

Process for the hydroformylation of olefins using a cobalt precatalyst and a diphosphine ligand

The invention relates to a process for the hydroformylation of olefins using a cobalt precatalyst and a diphosphine ligand.

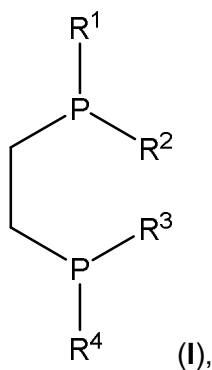
The use of cobalt catalysts in hydroformylation is described in Hood et al. "Highly active cationic cobalt (II) hydroformylation catalysts", Science, volume 367, number 6477, pages 542-548 (2020). In this process, the diphosphine ligands used are always employed in a ratio of 1:1 to cobalt. In the case of Rh, the ligand was employed in a significant excess ($L/Rh = 400-1600:1$).

The technical object underlying the present invention is that of providing a process with which olefins can be hydroformylated. In the process, an increased yield should be achieved.

This object is achieved by a process according to Claim 1.

Process comprising the process steps of:

- a) adding an olefin;
- b) adding a cobalt precatalyst;
- c) adding a ligand (L) having the structure (I):



where R^1 , R^2 , R^3 , R^4 are selected from:

-H, $-(C_1-C_{12})$ -alkyl, $-(C_6-C_{20})$ -aryl;

wherein the ligand is added in a molar ratio to cobalt of $L/Co = < 0.95/1$;

- d) supplying of syngas;
- e) heating the reaction mixture from a) to d), to convert the olefin into an aldehyde.

Process steps a) to d) can take place here in any desired order.

Addition of the ligand in a molar ratio to cobalt of $L/Co = \text{less than } 0.95 \text{ to } 1$ means that the ligand (L) is being added substoichiometrically in respect of the metal (Co).

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In one variant of the process, R^1, R^2, R^3, R^4 are selected from: $-(C_1-C_{12})\text{-alkyl}$, $-(C_6-C_{20})\text{-aryl}$.

In one variant of the process, R^1, R^2 are $-(C_6-C_{20})\text{-aryl}$.

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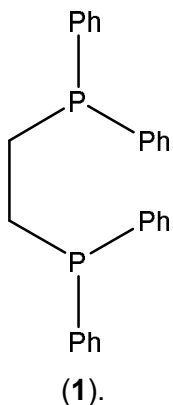
In one variant of the process, R^1, R^2 are $-\text{Ph}$.

In one variant of the process, R^1, R^3 are $-(C_6-C_{20})\text{-aryl}$.

In one variant of the process, R^1, R^3 are $-\text{Ph}$.

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In one variant of the process the ligand has the structure (1):

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In one variant of the process, the ligand is added in a molar ratio to cobalt of $L/Co = < 0.90/1$.

In one variant of the process, the ligand is added in a molar ratio to cobalt of $L/Co = < 0.80/1$.

In one variant of the process, the ligand is added in a molar ratio to cobalt of $L/Co = < 0.70/1$.

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In one variant of the process, the ligand is added in a molar ratio to cobalt of $L/Co = < 0.60/1$.

In one variant of the process, the ligand is added in a molar ratio to cobalt of $L/Co = < 0.50/1$.

In one variant of the process, the ligand is added in a molar ratio to cobalt of $L/Co = < 0.40/1$.

In one variant of the process, the ligand is added in a molar ratio to cobalt of $L/Co = < 0.30/1$.

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In one variant of the process, the ligand is added in a molar ratio to cobalt of $L/Co = < 0.20/1$.

In one variant of the process, the cobalt precatalyst is initially charged in the form of a solution.

10 In one variant of the process, the olefin is added to the initially charged cobalt precatalyst solution.

In one variant of the process, the syngas in process step d) is supplied at a pressure within a range from 1 to 8 MPa (10 to 80 bar).

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In one variant of the process, the syngas in process step d) is supplied at a pressure within a range from 4 to 6 MPa (40 to 60 bar).

20 In one variant of the process, the heating of the reaction mixture in process step e) is to a temperature within a range from 80°C to 180°C.

In one variant of the process, the heating of the reaction mixture in process step e) is to a temperature within a range from 120°C to 160°C.

25 In one variant of the process, the cobalt precatalyst is $[Co(acac)(C_4H_8O_2)_4]^+[BF_4]^-$ (**V1**).

In one variant of the process, the olefin is selected from:

ethene, propene, 1-butene, cis-2-butene, trans-2-butene, mixture of cis- and trans-2-butene, raffinate 1, raffinate 2, isobutene, 1-pentene, 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 1-methylcyclohexene, tetramethylethene, 1-octene, 2-octenes, cyclooctene, di-n-butene, diisobutene, undecenes, dodecenes, triisobutene, tri-n-butene.

