

# Rhodium cationic complexes using macrocyclic diphosphines as chiral ligands: Application in asymmetric hydroformylation

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## Abstract

The mononuclear complexes  $[\text{Rh}(\text{COD})(\text{OC}_n\text{P})]\text{BF}_4$  were prepared by adding 1,1'-binaphthyl-based diphosphine macrocyclic ligands ( $\text{OC}_n\text{P}$ ,  $n = 4-6$ ) to a dichloromethane solution of  $[\text{Rh}(\text{COD})_2]\text{BF}_4$  ( $\text{COD} = 1,5\text{-cyclooctadiene}$ ). Hydroformylation of styrene was carried out using solutions of rhodium-diphosphine catalyst prepared from  $[\text{Rh}(\text{acac})(\text{CO})_2]$  and chiral macrocyclic diphosphines  $\text{OC}_n\text{P}$ ,  $n = 2, 4-6$ . At 30 bar of  $\text{CO}/\text{H}_2$  (1:1) and  $65^\circ\text{C}$  regioselectivities in 2-phenylpropanal were  $> 92\%$  when all the chiral diphosphine was added in a P-P/Rh ratio of 2. The solution structure of the dominant species formed during the reaction of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  with  $(\text{rac})\text{-OC}_6\text{P}$  under hydroformylation conditions has been determined. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Asymmetric hydroformylation; Chiral macrocyclic diphosphine; Rhodium

## 1. Introduction

One interesting use of chiral macrocycles is as chiral auxiliaries in asymmetric catalysis [1]. Moderate conformational stability, allowing only tuned changes in

geometry, is a crucial feature and a necessary condition for chiral macrocycles if they are to be of use in asymmetric catalysis [2].

The conformational changes when the ligand is complexed with transition metals are expected to be dramatic and should significantly influence the reactivity and stereoselectivity in a transition metal-catalyzed reaction.

For a more detailed understanding of how and to what extent the intramolecular distances of complexing sites and asymmetric units affect asymmetric induction, a group of 1,1'-binaphthyl-based diphosphine macrocyclic ligands ( $\text{OC}_n\text{P}$ ,  $n = 2-6$ ) was synthesized by Widhalm and Klitschar [3] (Fig. 1). Their coordination to Ni and Pd and their use in asymmetric carbon-carbon coupling reactions were also studied [4].

This paper studies the coordination of some of these macrocyclic diphosphine ligands to rhodium complexes with a view to applying these systems as catalyst precursors in the asymmetric hydroformylation of styrene.

Rhodiumphosphine-catalyzed hydroformylation of alkenes is one of the most important applications of

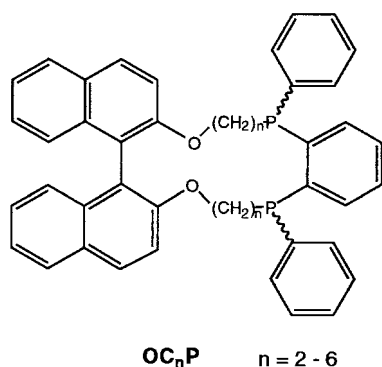


Fig. 1. 1,1'-Binaphthyl-based diphosphine macrocyclic ligands.

