

## Supplementary information

### Diastereoisomeric Bisphosphite Ligands in the Hydroformylation of Octenes: Rhodium Catalysis and HP-NMR investigations

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## 1. Experimental section

### 1.1. General

All reactions were carried out using standard Schlenk techniques under an atmosphere of argon (Linde AG). Chemicals were purchased from Aldrich Chemical Co.. NMR spectra were obtained on a Bruker ARX 400 spectrometer using a standard 10 mm NMR probe and mass spectra were measured on an Intectra AMD 402 facility. IR data were acquired with a Nicolet 6700 FT-IR spectrometer (CaF<sub>2</sub>, 0.1 mm). IR measurement was performed using the depressurized hydride complex solutions in toluene-d<sub>8</sub> obtained from HP-NMR. Mass spectra were obtained on Finnigan MAT 95-XP (Thermo Electron) spectrometer. Elemental analyses (C, H, P) were performed using a Leco 932 Analyzer and a Perkin Elmer Lambda 2 UV-Vis spectrophotometer. For catalytic batches, a 200 ml Premex AG autoclave equipped with a gasinlet stirrer, Bronkhorst pressure control and gas flow metering devices was used.

### 1.2. Synthesis of **1**-(*S,S,R*)

a) Preparation of intermediate hydroxymonophosphite 2'-((*S*)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yloxy)-1,1'-(*S*)-binaphthyl-2-ol

*S*-(-)-Binol (1.970 g, 5.617 mmol) in thf (20 ml) is treated dropwise with a solution of *n*-butyl lithium (5.617 mmol) in hexane (18 ml) at -20°C. The reaction mixture is stirred for 20 min, brought to room temperature and then added to a solution of 4-chlorodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine (1.608 g, 5.617 mmol, obtained from phosphorus trichloride and *S*-(-)-binol) in thf (25 ml) at 0°C. After stirring overnight the solvent is removed in vacuo. The obtained residue is dissolved in toluene (100 ml), followed by filtration. Removal of solvent in vacuo and workup by column chromatography (dichloromethane/hexane= 2:1) gives a white solid (*R*<sub>f</sub>= 0.3, yield: 1.374 g, 40%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 4.89 (s, 1H, OH), 6.52-7.99 (m, 24H) ppm; <sup>31</sup>P-NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 145.6 (s) ppm. Elemental analysis (calc. for C<sub>40</sub>H<sub>25</sub>O<sub>4</sub>P= 600.6 g/mol): C 79.54 (79.99), H 4.36 (4.20)%.

b) **1**-(*S,S,R*). A mixture of the hydroxymonophosphite (0.944 g, 1.572 mmol) and triethyl amine (0.229 g, 2.26 mmol) in toluene (17 ml) is added dropwise to a solution of 4-chlorodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine (0.551 g, 1.572 mmol, obtained from phosphorus trichloride and *R*-(+)-binol) in toluene (12 ml) at 0°C. After stirring overnight at room temperature the reaction solution is filtered and the solvent is removed in vacuo. Toluene (15 ml) is added, followed by filtration and evaporation of the filtrate to dryness. The residue obtained is stirred with hexane (20 ml) for 5 h, separated by filtration and dried at 0.1 mbar/ 60°C. Yield: 1.37 g (95%). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 6.07 (d, 1H), 6.40 (d, 1H), 6.97-8.02 (m, 34 H) ppm; <sup>31</sup>P-NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 144.8 (d, *J*<sub>PP</sub>= 20.8 Hz), 146.5 (d, *J*<sub>PP</sub>= 20.8 Hz) 145.2

(s, impurity of **1**-(*S,S,S*) holding 5% of signal intensity) ppm. Elemental analysis (calc. for  $C_{60}H_{36}O_6P_2$  = 914.88 g/mol): C 78.76 (78.77), H 4.44 (3.97), P 6.75 (6.77)%. CI-MS (pos., isobutene):  $m/e$  915 ( $M^+$ , 1 %), 273 (100%).

