

Pt-xanthene-bromine complex

The present invention relates to a Pt-xanthene-bromine complex, and the use thereof for catalysis of a hydroformylation reaction.

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C. Botteghi et al., Journal of Molecular Catalysis A: Chemical 200, (2003), 147-156 describes the use of Pt(Xantphos)Cl₂ for hydroformylation of 2-tosyloxystyrene.

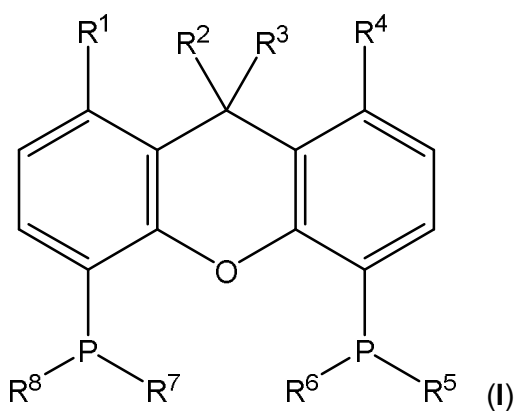
10 The problem addressed by the present invention is that of providing a novel complex. The complex here is to afford an enhanced yield in the catalysis of hydroformylation reactions compared to the Pt(Xantphos)Cl₂ complex described in the prior art.

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

15 Complex comprising:

a) Pt;

b) a ligand conforming to the formula (I):



where R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ are selected from: -H, -(C₁-C₁₂)-alkyl, -(C₆-C₂₀)-aryl;

20 and, if R¹, R², R³, R⁴, R⁵, R⁶, R⁷, R⁸ are -(C₆-C₂₀)-aryl, the aryl ring may have substituents selected from: -(C₁-C₁₂)-alkyl, -O-(C₁-C₁₂)-alkyl;

c) a bromine ligand.

25 The expression (C₁-C₁₂)-alkyl encompasses straight-chain and branched alkyl groups having 1 to 12 carbon atoms. These are preferably (C₁-C₈)-alkyl groups, more preferably (C₁-C₆)-alkyl, most preferably (C₁-C₄)-alkyl.

Suitable (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,
 5 1-propylbutyl, *n*-octyl, 2-ethylhexyl, 2-propylheptyl, nonyl, decyl.

The expression (C₆-C₂₀)-aryl encompasses mono- or polycyclic aromatic hydrocarbyl radicals having 6 to 20 carbon atoms. These are preferably (C₆-C₁₄)-aryl, more preferably (C₆-C₁₀)-aryl.

10 Suitable (C₆-C₂₀)-aryl groups are especially phenyl, naphthyl, indenyl, fluorenyl, anthracenyl, phenanthrenyl, naphthacenyl, chrysenyl, pyrenyl, coronenyl. Preferred (C₆-C₂₀)-aryl groups are phenyl, naphthyl and anthracenyl.

In one embodiment, R², R³, R⁵, R⁶, R⁷, R⁸ are selected from: -(C₁-C₁₂)-alkyl, -(C₆-C₂₀)-aryl.
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In one embodiment, R⁵, R⁶, R⁷, R⁸ are -(C₆-C₂₀)-aryl.

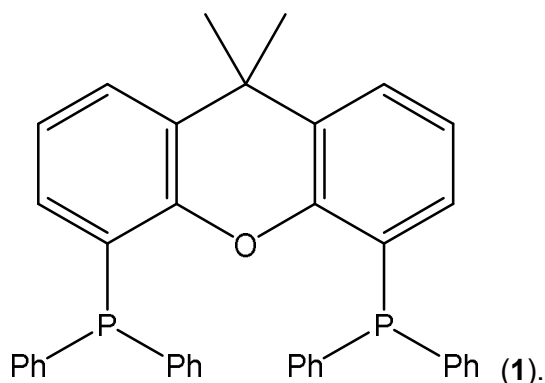
In one embodiment, R⁵, R⁶, R⁷, R⁸ are -Ph.

20 In one embodiment, R² and R³ are -(C₁-C₁₂)-alkyl.

In one embodiment, R² and R³ are -CH₃.

