

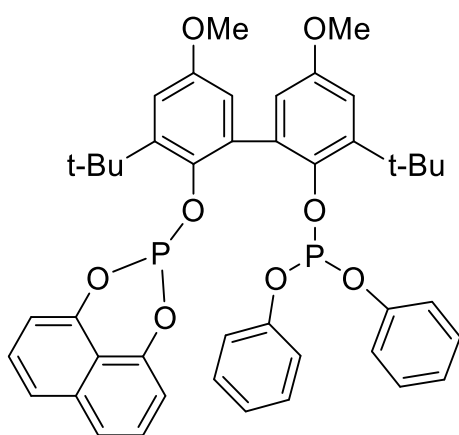
Bisphosphites with *tert*-butyl radicals on the central unit and substituted outer unit

The invention relates to bisphosphites with *tert*-butyl radicals on the central unit and substituted outer unit. Furthermore, the invention relates to the use of the bisphosphites in hydroformylation.

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

WO 02/00670 A1 describes bisphosphite compounds, metal complexes thereof and use of the compounds and complexes in olefin hydroformylation. Disclosed here, inter alia, is the compound (IIa):

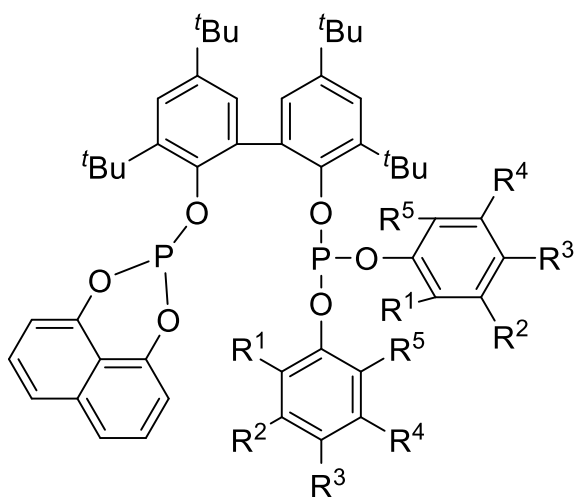


(IIa).

15 The technical object of the invention is to provide a compound with which a good yield can be achieved in the hydroformylation of olefins.

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

20 Compound of formula (I):



(I)

wherein R^1, R^2, R^3, R^4, R^5 are selected from: -H, -(C₁-C₄)-alkyl, -O-(C₁-C₄)-alkyl and at least one of the radicals R^1, R^2, R^3, R^4, R^5 is not -H.

In one embodiment, R^1, R^2, R^3, R^4, R^5 are selected from: -H, -CH₃, -CH₂-CH₃, -*tert*Bu, -O-CH₃.

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In one embodiment, at least two of the radicals R^1, R^2, R^3, R^4, R^5 are -H.

In one embodiment, at least three of the radicals R^1, R^2, R^3, R^4, R^5 are -H.

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In one embodiment, R^1, R^2, R^3, R^4, R^5 are selected from: -H, -CH₃.

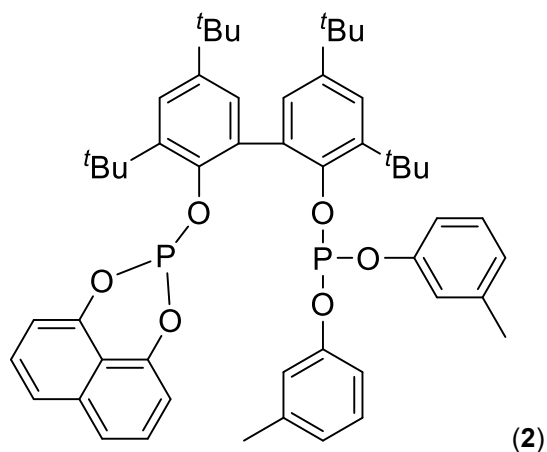
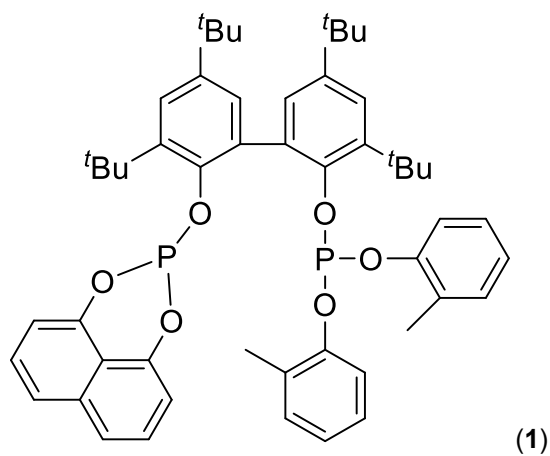
In one embodiment, R^1, R^2, R^3, R^4, R^5 are selected from: -H, -CH₂-CH₃.

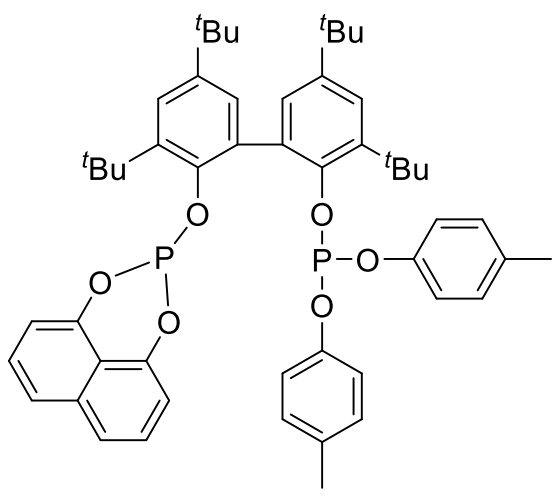
In one embodiment, R^1, R^2, R^3, R^4, R^5 are selected from: -H, -*tert*Bu.

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In one embodiment, R^1, R^2, R^3, R^4, R^5 are selected from: -H, -O-CH₃.

