

Process for hydroformylation of olefins using Pt and bromine

The present invention relates to a process for hydroformylation of olefins using Pt and bromine.

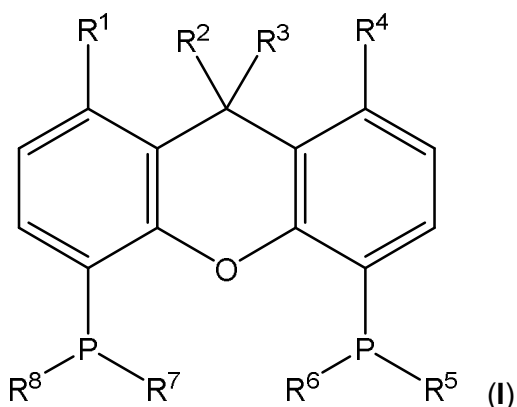
- 5 C. Botteghi et al., Journal of Molecular Catalysis A: Chemical 200, (2003), 147-156 describes the use of $\text{Pt}(\text{Xantphos})\text{Cl}_2$ for hydroformylation of 2-tosyloxystyrene.

The problem addressed by the present invention is that of providing a novel hydroformylation process. The process here is to afford an increased yield compared to the process known from
10 the prior art using $\text{Pt}(\text{Xantphos})\text{Cl}_2$.

This problem is solved by a process according to Claim 1.

Process comprising the process steps of:

- 15 a) initially charging an olefin;
b) adding a compound of formula (I):



where $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7, \text{R}^8$ are selected from: -H, $-(\text{C}_1\text{-C}_{12})\text{-alkyl}$, $-(\text{C}_6\text{-C}_{20})\text{-aryl}$;

and, if $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4, \text{R}^5, \text{R}^6, \text{R}^7, \text{R}^8$ are $-(\text{C}_6\text{-C}_{20})\text{-aryl}$, the aryl ring may have substituents
20 selected from: $-(\text{C}_1\text{-C}_{12})\text{-alkyl}$, $-\text{O}-(\text{C}_1\text{-C}_{12})\text{-alkyl}$;

- c) adding a Pt compound capable of forming a complex;
d) adding a bromine compound;
e) feeding in CO and H_2 ;
f) heating the reaction mixture from steps a) to e), to convert the olefin to an aldehyde.

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In this process, process steps a) to e) can be effected in any desired sequence. Typically, however, CO and H_2 are added after the co-reactants have been initially charged in steps a) to d).

It is possible here for process steps c) and d) to be effected in one step, by adding PtBr_2 .

In a preferred variant of the process, the Pt compound and the bromine compound are added in one step, by adding PtBr_2 .

- 5 The expression $(\text{C}_1\text{-C}_{12})$ -alkyl encompasses straight-chain and branched alkyl groups having 1 to 12 carbon atoms. These are preferably $(\text{C}_1\text{-C}_8)$ -alkyl groups, more preferably $(\text{C}_1\text{-C}_6)$ -alkyl, most preferably $(\text{C}_1\text{-C}_4)$ -alkyl.

Suitable $(\text{C}_1\text{-C}_{12})$ -alkyl groups are especially methyl, ethyl, propyl, isopropyl, *n*-butyl, *isobutyl*,
 10 *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,
 15 1-propylbutyl, *n*-octyl, 2-ethylhexyl, 2-propylheptyl, nonyl, decyl.

The expression $(\text{C}_6\text{-C}_{20})$ -aryl encompasses mono- or polycyclic aromatic hydrocarbyl radicals having 6 to 20 carbon atoms. These are preferably $(\text{C}_6\text{-C}_{14})$ -aryl, more preferably $(\text{C}_6\text{-C}_{10})$ -aryl.

20 Suitable $(\text{C}_6\text{-C}_{20})$ -aryl groups are especially phenyl, naphthyl, indenyl, fluorenyl, anthracenyl, phenanthrenyl, naphthacenyl, chrysenyl, pyrenyl, coronenyl. Preferred $(\text{C}_6\text{-C}_{20})$ -aryl groups are phenyl, naphthyl and anthracenyl.