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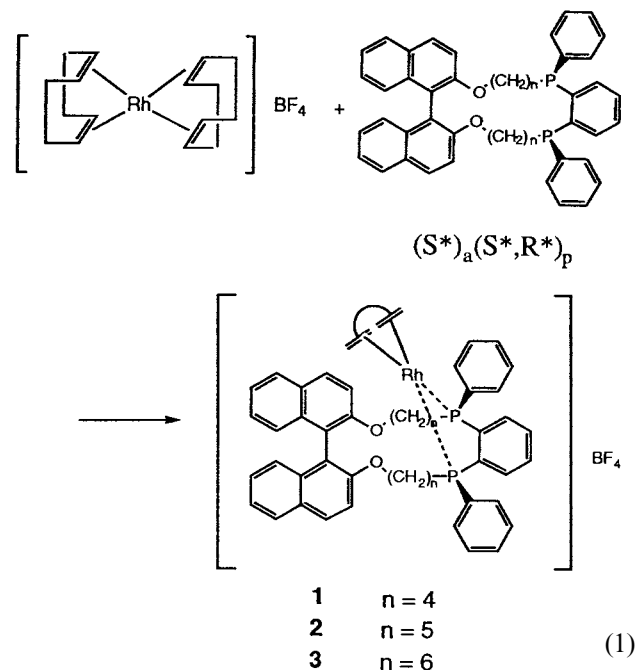
homogeneous catalysis in industry [5]. The regioselectivity depends on the stereochemistry of the trigonal bipyramidal complex  $[\text{RhH}(\text{CO})_2\text{L}_2]$  ( $\text{L}$  = monophosphine,  $\text{L}_2$  = diphosphine) formed under hydroformylation conditions; high regioselectivities in the hydroformylation of 1-alkenes have been obtained for both diphosphite- and diphosphine-modified catalysts [6]. Asymmetric hydroformylation is a potentially powerful process for synthesising a number of pharmacologically important compounds and different chiral building blocks [7]. Results for the enantioselective hydroformylation of a variety of olefins are best when the rhodium catalyst is used with the phosphine-phosphito ligand (*R,S*)-binaphos [8]. To the best of our knowledge macrocyclic diphosphine ligands have not been explored.

It is known that the stereo-electronic properties of phosphorus ligands have a dramatic influence on the reactivity of hydroformylation catalysts. Leitner and co-workers [9] recently investigated how structural changes in chelating ligands affect the coordination geometry of the  $[(\text{P}2)\text{Rh}]$  ( $\text{P}2 = \text{R}_2\text{P}-(\text{X})-\text{PR}_2$ ) fragment and attempted to correlate the results with catalytic activity. This influence varied according to the nature and length or, more precisely, the rigidity of the backbone ( $\text{X}$ ). From these results, Leitner et al. introduced the *accessible molecular surface* (AMS) model as a unique approach for describing steric ligand effects in homogeneous catalysis. This concept may serve as a general approach for understanding ligand effects on activity, and especially selectivity, in processes that are mainly governed by steric interactions. The fact that not only the size but also the shape of the cavity of the active fragment can be analysed opens up a whole range of possible applications. With a better insight into steric requirements at the substrate complexation sites, the attempts to optimize the ligand structure and so obtain high enantioselection will be made on a more rational basis.

## 2. Results and discussion

### 2.1. Preparation of $[\text{Rh}(\text{COD})(\text{OC}_n\text{P})]\text{BF}_4$ ( $n = 4-6$ ) complexes

The  $[\text{Rh}(\text{COD})(\text{OC}_n\text{P})]\text{BF}_4$  complexes ( $\text{COD} = 1,5$ -cyclooctadiene,  $n = 4$  (**1**),  $5$  (**2**),  $6$  (**3**)) were prepared by adding the corresponding racemic  $(S^*)_a(S^*,R^*)_p$  macrocyclic diphosphine ligand  $\text{OC}_n\text{P}$  ( $C_1$  symmetry) to a dichloromethane solution of  $[\text{Rh}(\text{COD})_2]\text{BF}_4$  (Eq. (1)). After stirring, the brown solution turned yellow. By addition of diethyl ether the complexes were isolated as moderately air-stable powders.



Elemental analysis of C and H matches the stoichiometry  $\{[\text{Rh}(\text{COD})(\text{OC}_n\text{P})]\}_x[\text{BF}_4]_x$  for all complexes. The FAB mass spectra show the heaviest ions at  $m/z = 899$  for complex **1**,  $927$  for complex **2** and  $955$  for complex **3**. This is indicative of the mononuclear cations  $[\text{Rh}(\text{COD})(\text{OC}_n\text{P})]^+$ . The IR spectra show a strong band between  $1090-1050\text{ cm}^{-1}$  and a medium band around  $450\text{ cm}^{-1}$  for all complexes. This is characteristic of the noncoordinated  $\text{BF}_4^-$  anion in cationic complexes [10].

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data for complexes **1**, **2** and **3** were assigned using HETCOR,  $^1\text{H}$ -,  $^{13}\text{C}$ - and COSY  $^1\text{H}$ - $^1\text{H}$ .