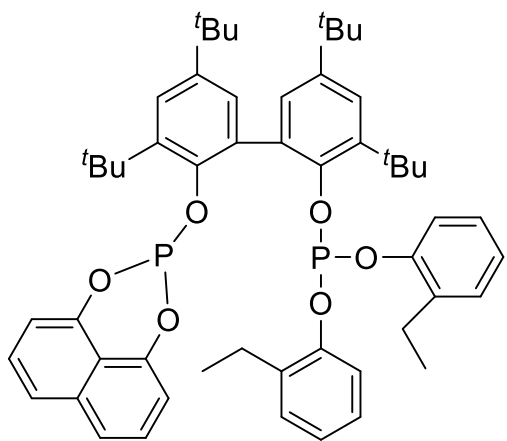
In one embodiment, the compound has one of the structures (1) to (3):



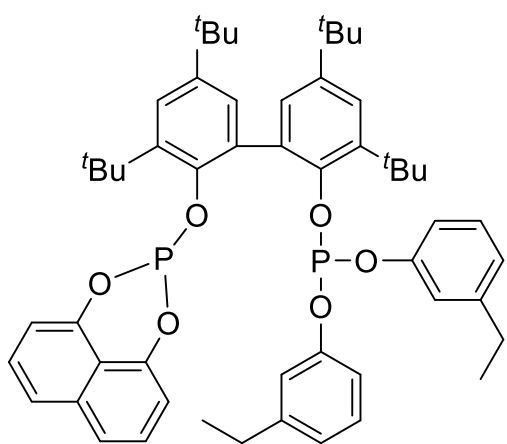


(3).

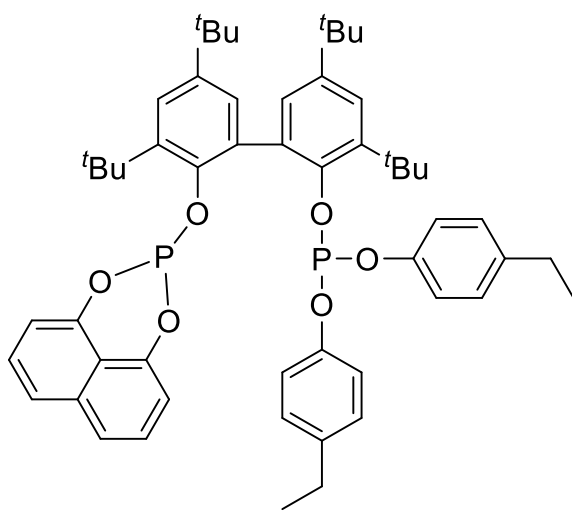
In one embodiment, the compound has one of the structures (4) to (6):



(4)

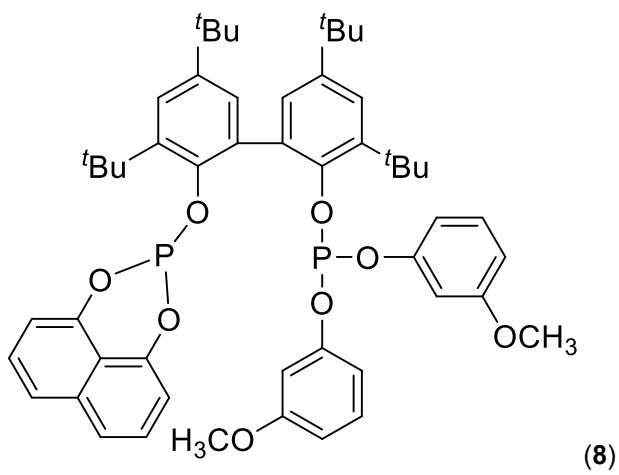
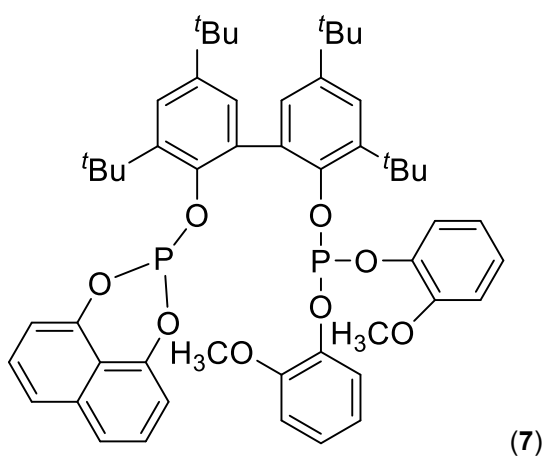


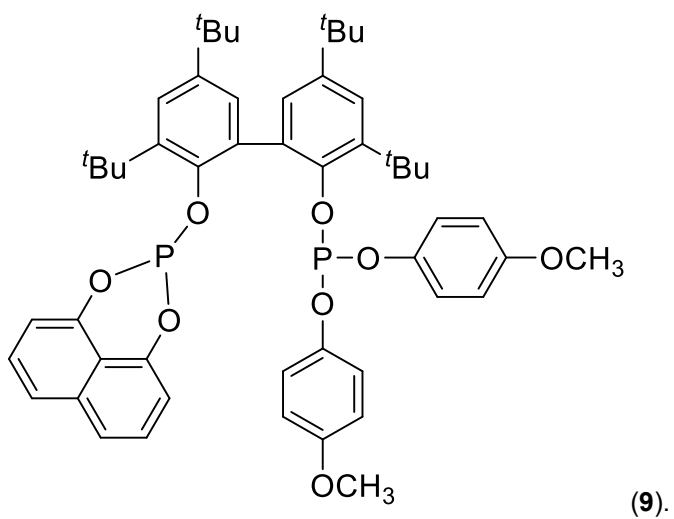
(5)



In one embodiment, the compound has one of the structures (7) to (9):