In one variant of the process, R^2 , R^3 , R^5 , R^6 , R^7 , R^8 are selected from: $(\text{C}_1\text{-C}_{12})$ -alkyl, $(\text{C}_6\text{-C}_{20})$ -
 25 aryl.

In one variant of the process, R^5 , R^6 , R^7 , R^8 are $(\text{C}_6\text{-C}_{20})$ -aryl.

In one variant of the process, R^5 , R^6 , R^7 , R^8 are -Ph.

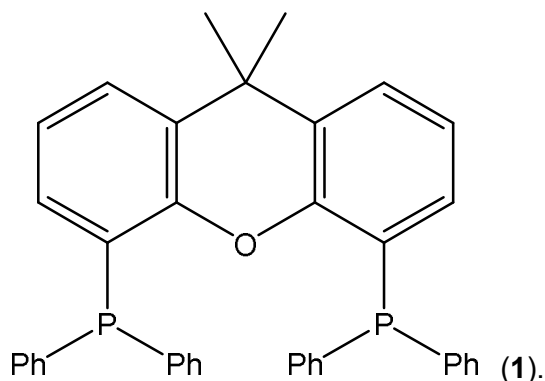
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In one variant of the process, R^2 and R^3 are $(\text{C}_1\text{-C}_{12})$ -alkyl.

In one variant of the process, R^2 and R^3 are $-\text{CH}_3$.

35 In one variant of the process, R^1 and R^4 are each -H.

In one variant of the process, the compound (I) has the structure (1):



In one variant of the process, the Pt compound is selected from: Pt(II)Br₂, Pt(IV)Br₄, diphenyl(1,5-COD)Pt(II), Pt(II)(acac)₂, Pt(0)(PPh₃)₄, Pt(0)(DVTS) solution (CAS: 68478-92-2), Pt(0)(ethylene)(PPh₃)₂, Pt(II)Br₂(COD), tris(benzylideneacetone)Pt(0), Pt(II)(OAC)₂ solution, Pt(0)(t-Bu)₂, Pt(II)(COD)Me₂, Pt(II)(COD)I₂, Pt(IV)I Me₃, Pt(II)(hexafluoroacetylacetonate)₂.

In one variant of the process, the Pt compound is selected from: Pt(II)Br₂, Pt(II)(acac)₂.

In one variant of the process, the bromine compound is selected from: alkali metal halide, alkaline earth metal halide, NH₄X, alkylammonium halide, dialkyl halide, trialkyl halide, tetraalkyl halide, cycloalkylammonium halide.

In one variant of the process, the bromine compound is selected from: Pt(II)Br₂, LiBr.

In one variant of the process, the bromine compound is added in an amount in the range of 0.1 to 10, measured in equivalents based on Pt.

In one variant of the process, this process comprises the additional process step e'): e') adding a solvent.

In one variant of the process, the solvent is selected from: THF, DCM, ACN, DMF, toluene, texanol, pentane, hexane, octane, isooctane, decane, dodecane, cyclohexane, benzene, xylene, Marlotherm, propylene carbonate, MTBE, diglyme, triglyme, diethyl ether, dioxane, isopropanol, tert-butanol, isononanol, isobutanol, isopentanol, ethyl acetate.

In one variant of the process, the solvent is selected from: THF, DCM, ACN, DMF, toluene, Texanol.

In one variant of the process, CO and H₂ are fed in at a pressure in a range from 1 MPa (10 bar) to 6 MPa (60 bar).

- 5 In one variant of the process, CO and H₂ are fed in at a pressure in a range from 1 MPa (20 bar) to 6 MPa (50 bar).

In one variant of the process, the mixture is heated at a temperature in the range from 25°C to 150°C.

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In one variant of the process, the mixture is heated at a temperature in the range from 30°C to 130°C.