As expected, for a  $C_1$ -symmetrical ligand, the  $^1\text{H}$ -NMR spectrum for complex **1** shows the olefinic  $-\text{CH}=\text{CH}-$  protons of the coordinated COD ligand as four multiplet signals at 4.82, 4.89, 5.16 and 5.24 ppm. For complex **2**, three multiplet signals were observed and for complex **3** only two. For the *endo*- and *exo*-methylene protons of cyclooctadiene, two signals were observed in all complexes. Also as expected, four resonances were observed around 100 ppm in the  $^{13}\text{C}$ -NMR for the olefinic carbons of coordinated COD of complex **1** and **2**. For complex **3** only three resonances were observed. The rest of the  $^{13}\text{C}$ -NMR signals were in accordance with the coordination of the cyclooctadiene and diphosphine ligand (Table 1)

The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of **1-3** at room temperature in trichloromethane- $d_1$  show two doublets of doublets between 54 and 57 ppm ( $^1J_{\text{Rh-P}}$  around 150 Hz,  $^2J_{\text{P-P}}$  around 27 Hz) corresponding to the two nonequivalent phosphorus atoms of the diphosphine ligand, as expected for a  $C_1$ -symmetrical ligand.

Table 1  
 $^{13}\text{C}$ -NMR data for the rhodium complexes **1–3**<sup>a</sup>

	$\delta$ CH <sub>2</sub>	$\delta$ CH=	$\delta$ Car
1	21.43, 21.94, 26.54, <u>26.88</u> , 27.25, <u>27.61</u> , <u>27.85</u> , 29.43, 29.83, 30.31, 31.49, 31.69, 67.62, 68.81	98.61 (dd, $a = 6.2$ , $a = 8.5$ ), 100.67 ( $t$ , $a =$ 6.3), 102.94 ( $t$ , $a = 6.9$ ), 103.41 ( $t$ , $a = 7.4$ )	115.07, 116.42, 119.29 (C), 120.31 (C), 123.46, 123.56, <u>125.29</u> , 125.45 (C), 126.12, 126.34, 126.42 (C), <u>127.80</u> , <u>129.39</u> , 130.94, <u>131.21</u> , <u>131.43</u> , <u>131.55</u> (C), <u>132.23</u> , <u>133.21</u> , <u>133.90</u> (C), 155.32 (C), 155.41 (C)
2	25.50 (d, $J = 3.5$ ), 26.18 (d, $J = 6.3$ ), 26.30 (d, $J = 7.5$ ), 26.49 (d, $J = 8.3$ ), <u>26.79</u> , <u>27.15</u> , 27.34, 27.71, 29.08 (cod), 29.64 (cod), <u>30.15</u> (cod), 67.69, 67.78.	99.75 ( $t$ , $a = 8.3$ ), 100.12 ( $t$ , $a = 6.7$ ), 103.22 ( $t$ , $a = 7.5$ ), 103.71 ( $t$ , $a = 8.0$ )	114.73, 114.95, 120.11 (C), 120.59 (C), 123.33, 125.39, 126.19, 126.23, 127.39 (C), 127.80, 127.86, 129.13, 129.19 (C), 129.29, <u>129.51</u> (C), 129.64, 129.77, 130.89, <u>131.06</u> , <u>131.20</u> , <u>131.24</u> , <u>131.51</u> , <u>131.63</u> (C), 132.42 (C), <u>133.37</u> , <u>133.47</u> , <u>134.24</u> (C), 153.81 (C), 153.95 (C)
3	25.38, 25.51 (m), 25.57 (m), 26.91 (m), 27.28 (m), 27.62 (m), 27.82, 28.84, 29.16, 29.57 (cod), 29.66 (cod), 30.10 (m, cod), <u>30.15</u> , <u>30.73</u> , <u>30.94</u> , 68.93, 69.39	99.73 (m), 102.92 ( $t$ , $a = 7.5$ ), 103.38 ( $t$ , $a = 8.2$ )	115.63, 116.49, 120.36 (C), 120.95(C), 123.42, 123.54, 125.28, 125.36, 126.13, 127.74, <u>129.03</u> , <u>129.10</u> , <u>129.18</u> (C), <u>129.37</u> (C), 129.60, 129.72, <u>130.85</u> (C), <u>130.90</u> (C), <u>131.02</u> , <u>131.13</u> , <u>131.27</u> , <u>133.29</u> , 134.21 (C), 134.32 (C), 154.44 (C), 154.52 (C)