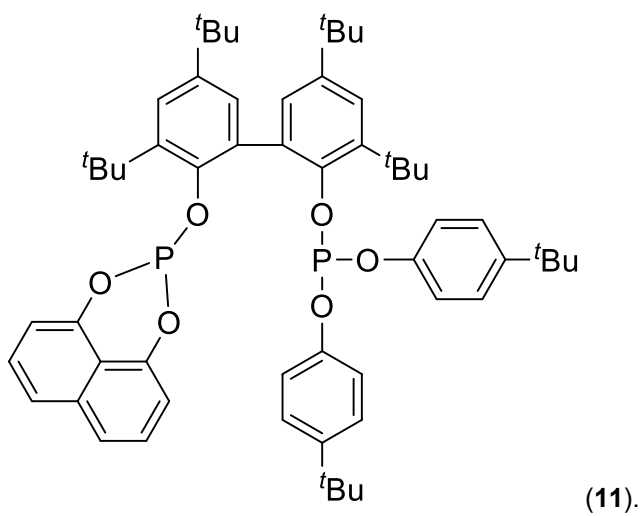
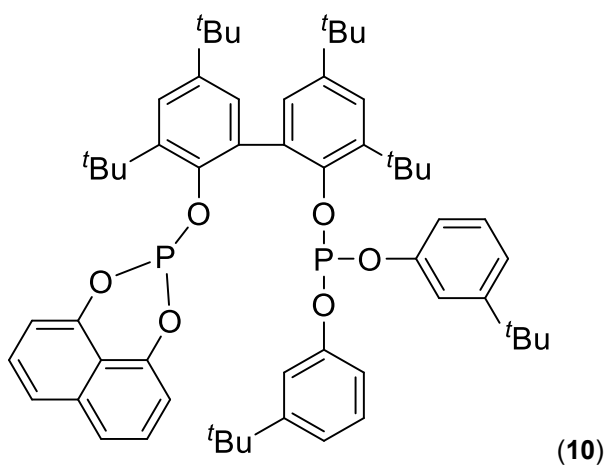
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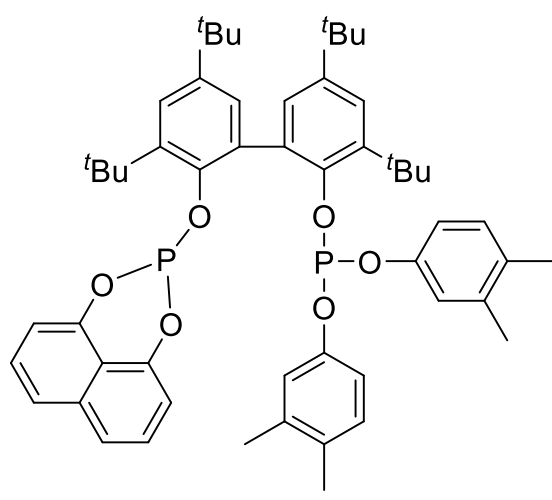


In one embodiment, the compound has either of the structures (10) or (11):

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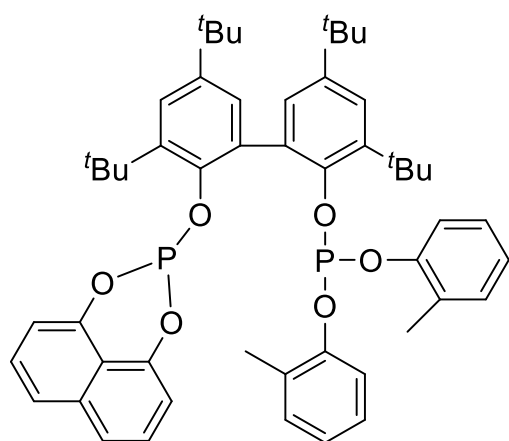


In one embodiment, the compound has the structure (12):



(12).

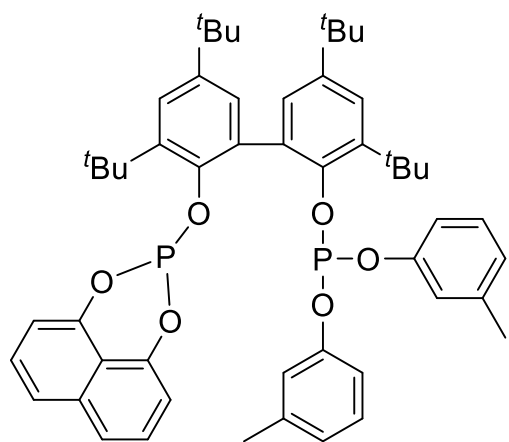
In one embodiment, the compound has the structure (1):



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(1).

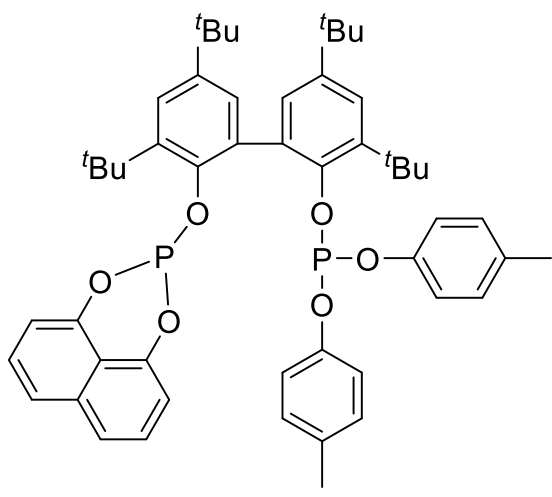
In one embodiment, the compound has the structure (2):



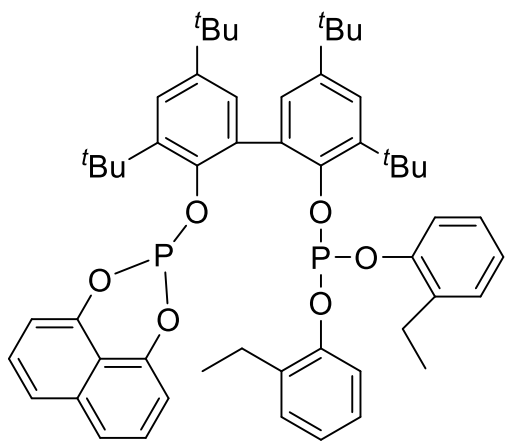
(2).

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In one embodiment, the compound has the structure (3):

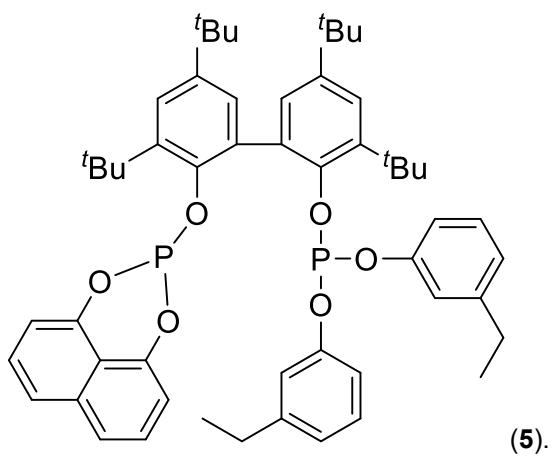


In one embodiment, the compound has the structure (4):



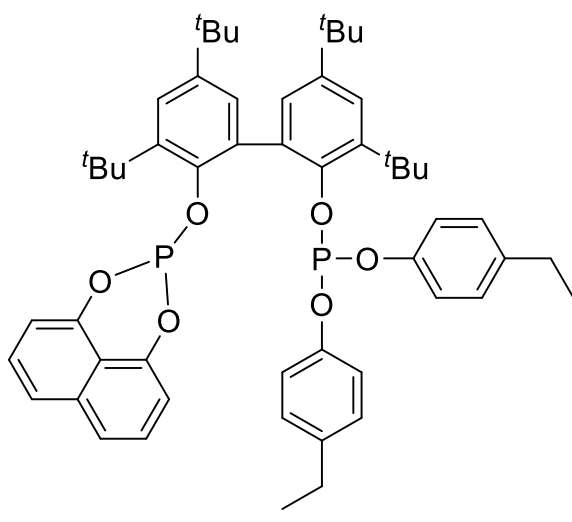
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In one embodiment, the compound has the structure (5):

