched aldehyde (= iso). The selectivity here in respect of the n-aldehyde signifies that this amount of linear product was formed. The remaining percentages then correspond to the branched isomer. Thus, at a regioselectivity of 50%, n-aldehyde and iso-aldehyde are formed in
15 equal proportions.

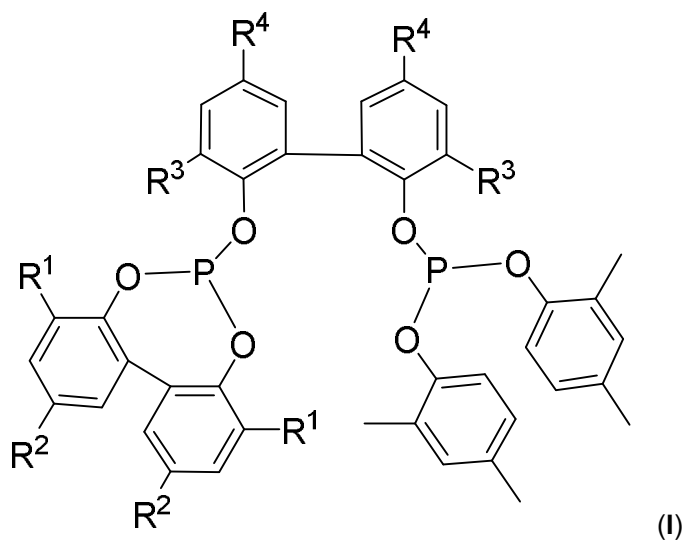
The compound of the invention (**1**) achieved an increase in n/iso selectivity compared with the comparative ligand (**2**).

- 20 The experiments carried out demonstrate that the stated object is achieved by the compound of the invention.

Claims

1. Compound of the structure (I):

5



where R^1 , R^2 , R^3 , R^4 are selected from: -H, -(C₁-C₁₂)-alkyl, -O-(C₁-C₁₂)-alkyl.

10 2. Compound according to Claim 1,
where R^1 , R^3 are selected from: -H, -(C₁-C₁₂)-alkyl.

3. Compound according to either of Claims 1 and 2,
where R^1 , R^3 are -(C₁-C₁₂)-alkyl.

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4. Compound according to any of Claims 1 to 3,
where R^1 , R^3 are the same radical.

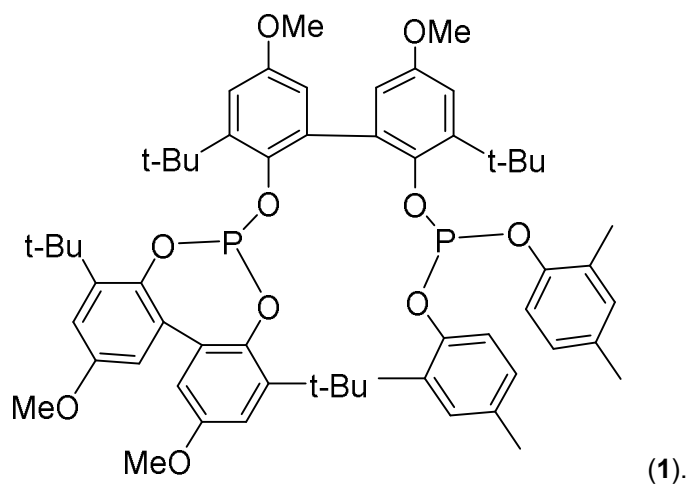
5. Compound according to any of Claims 1 to 4,
20 where R^2 , R^4 are selected from: -H, -O-(C₁-C₁₂) alkyl.

6. Compound according to any of Claims 1 to 5,
wherein R^2 , R^4 are -O-(C₁-C₁₂)-alkyl.

25 7. Compound according to any of Claims 1 to 6,
where R^2 , R^4 are the same radical.

8. Compound according to any of Claims 1 to 7,
where R^1 , R^2 , R^3 , R^4 are not all simultaneously -CH₃.

9. Compound according to any of Claims 1 to 8,
where the compound has the structure (1):



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10. Use of a compound according to any of Claims 1 to 9
in a ligand-metal complex for catalysis of a hydroformylation reaction.

11. Process comprising the process steps of:

- 10 a) initially charging an olefin,
b) adding a compound according to any of Claims 1 to 9 and a substance containing a metal selected from: Rh, Ru, Co, Ir,
c) supplying H₂ and CO,
d) heating the reaction mixture from steps a) to c), with conversion of the olefin to an aldehyde.

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