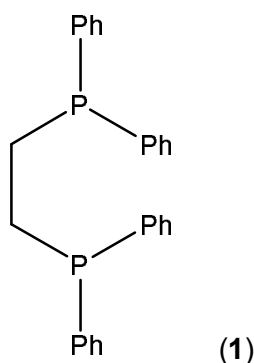
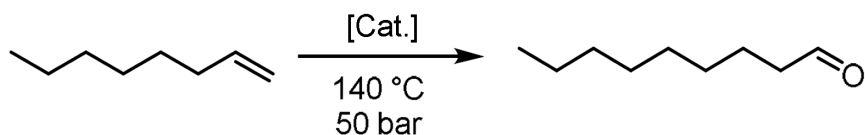
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In one variant of the process, the olefin is selected from:

1-butene, cis-2-butene, trans-2-butene, isobutene, 1-pentene, 2-pentene, 1-octene, 2-octenes, di-n-butene, diisobutene, triisobutene, tri-n-butene.

The invention shall be elucidated in more detail hereinbelow with reference to a working example.

Hydroformylation of 1-octene with $[\text{Co}(\text{acac})(\text{C}_4\text{H}_8\text{O}_2)](\text{BF}_4)$



(1): 1,2-Bis(diphenylphosphino)ethane (DPPE)

(V1): $[\text{Co}(\text{acac})(\text{C}_4\text{H}_8\text{O}_2)](\text{BF}_4)$

A solution of the Co precatalyst (V1) and diphosphine (1) in diglyme (24 mL) was introduced into a 150 mL Premex autoclave with sparging stirrer and pressurized with 32 bar of syngas. The solution was heated to 160°C and the pressure readjusted to 50 bar. After 5 minutes, the temperature was lowered to 140°C. The olefin (4.74 mL) was then added to the catalyst solution by means of a pressure pipette and the reaction solution (1 M olefin) stirred at 50 bar and 140°C. The reaction mixture was then cooled to room temperature and the pressure released. The yields were determined by gas chromatography.

Reaction conditions:

[Co]: 2.6 mM, T: 140°C, p(syngas): 50 bar, t: 1 h, precatalyst: V1

Hydroformylation of 1-octene

Ligand	Precatalyst	P/Co	L/Co	T (°C)	t (h)	Yield (%)
(1)	V1	2:1	1:1	140	1	35.9
(1)*	V1	0.23:1	0.115:1	140	1	69.9

5 * process according to the invention

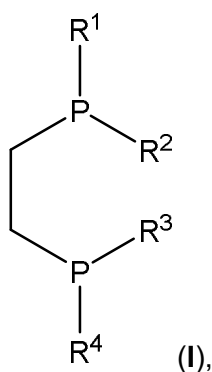
With the ligand-cobalt ratio (L/Co) according to the invention, it was possible to increase the yield.

As demonstrated by the working example, the object is achieved by the process according to
 10 the invention.

Claims

1. Process comprising the process steps of:

- a) adding an olefin;
- 5 b) adding a cobalt precatalyst;
- c) adding a ligand (L) having the structure (I):



where R^1 , R^2 , R^3 , R^4 are selected from:

-H, -(C₁-C₁₂)-alkyl, -(C₆-C₂₀)-aryl;

10 wherein the ligand is added in a molar ratio to cobalt of L/Co = < 0.95/1;

- d) supplying of syngas;
- e) heating the reaction mixture from a) to d), to convert the olefin into an aldehyde.

2. Process according to Claim 1,

15 where R^1 , R^2 , R^3 , R^4 are selected from: -(C₁-C₁₂)-alkyl, -(C₆-C₂₀)-aryl.

3. Process according to either of Claims 1 and 2,

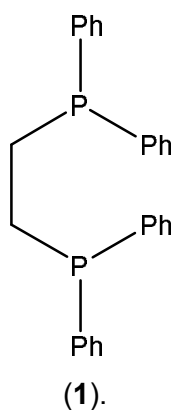
where R^1 , R^2 are -Ph.

20 4. Process according to any of Claims 1 to 3,

where R^1 , R^3 are -Ph.

5. Process according to any of Claims 1 to 4,

where the ligand has the structure (1):



6. Process according to any of Claims 1 to 5,
- 5 wherein the ligand is added in a molar ratio to cobalt of $L/Co = < 0.90/1$.
7. Process according to any of Claims 1 to 6,
- wherein the ligand is added in a molar ratio to cobalt of $L/Co = < 0.80/1$.
- 10 8. Process according to any of Claims 1 to 7,
- wherein the Co precatalyst is initially charged in the form of a solution.
9. Process according to Claim 8,
- wherein the olefin is added to the initially charged Co precatalyst solution.
- 15 10. Process according to any of Claims 1 to 9,
- wherein the syngas is supplied in process step d) at a pressure within a range from 1 to 8 MPa (10 to 80 bar).
- 20 11. Process according to any of Claims 1 to 10,
- wherein the heating of the reaction mixture in process step e) is to a temperature within a range from 80°C to 180°C.
12. Process according to any of Claims 1 to 11,
- 25 wherein the cobalt precatalyst is $[Co(acac)(C_4H_8O_2)_4]^+[BF_4]^-$ (**V1**).
13. Process according to any of Claims 1 to 12,
- wherein the olefin is selected from:

ethene, propene, 1-butene, cis-2-butene, trans-2-butene, mixture of cis- and trans-2-butene, raffinate 1, raffinate 2, isobutene, 1-pentene, 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 1-methylcyclohexene, tetramethylethene, 1-octene, 2-octenes, cyclooctene, di-n-butene, diisobutene, undecenes, dodecenes, triisobutene, tri-n-butene.