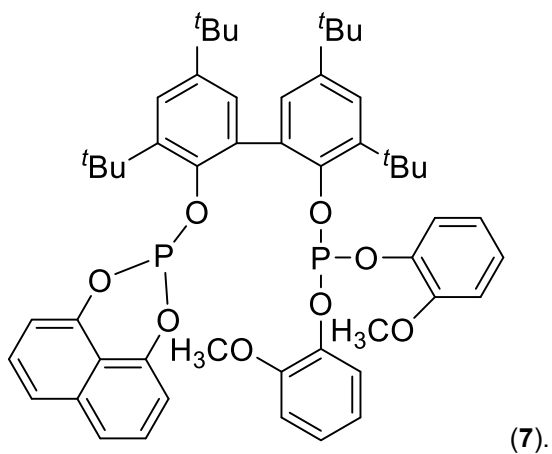


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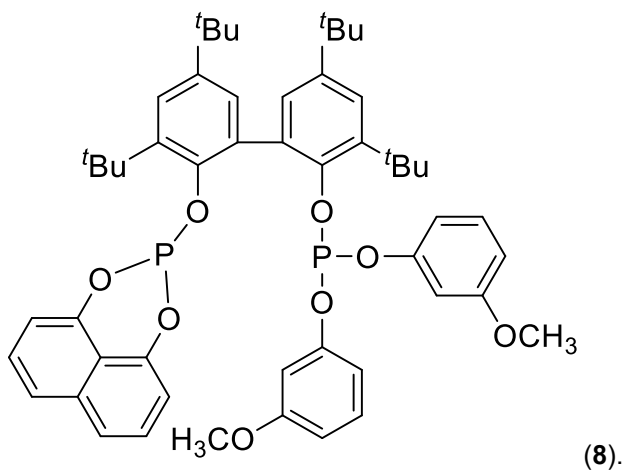
In one embodiment, the compound has the structure (6):



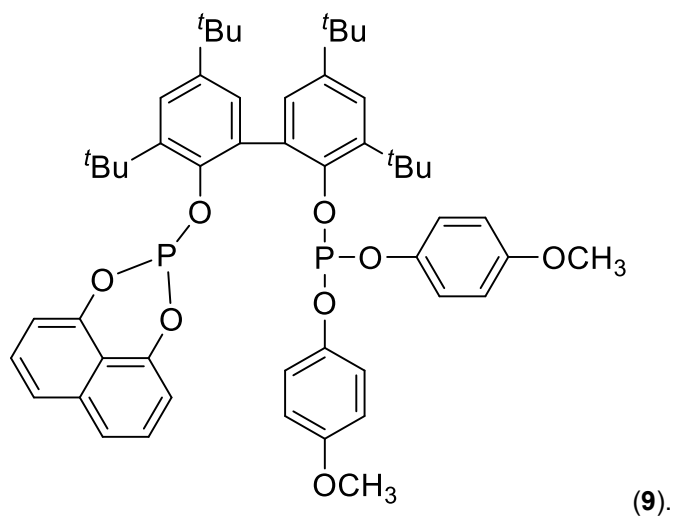
5 In one embodiment, the compound has the structure (7):



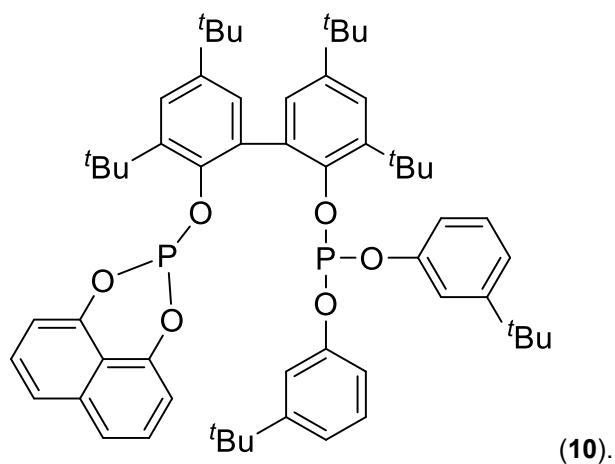
In one embodiment, the compound has the structure (8):



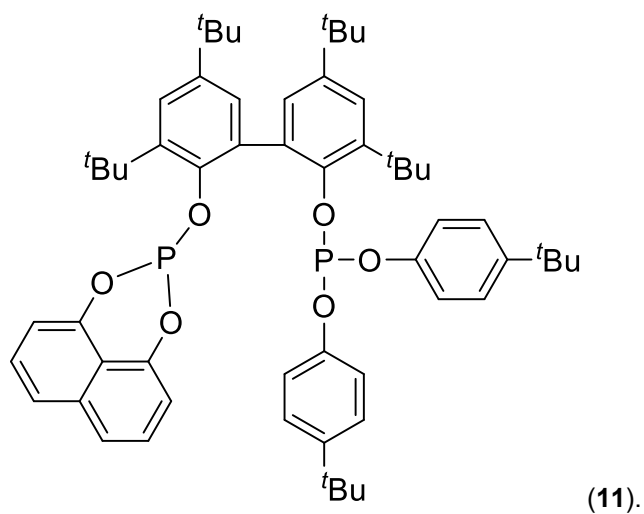
In one embodiment, the compound has the structure (9):



In one embodiment, the compound has the structure (10):



In one embodiment, the compound has the structure (11):



10 In addition to the compounds themselves, a process in which the compounds described above are used is also claimed.

Process comprising the process steps of:

- a) initially charging an olefin;
- b) adding the compound described above;
- 5 c) adding a substance comprising Rh;
- d) feeding in H₂ and CO;
- e) heating the reaction mixture from a) to d), with conversion of the olefin to an aldehyde.

In one variant of the process, the substance comprising Rh is selected from: Rh(acac)(CO)₂,
 10 Rh(acac)(cod) (Umicore, acac = acetylacetonate anion; cod = 1,5-cyclooctadiene), Rh₄CO₁₂.