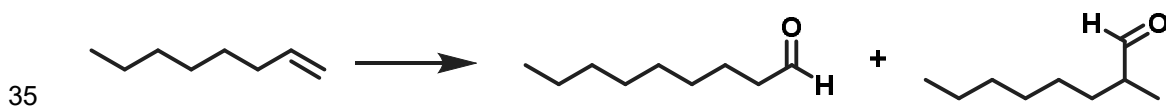
- 15 In one variant of the process, the olefin is selected from: ethene, propene, 1-butene, cis- and/or trans-2-butene, isobutene, 1,3-butadiene, 1-pentene, cis- and/or trans-2-pentene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, hexene, tetramethylethylene, heptene, 1-octene, 2-octene, di-n-butene, or mixtures thereof.

- 20 The invention shall be elucidated in more detail hereinbelow with reference to working examples.

Experimental description

- 25 A vial was charged with PtX₂ (X = halogen), ligand, and an oven-dried stirrer bar. The vial is then sealed with a septum (PTFE-coated styrene-butadiene rubber) and phenolic resin cap. The vial is evacuated and refilled with argon three times. Toluene and olefin were added to the vial using a syringe. The vial was placed in an alloy plate, which was transferred to an autoclave (300 ml) of the 4560 series from Parr Instruments under an argon atmosphere. After purging the autoclave three times with CO/H₂, the synthesis gas pressure was increased to 40 bar at
- 30 room temperature. The reaction was conducted at 120°C for 20 h/18 h. On termination of the reaction, the autoclave was cooled to room temperature and cautiously decompressed. Yield and selectivity were determined by GC analysis.

Hydroformylation of 1-octene



Reaction conditions:

20 mmol of 1-octene, 1.0 mol% Pt, 2.2 equivalents of Xantphos (**1**), solvent: toluene,
p(CO/H₂): 40 bar, T: 120°C, t: 20 h.

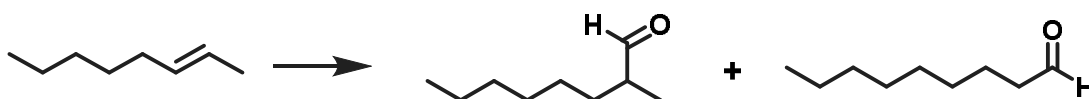
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Yields:

PtBr₂: 99%

PtCl₂: 30%

10 Variation of the halogen (2-octene)



Reaction conditions:

20 mmol of 2-octene, 1.0 mol% Pt, 1.1 equivalents of Xantphos (**1**), solvent: toluene,
p(CO/H₂): 40 bar, T: 120°C, t: 20 h.

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Yields:

PtBr₂: 99%

PtCl₂: 16%

20 Variation of the halogen (1-octene)

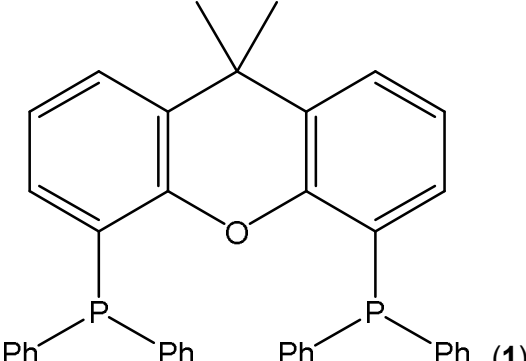
Reaction conditions:

10.0 mmol of 1-octene, 0.1 mol% PtX₂, 2.2 equivalents of ligand, solvent: toluene, p(CO/H₂):
40 bar, T: 120°C, t: 20 h.