In one embodiment, R¹ and R⁴ are -H.
 25

In one embodiment, the ligand conforming to the formula (I) has the structure (1):



(1): Xantphos

In one embodiment, the complex has exactly one ligand corresponding to formula (I).

In one embodiment, the complex has at least two bromine ligands.

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In one embodiment, the complex has exactly two bromine ligands.

In one embodiment, the complex has the following structure: $\text{Pt}(\text{Xantphos})\text{Br}_2$.

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

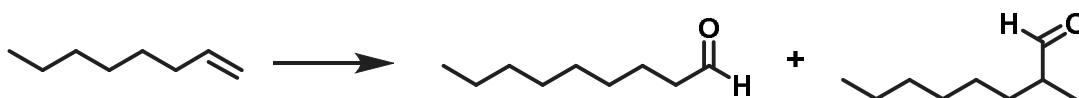
Use of a complex as described above for catalysis of a hydroformylation reaction.

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

Experimental description

20 A vial was charged with PtX_2 (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 of the 4560 series from Parr Instruments under an argon atmosphere. After purging the
 25 autoclave three times with CO/H_2 , the synthesis gas pressure was increased to 40 bar at 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.

30 Hydroformylation of 1-octene



Reaction conditions:

20 mmol of 1-octene, 1.0 mol% of Pt, 2.2 equivalents of Xantphos (**1**), solvent: toluene,

35 $p(\text{CO}/\text{H}_2)$: 40 bar, T: 120°C , t: 20 h.

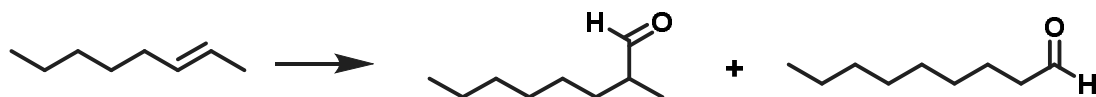
Yields:

PtBr₂: 99%

PtCl₂: 30%

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Variation of the halogen (2-octene)



Reaction conditions:

20 mmol of 2-octene, 1.0 mol% of Pt, 1.1 equivalents of Xantphos (**1**), solvent: toluene,

10 p(CO/H₂): 40 bar, T: 120°C, t: 20 h.

Yields:

PtBr₂: 99%

PtCl₂: 16%

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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):

20 40 bar, T: 120°C, t: 20 h.

Yields:

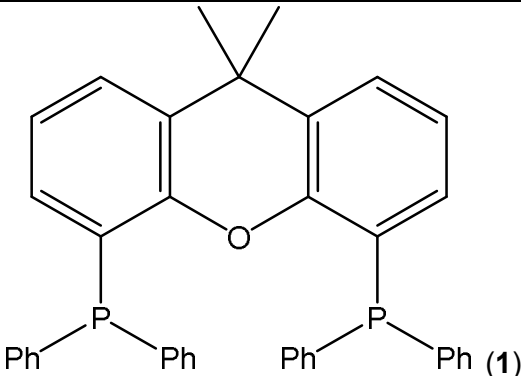
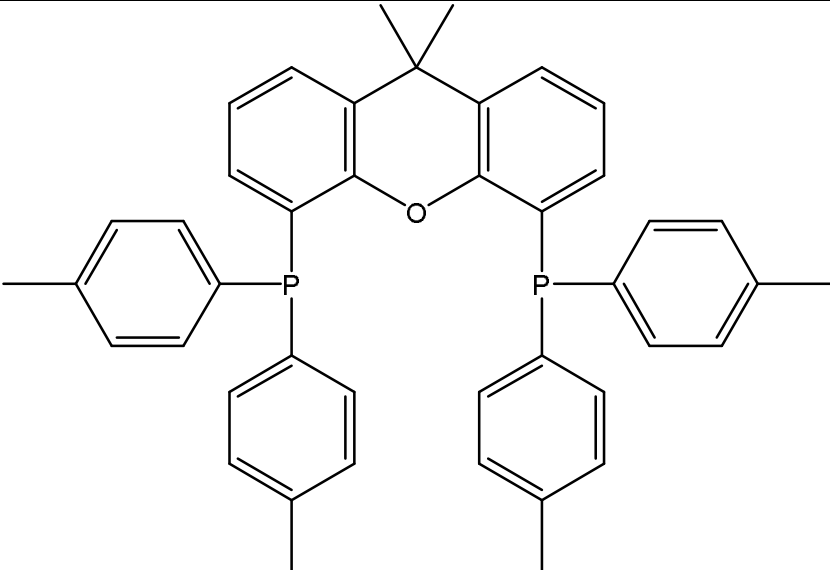
Ligand	Halogen	Yield [%]
	Br / Cl	97 / 5