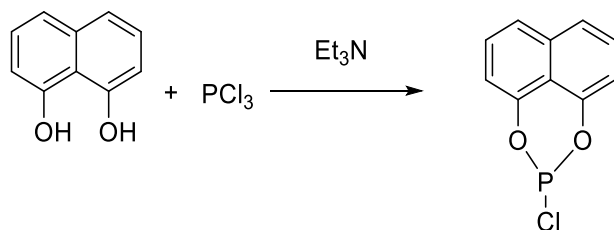
In one variant of the process, the substance comprising Rh is Rh(acac)(CO)₂.

The invention is to be elucidated in more detail hereinafter with reference to exemplary embodiments.

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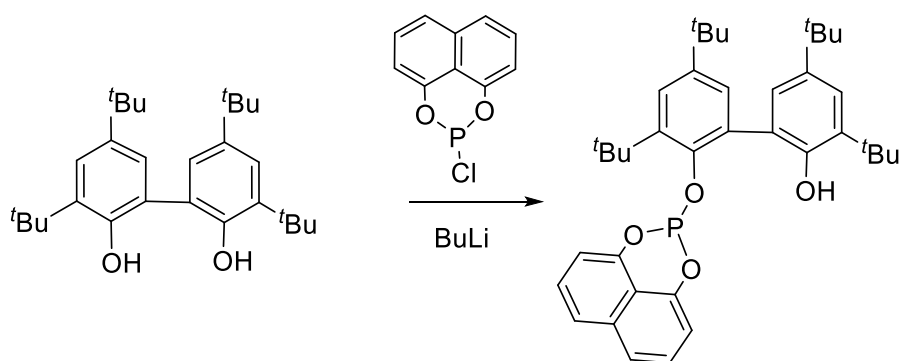
Synthesis

First stage



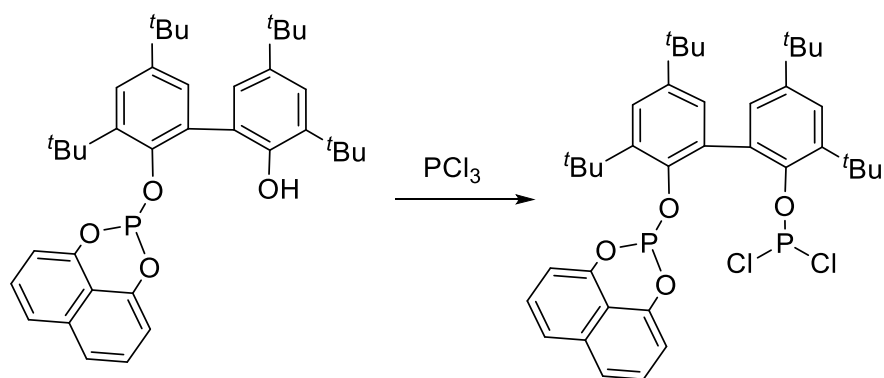
- 20 0.076 mol of naphthalene-1,8-diol was dried overnight at 50°C by means of oil-pump vacuum. The following day, the Schlenk flask was flooded with argon and the naphthalene-1,8-diol was dissolved in 350 ml of dried toluene. In a Schlenk flask which had been repeatedly evacuated and filled with inert gas, 0.114 mol of phosphorus trichloride was dissolved in 120 ml of dried toluene. Subsequently, the naphthalene-1,8-diol solution was slowly and steadily added dropwise at -20°C to the PCl₃ solution.
- 25 Thereafter, 0.165 mol of triethylamine was slowly added dropwise at -20°C to the solution under high stirring speed. The solution was brought to room temperature and stirring was continued overnight. The next day, the reaction mixture was filtered using a frit, the filter cake was washed twice with in each case 25 ml of toluene and the filtrate was concentrated at 40°C by means of oil-pump vacuum.

30 Yield: 86%

Second stage

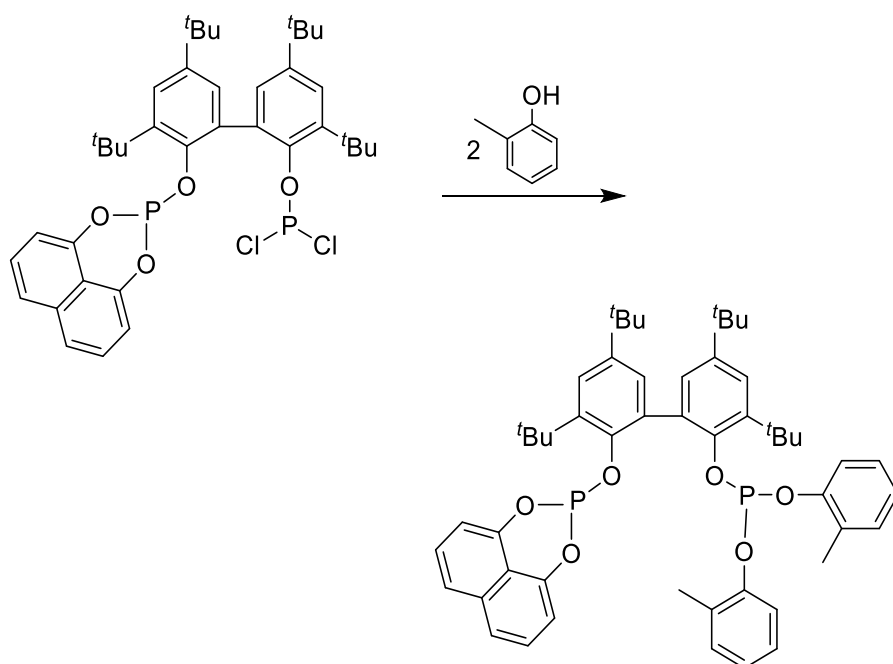
0.016 mol of biphenol was weighed out, dried overnight by means of oil-pump vacuum and the next morning flooded with argon. The biphenol was dissolved in 40 ml of toluene. Under an inert gas atmosphere, 0.016 mol of chlorophosphite was weighed out, dissolved in 40 ml of toluene and admixed with 0.016 mol of degassed triethylamine. The chlorophosphite-toluene solution was added dropwise at room temperature to the biphenol solution over the course of 1 h and stirring was performed at 40°C for 24 h. The reaction mixture was filtered using a frit and the filter cake was washed twice with in each case 20 ml of toluene. The filtrate obtained was concentrated and dried at 40°C under oil-pump vacuum.