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Yields:

Ligand	Halogen	Yield [%]
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	Br / Cl	97 / 5
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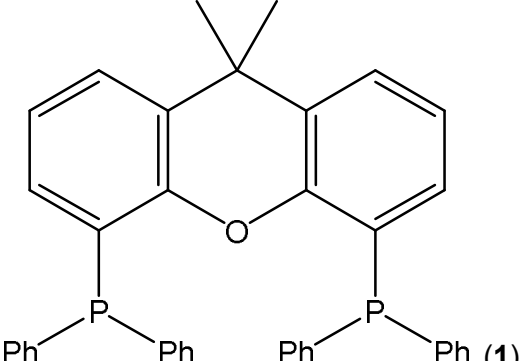
Variation of the ligand and of the halogen

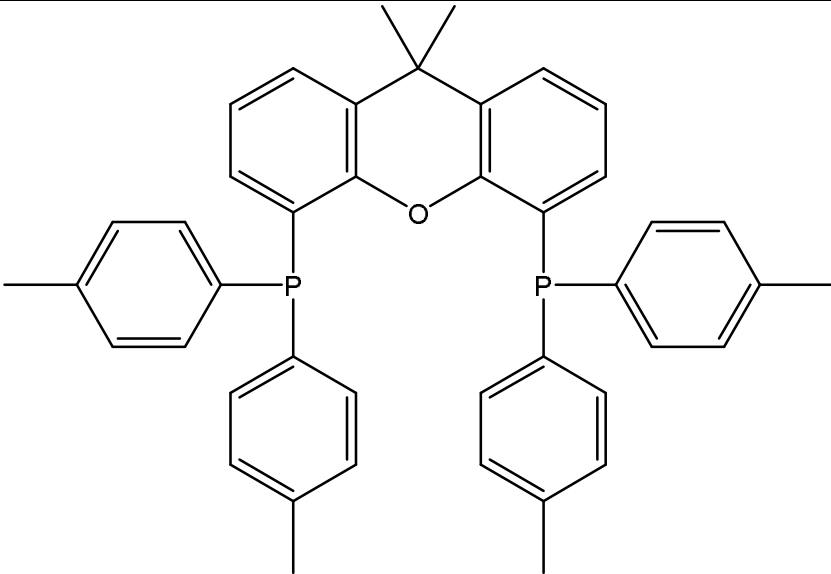
5 Reaction conditions:

1.0 mmol of 2-octene, 0.5 mol% PtX_2 , 2.0 equivalents of ligand, solvent: toluene, $p(\text{CO}/\text{H}_2)$: 40 bar, T: 120°C, t: 18 h.

Yields:

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Ligand	Halogen	Yield [%]
	Br / Cl	85 / <1

	Br / Cl	81 / <1
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Variation of the equivalents and of the halogen

5 Reaction conditions:

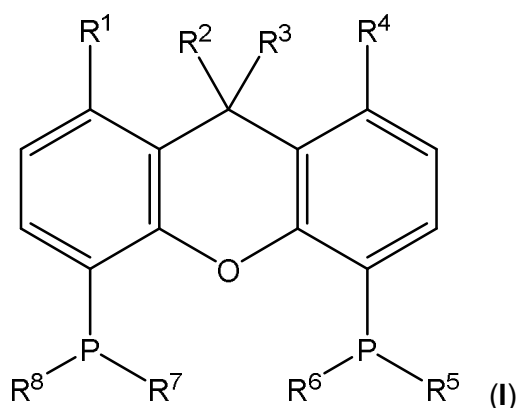
1.0 mmol of 1-octene, 1.0 mol% Pt(acac)₂, LiX (X= halogen), 2.2 equivalents of Xantphos (**1**), solvent: toluene, p(CO/H₂): 40 bar, T: 120°C, t: 20 h.

Equivalents of LiX	X	Yield [%]
0.5	Br	68
2.0	Br	71
1.5	Cl	0
4.0	Cl	0

- 10 As the experimental results show, the problem is solved by the process according to the invention.

Claims

- 5 1. Process comprising the process steps of:
 a) initially charging an olefin;
 b) adding a compound of formula (I):



- where $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8$ are selected from: -H, -(C₁-C₁₂)-alkyl, -(C₆-C₂₀)-aryl;
 10 and, if $R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8$ are -(C₆-C₂₀)-aryl, the aryl ring may have substituents selected from: -(C₁-C₁₂)-alkyl, -O-(C₁-C₁₂)-alkyl;
 c) adding a Pt compound capable of forming a complex;
 d) adding a bromine compound;
 e) feeding in CO and H₂;
 15 f) heating the reaction mixture from steps a) to e), to convert the olefin to an aldehyde.