### 1.3. Selenium adducts

The distinct diastereomer of **1** (91.5 mg, 0.1 mmol) was reacted with selenium (473.8 mg, 6 mmol) in boiling toluene (5 ml) for 17 h. After filtration, the filtrate was evaporated to dryness and the resulting residue dried in vacuo (0.1 mbar, 70°C, 4 h). Nearly quantitative yields of diselenides were obtained.

#### **1**-(*S,R,S*)Se<sub>2</sub>-toluene.

Elemental analysis (calc. for  $C_{67}H_{44}O_6P_2Se_2$ , M = 1164.93 g/mol): C 69.15 (69.08), H 3.87 (3.82), P 5.70 (5.32) %. ESI-MS ( $CH_3CN$ ,  $H_2O$ , 2%  $HCOOH$ ):  $m/e$  1090 ( $[M^+$ -toluene+O], 85%), 1073 ( $[M^+$ -toluene-H], 27%), 663 (100%).

#### **1**-(*R,R,R*)Se<sub>2</sub>.

Elemental analysis (calc. for  $C_{60}H_{36}O_6P_2Se_2$ , M = 1072.81 g/mol): C 67.75 (67.18), H 3.78 (3.38), P 5.42 (5.77) %. ESI-MS ( $CH_3CN$ ,  $H_2O$ , 2%  $HCOOH$ ):  $m/e$  1075 ( $[M^+$ +H], 10%), 1011 (30%), 947 (100%).

#### **1**-(*S,S,R*)Se<sub>2</sub>.

Elemental analysis (calc. for  $C_{60}H_{36}O_6P_2Se_2$ , M = 1072.81 g/mol): C 67.81 (67.18), H 3.76 (3.38), P 5.81 (5.77) %. ESI-MS ( $CH_3CN$ ,  $H_2O$ , 2%  $HCOOH$ ):  $m/e$  1137 ( $[M^+$ + $HCOO$ + $H_2O$ ], 44%), 1073 ( $M^+$ -H, 63%), 1011 (100%).

### 1.4. HP-NMR investigations

The samples for HP-NMR investigations contained the following amounts of precursors: [acacRh(COD-1.5)] (31 mg, 0.1 mmol), diastereomer of **1** (91.5 mg, 0.1 mmol). Compounds were dissolved in 2.2 ml toluene- $d_8$  under an atmosphere of argon and then transferred to a 10 mm sapphire HP-NMR tube under the exclusion of air. Syngas was fed into the solutions via capillary. Gas circulation, flow regulation and pressure adjustment, respectively, were performed as described in DE 103 33 143 (to LIKAT e.V., 17.07. 2003).

Spectroscopic data for hydride complexes:

[HRh(CO)<sub>2</sub>(**1**-(*S,R,S*))]. <sup>1</sup>H-NMR:  $\delta$  -10.57 ppm (d, <sup>1</sup> $J_{HRh}$  = 2.9 Hz, <sup>2</sup> $J_{HP}$  not resolved), <sup>31</sup>P-NMR:  $\delta$  167.5 ppm (d, <sup>1</sup> $J_{PRh}$  = 237.5 Hz). IR (CaF<sub>2</sub>, 0.1mm, toluene- $d_8$ ):  $\nu(CO)$  = 2020, 2070  $cm^{-1}$ .

[HRh(CO)<sub>2</sub>(**1**-(*R,R,R*))]. <sup>1</sup>H-NMR:  $\delta$  -10.37 ppm (dt, <sup>1</sup> $J_{HRh}$  = 4.8 Hz, <sup>2</sup> $J_{HP}$  = 6.8 Hz), <sup>31</sup>P-NMR:  $\delta$  167.0 ppm (<sup>1</sup> $J_{PRh}$  = 232.8 Hz). IR (CaF<sub>2</sub>, 0.1mm, toluene- $d_8$ ):  $\nu(CO)$  = 2013, 2023, 2067  $cm^{-1}$ .  $\nu(Rh-H)$  = 1991  $cm^{-1}$ .