25 Variation of the ligand and of the halogen

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.

5 Yields:

Ligand	Halogen	Yield [%]
 $\text{Ph}-\text{P}(\text{Ph})_2$ $\text{Ph}-\text{P}(\text{Ph})_2$ (1)	Br / Cl	85 / <1
	Br / Cl	81 / <1

Variation of the equivalents and of the halogen

10 Reaction conditions:

1.0 mmol of 1-octene, 1.0 mol% $\text{Pt}(\text{acac})_2$, LiX (X= halogen), 2.2 equivalents of Xantphos (**1**), solvent: toluene, $p(\text{CO}/\text{H}_2)$: 40 bar, T: 120°C, t: 20 h.

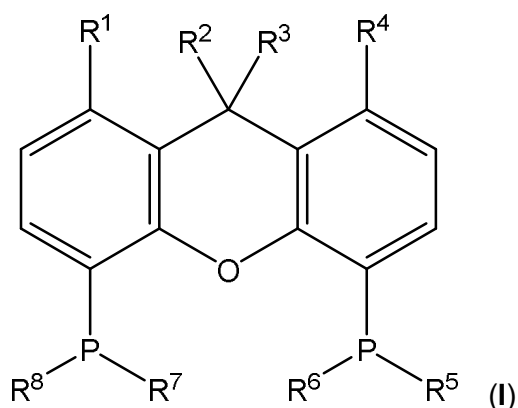
Equivalents of LiX	X	Yield [%]
0.5	Br	68

2.0	Br	71
1.5	Cl	0
4.0	Cl	0

As the experimental results show, the object is achieved by the complex according to the invention.

Claims

- 5 1. Complex comprising:
 a) Pt;
 b) a ligand conforming to the 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) a bromine ligand.

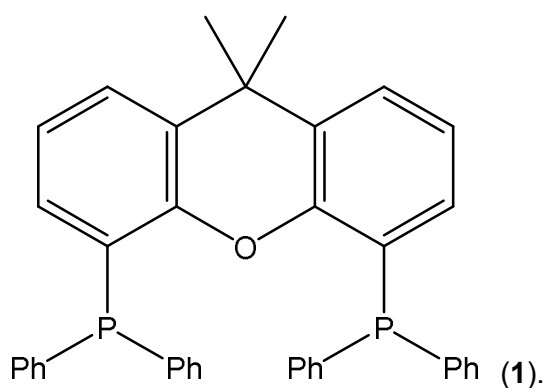
2. Complex according to Claim 1,
 15 where $R^2, R^3, R^5, R^6, R^7, R^8$ are selected from: -(C₁-C₁₂)-alkyl, -(C₆-C₂₀)-aryl.

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

- 20 4. Complex according to any of Claims 1 to 3,
 where R^2 and R^3 are -(C₁-C₁₂)-alkyl.

5. Complex according to any of Claims 1 to 4,
 where R^1 and R^4 are -H.

- 25 6. Complex according to any of Claims 1 to 5,
 wherein the ligand conforming to the formula (I) has the structure (1):



7. Complex according to any of Claims 1 to 6,
wherein the complex has exactly one ligand conforming to the formula (I).

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8. Complex according to any of Claims 1 to 7,
wherein the complex has at least two bromine ligands.

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

10 wherein the complex has exactly two bromine ligands.

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

wherein the complex has the following structure: $\text{Pt}(\text{Xantphos})\text{Br}_2$.

15 11. Use of a complex according to any of Claims 1 to 10 for catalysis of a hydroformylation reaction.