Yield: 75%

Third stage

Under an inert gas atmosphere, 11.9 mmol of the monophosphite was weighed out and dissolved in 150 ml of dried toluene and 29.8 mmol of degassed triethylamine. In a Schlenk flask which had been repeatedly evacuated and filled with inert gas, 14.9 mmol of phosphorus trichloride was dissolved in 100 ml of dried toluene and cooled to 0°C. The organochlorophosphite-triethylamine solution was then added at 0°C to the phosphorus trichloride solution. The reaction mixture was stirred at room temperature for 24 h. The ammonium hydrochloride formed was filtered off using a frit and washed twice with in each case 50 ml of dried toluene. The filtrate obtained was subsequently concentrated to dryness at 45°C under oil-pump vacuum.

Yield: 87%

Synthesis (1)

5 (1)

Under an inert gas atmosphere, 2.9 mmol of organodichlorophosphite was weighed out and suspended in 30 ml of dried toluene. 6.7 mmol of the phenol was weighed out in a Schlenk flask and repeated evacuation and filling with inert gas was briefly performed by means of oil-pump vacuum. Subsequently, the Schlenk flask was flooded with argon and the phenol was dissolved in 20 ml of dried toluene and

10 14.3 mmol of degassed triethylamine was added. Subsequently, the phenol solution was slowly and steadily added at room temperature to the chlorophosphite suspension. The reaction solution was stirred at room temperature overnight. The ammonium hydrochloride formed was filtered off using a frit and washed twice with in each case 10 ml of dried toluene. The filtrate obtained was subsequently concentrated to dryness at 40°C by means of oil-pump vacuum. The dried filtrate was purified by means

15 of column chromatography.

Yield: 60%

Compounds (2) to (12) were prepared analogously, as was Comparative Compound (IIa).

Catalysis experiments

An argon atmosphere is employed. Reaction vessels have been dried beforehand at high temperature (80°C) and under oil-pump vacuum. Liquid substances were degassed by bubbling in argon for at least 15 minutes. The hydroformylation was carried out in a 0.5 l autoclave from Berghof Products +

25 Instruments GmbH, equipped with a constant-pressure apparatus. The reactor is heated by means of oil bath from IKA. The reactor serves for gas exchange and as a temperature control unit. Five glass vials (20 ml), filled with catalyst solution and magnetic stirrer bars and crimped under argon, were

placed inside this reactor such that gas exchange between vials and reactor space is possible. The temperature of the glass vials was controlled by thermal oil present in the reactor. Reaction temperatures specified were measured inside the glass vials. The substrate used was n-octene (Oxeno GmbH, octene isomer mixture of 1-octene: 3%; cis+trans-2-octene: 49%; cis+trans-3-octene: 29%; cis+trans-4-octene: 16%; structurally isomeric octenes: 3%).

For an experiment run, a stock solution was prepared in advance under an argon atmosphere. For this purpose, 0.0127 g of $\text{Rh}(\text{acac})(\text{CO})_2$ and the corresponding amount of phosphite compound (MV Lig:Rh = 5:1) were weighed out and made up with 48.0 ml of toluene. Approx. 8 ml of this solution was distributed to each of the vials and the exact amount was weighed. The vials were placed in the reactor and the latter was closed. Purging was performed three times with argon and three times with synthesis gas (Linde; H_2 (99.999%) : CO (99.997%) = 1:1). On completion of pressure testing, the autoclave was heated to the desired temperature of 120°C at an overall pressure of 10 bar with stirring (900 rpm). After reaching the reaction temperature, the synthesis gas pressure was increased to 20 bar and 2 ml of the substrate in each case was metered in by means of HPLC pump to start the reaction. This results in an Rh concentration of 100 ppm. 1 h after the start of the reaction at constant pressure, a sample was taken from each vial and analysed undiluted by gas chromatography: HP 6890, Petrocol® DH 150, 150 m x 0.25 mm x 1 µm. Residual olefin and aldehyde were quantitatively determined against the solvent toluene as internal standard. The results listed in the table below are the average over one experiment run.

Results of the catalysis experiments

[Rh]: 100 ppm, p: 20 bar, T: 120°C; t: 1 h

The n-octene mixture used consisted of the C8 isomers: 1-octene, cis-2-octene, trans-2-octene, cis-3-octene, trans-3-octene, cis-4-octene and trans-4-octene.

Table 1:

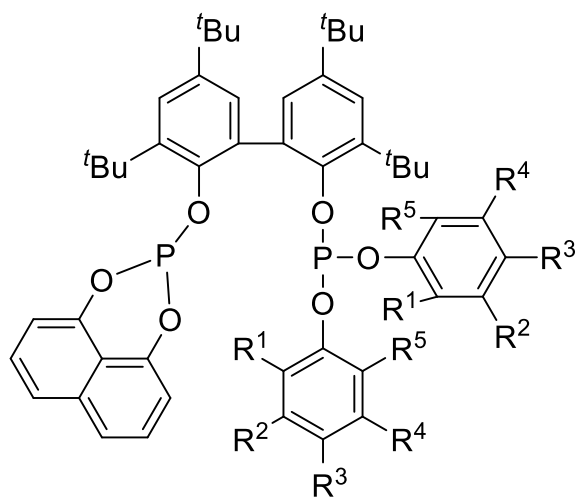
Ligand	Yield [%]
(1)	40
(2)	47
(3)	48
(4)	41
(5)	43
(6)	45
(7)	46
(8)	45
(9)	45
(10)	44
(11)	41
(12)	46
(IIa)*	39

* non-inventive exemplary embodiment

The experiments carried out demonstrate that the stated object is achieved by the compounds according to the invention.

Claims

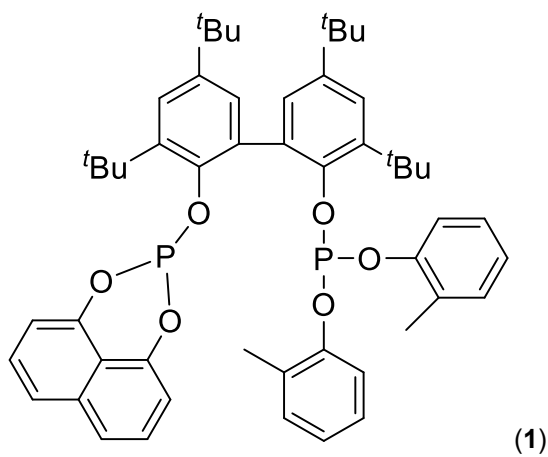
1. Compound of formula (I):