[HRh(CO)<sub>2</sub>(**1**-(*S,S,R*))]. <sup>1</sup>H-NMR:  $\delta$  -10.37 ppm (<sup>1</sup> $J_{HRh}$  = 3.8 Hz, <sup>2</sup> $J_{HP}$  not resolved); <sup>31</sup>P-NMR:  $\delta$  169.4 ppm (<sup>1</sup> $J_{PRh}$  = 240 Hz, <sup>2</sup> $J_{PP}$  = 254 Hz), 164.6 ppm (<sup>1</sup> $J_{PRh}$  = 234 Hz, <sup>2</sup> $J_{PP}$  = 255 Hz). IR (Toluene- $D_8$ ):  $\nu(CO)$  = 2018, 2078  $cm^{-1}$ .

## 2. Semi-empirical calculations for complexes [HRh(CO)<sub>2</sub>(**1**)].

PM3 calculations for geometry optimization were performed within the WAVEFUNCTION Spartan06 software package. Based on *tbp*-geometry at rhodium, twelve complexes [HRh(CO)<sub>2</sub>(**1**)] were identified. **1**-(*R*<sub>eq</sub>,*R*,*R*<sub>eq</sub>) and **1**-(*S*<sub>eq</sub>,*R*,*S*<sub>eq</sub>) resulted in structural different rhodium complexes, (a) and (b), by exchanging axial hydride with the axial CO ligand. With the same operation applied to *ax,eq* coordinated **1**, only the (*S,S,R*)-diastereomer yielded in additional complexes by exchange of hydride<sub>*ax*</sub> with a CO<sub>*eq*</sub>.

Coordination modes of <b>1</b> in complexes <i>tbp</i> -[HRh(CO) <sub>2</sub> ( <b>1</b> )]	P-Rh-P (°)	Heat of formation (kcal/mol)
<i>S</i> <sub>eq</sub> , <i>S</i> , <i>R</i> <sub>eq</sub> (a)	<b>119.35</b>	<b>-519.63</b>
<i>S</i> <sub>eq</sub> , <i>S</i> , <i>R</i> <sub>ax</sub> (a)	107.90	-510.16
<i>S</i> <sub>ax</sub> , <i>S</i> , <i>R</i> <sub>eq</sub> (a)	107.45	-511.15
<i>S</i> <sub>eq</sub> , <i>S</i> , <i>R</i> <sub>eq</sub> (b)	<b>118.61</b>	<b>-520.70</b>
<i>S</i> <sub>eq</sub> , <i>S</i> , <i>R</i> <sub>ax</sub> (b)	109.17	-513.06
<i>S</i> <sub>ax</sub> , <i>S</i> , <i>R</i> <sub>eq</sub> (b)	105.27	-517.32
<i>R</i> <sub>eq</sub> , <i>R</i> , <i>R</i> <sub>eq</sub> (a)	<b>122.38</b>	<b>-521.22</b>
<i>R</i> <sub>eq</sub> , <i>R</i> , <i>R</i> <sub>eq</sub> (b)	<b>122.39</b>	<b>-521.33</b>
<i>R</i> <sub>ax</sub> , <i>R</i> , <i>R</i> <sub>eq</sub>	108.02	-512.83
<i>S</i> <sub>eq</sub> , <i>R</i> , <i>S</i> <sub>eq</sub> (a)	<b>121.76</b>	<b>-522.78</b>
<i>S</i> <sub>eq</sub> , <i>R</i> , <i>S</i> <sub>eq</sub> (b)	106.53	-509.52
<i>S</i> <sub>ax</sub> , <i>R</i> , <i>S</i> <sub>eq</sub>	111.03	-514.07