2. Process according to Claim 1,

where $R^2, R^3, R^5, R^6, R^7, R^8$ are selected from: -(C₁-C₁₂)-alkyl, -(C₆-C₂₀)-aryl.

- 20 3. Process according to either of Claims 1 and 2,
 where R^5, R^6, R^7, R^8 are -(C₆-C₂₀)-aryl.

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

where R^2 and R^3 are -(C₁-C₁₂)-alkyl.

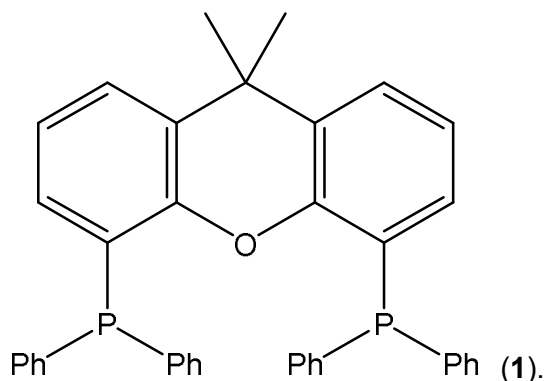
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5. Process according to any of Claims 1 to 4,

where R^1 and R^4 are each -H.

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

wherein the compound (I) has the structure (1):



7. Process according to any of Claims 1 to 6,

- 5 wherein the Pt compound is selected from: Pt(II)Br₂, Pt(IV)Br₄, diphenyl(1,5-COD)Pt(II), Pt(II)(acac)₂, Pt(0)(PPh₃)₄, Pt(0)(DVTs) solution (CAS: 68478-92-2), Pt(0)(ethylene)(PPh₃)₂, Pt(II)Br₂(COD), tris(benzylideneacetone)Pt(0), Pt(II)(OAc)₂ solution, Pt(0)(t-Bu)₂, Pt(II)(COD)Me₂, Pt(II)(COD)I₂, Pt(IV)I Me₃, Pt(II)(hexafluoroacetylacetonate)₂.

- 10 8. Process according to any of Claims 1 to 7,

wherein the Pt compound is selected from: Pt(II)Br₂, Pt(II)(acac)₂.

9. Process according to any of Claims 1 to 8,

wherein the bromine compound is selected from: Pt(II)Br₂, LiBr.

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10. Process according to any of Claims 1 to 9,

wherein the bromine compound is added in an amount in the range of 0.1 to 10, measured in equivalents based on Pt.

- 20 11. Process according to any of Claims 1 to 10,

comprising the additional process step e'):

e') adding a solvent.

12. Process according to Claim 11,

- 25 wherein the solvent is selected from: THF, DCM, ACN, DMF, toluene, texanol, pentane, hexane, octane, isooctane, decane, dodecane, cyclohexane, benzene, xylene, Marlotherm, propylene carbonate, MTBE, diglyme, triglyme, diethyl ether, dioxane, isopropanol, tert-butanol, isononanol, isobutanol, isopentanol, ethyl acetate.

13. Process according to any of Claims 1 to 12,
wherein CO and H₂ are fed in at a pressure in a range from 1 MPa (10 bar) to 6 MPa (60 bar).

5 14. Process according to any of Claims 1 to 13,
wherein the reaction mixture is heated to a temperature in the range from 25°C to 150°C.

15. Process according to any of Claims 1 to 14,
wherein the olefin is selected from: ethene, propene, 1-butene, cis- and/or trans-2-butene,
10 isobutene, 1,3-butadiene, 1-pentene, cis- and/or trans-2-pentene, 2-methyl-1-butene, 3-
methyl-1-butene, 2-methyl-2-butene, hexene, tetramethylethylene, heptene, 1-octene, 2-
octene, di-n-butene, or mixtures thereof.

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