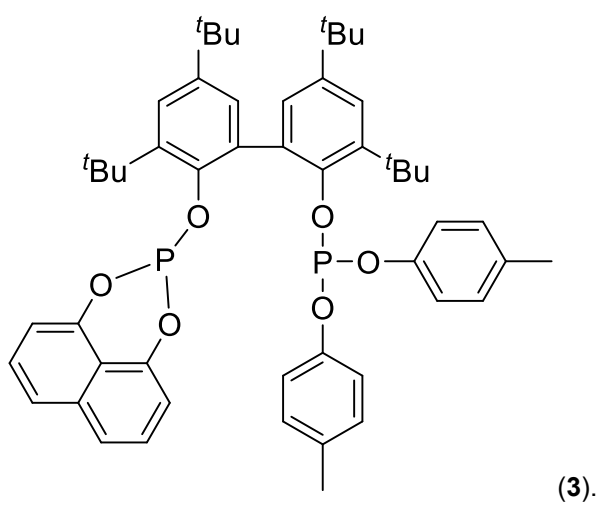
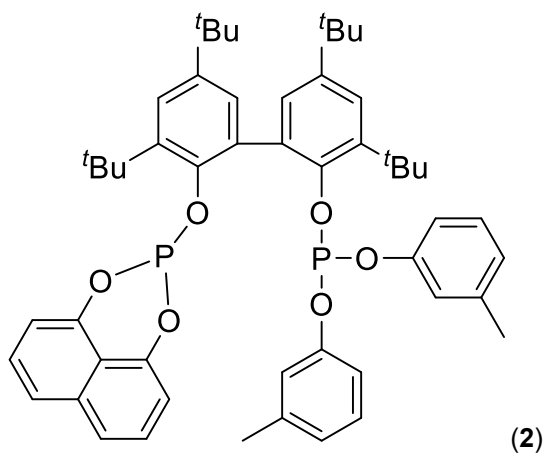
(I)

- 5 wherein R^1 , R^2 , R^3 , R^4 , R^5 are selected from: -H, -(C₁-C₄)-alkyl, -O-(C₁-C₄)-alkyl and at least one of the radicals R^1 , R^2 , R^3 , R^4 , R^5 is not -H.
2. Compound according to Claim 1,
wherein R^1 , R^2 , R^3 , R^4 , R^5 are selected from: -H, -CH₃, -CH₂-CH₃, -*tert*Bu, -O-CH₃.
- 10 3. Compound according to either of Claims 1 and 2,
wherein at least three of the radicals R^1 , R^2 , R^3 , R^4 , R^5 are -H.
4. Compound according to any of Claims 1 to 3,
15 wherein R^1 , R^2 , R^3 , R^4 , R^5 are selected from: -H, -CH₃.
5. Compound according to any of Claims 1 to 3,
wherein R^1 , R^2 , R^3 , R^4 , R^5 are selected from: -H, -CH₂-CH₃.
- 20 6. Compound according to any of Claims 1 to 3,
wherein R^1 , R^2 , R^3 , R^4 , R^5 are selected from: -H, -*tert*Bu.
7. Compound according to any of Claims 1 to 3,
wherein R^1 , R^2 , R^3 , R^4 , R^5 are selected from: -H -O-CH₃.

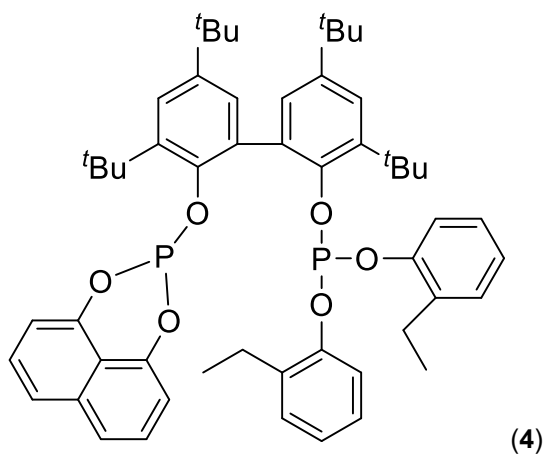
8. Compound according to any of Claims 1 to 3,
wherein the compound has one of the structures (1) to (3):



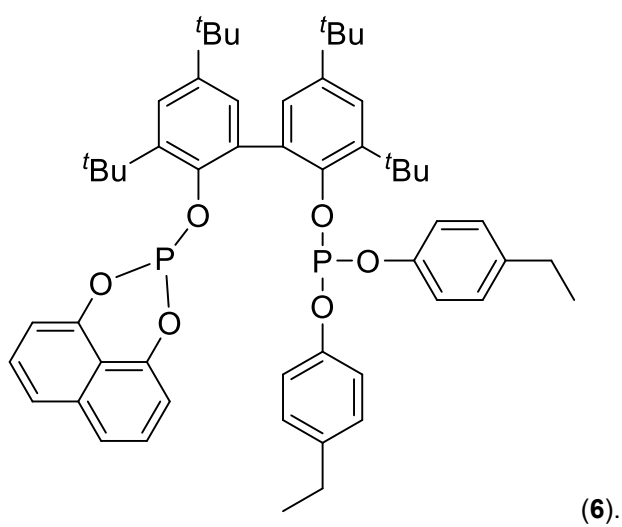
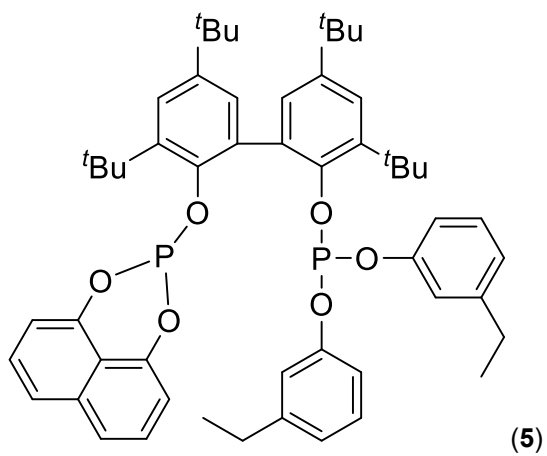
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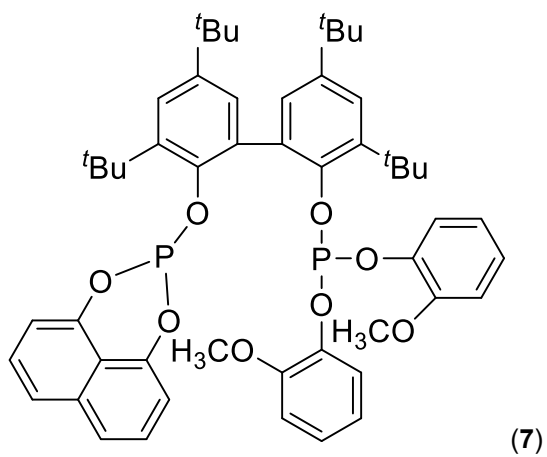
9. Compound according to any of Claims 1 to 3,
wherein the compound has one of the structures (4) to (6):



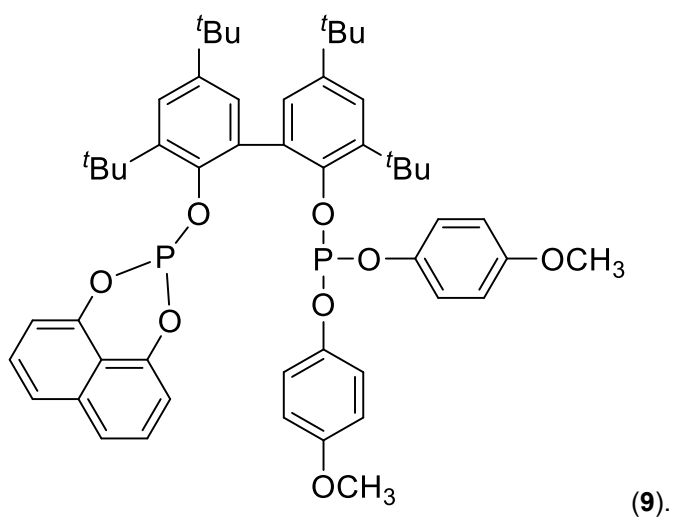
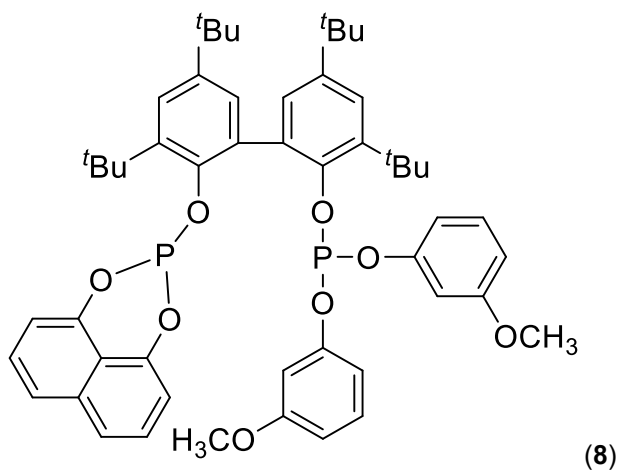
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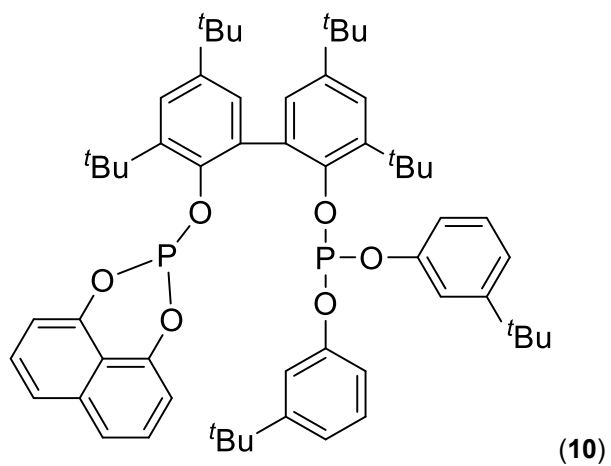
10. Compound according to any of Claims 1 to 3,
wherein the compound has one of the structures (7) to (9):



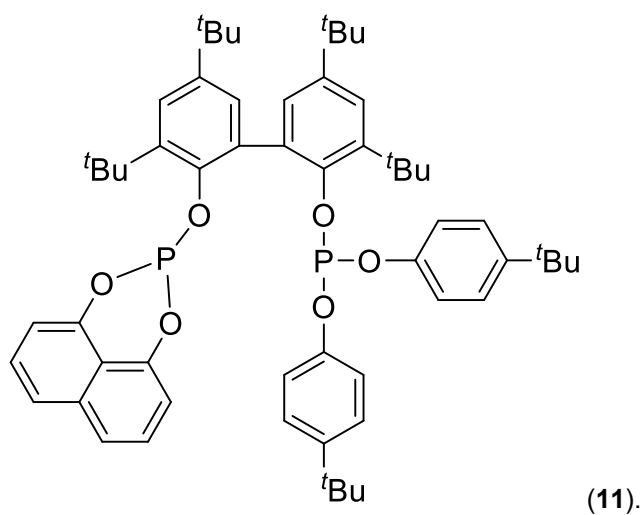
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11. Compound according to any of Claims 1 to 3,
wherein the compound has either of the structures (10) and (11):

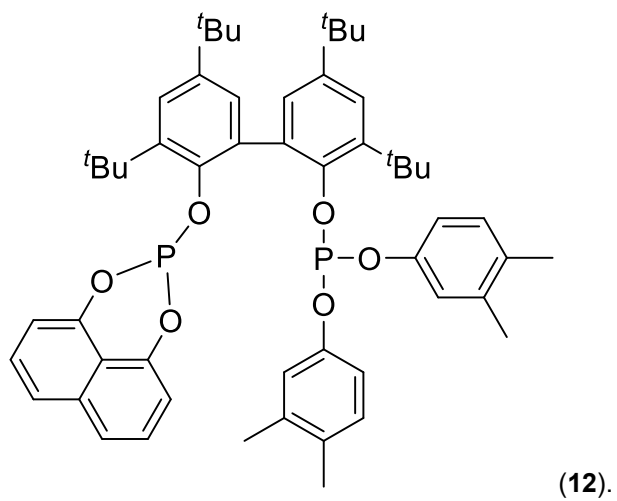


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12. Compound according to any of Claims 1 to 3,
wherein the compound has the structure (12):

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13. Process comprising the process steps of:
- a) initially charging an olefin;
 - b) adding a compound according to any of Claims 1 to 12;
 - 5 c) adding a substance comprising Rh;
 - d) feeding in H₂ and CO;
 - e) heating the reaction mixture from a) to d), with conversion of the olefin to an aldehyde.
14. Process according to Claim 13,
- 10 wherein the substance comprising Rh is selected from: Rh(acac)(CO)₂, Rh(acac)(cod) (Umicore, acac = acetylacetonate anion; cod = 1,5-cyclooctadiene), Rh₄CO₁₂.
15. Process according to either of Claims 13 and 14,
- wherein the substance comprising Rh is Rh(acac)(CO)₂.