<sup>a</sup>  $J$  refers to PC coupling constants in Hz,  $a$  refers to C–X (where X = P or Rh) coupling constants in Hz. In spectral areas with extensive signal overlapping, multiplets could not be assigned; those signals of unclear relationship are underlined, ignoring probable multiplet structures.

Table 2  
 Styrene hydroformylation with  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{diphosphine}$  catalytic systems<sup>a</sup>

Entry	Diphosphine	P–P/Rh	$P$ (atm)	$t$ (h)	%C <sub>ald</sub> <sup>b</sup>	% 2-PP <sup>c</sup>	ee% <sup>d</sup>
1	( <i>S</i> )-OC <sub>2</sub> P	1	30	20	33	87	12 ( <i>S</i> )
2	( <i>S</i> )-OC <sub>4</sub> P	1	30	20	26	82	5 ( <i>S</i> )
3	( <i>S</i> )-OC <sub>5</sub> P	1	30	20	72	75	0
4	( <i>S</i> )-OC <sub>6</sub> P	1	30	20	43	77	0
5	–	–	30	2	78	63	–
6	( <i>S</i> )-OC <sub>2</sub> P	2	30	20	77	97	10 ( <i>S</i> )
7	( <i>S</i> )-OC <sub>4</sub> P	2	30	20	25	92	0
8 <sup>e</sup>	<i>rac</i> -OC <sub>5</sub> P	2	30	20	75	94	nd
9	<i>rac</i> -OC <sub>6</sub> P	2	30	20	81	97	nd
10	( <i>S</i> )-OC <sub>2</sub> P	1	75	12	54	92	5 ( <i>S</i> )
11	( <i>S</i> )-OC <sub>4</sub> P	1	75	12	95	82	4 ( <i>S</i> )
12	( <i>S</i> )-OC <sub>5</sub> P	1	75	18	99	91	0
13	( <i>S</i> )-OC <sub>6</sub> P	1	75	18	100	85	0

<sup>a</sup> Reaction conditions:  $T = 338$  K, styrene (10.2 mmol),  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.015 mmol), toluene (7.5 ml),  $\text{CO}/\text{H}_2 = 1$ .

<sup>b</sup> Aldehyde conversion measured by GC.

<sup>c</sup> 2-PP = 2-phenylpropanal.

<sup>d</sup> %ee was measured by CG with chiral column on the 2-phenylpropanoic acids obtained by oxidating the aldehydes with  $\text{KMnO}_4$ .

<sup>e</sup> 18% of ethylbenzene was also obtained.

## 2.2. Styrene hydroformylation

The macrocyclic ligands OC<sub>*n*</sub>P ( $n = 2, 4–6$ ) were used to prepare precursor systems in the hydroformylation of styrene by adding one or two equivalents of diphosphine to  $[\text{Rh}(\text{acac})(\text{CO})_2]$  [11] solution in toluene. These ligands with different chain lengths could provide different steric effects and arrangements around the metal center. Racemic and enantiomeri-

cally pure ligands were used at 30 and 75 bar of *syn* gas at 338 K (Table 2).

Adding the macrocyclic diphosphine ligands in a P–P/Rh ratio of one at 30 bar produces conversions in aldehydes between 26 and 72% with complete chemoselectivity, as expected for Rh/P systems in the hydroformylation of styrene (entries 1–4). Although macrocyclic ligands with different chain lengths were used, catalytic activity did not depend systematically

on the chain length of the ligand; the best conversion was for the (*S*)-OC<sub>5</sub>P (72%).

For comparison purposes, an experiment using

[Rh(acac)(CO)<sub>2</sub>] without diphosphine ligand was carried out to give higher activity and lower regioselectivity (entry 5). As expected, for [Rh(acac)(CO)<sub>2</sub>]/OC<sub>*n*</sub>P

Table 3

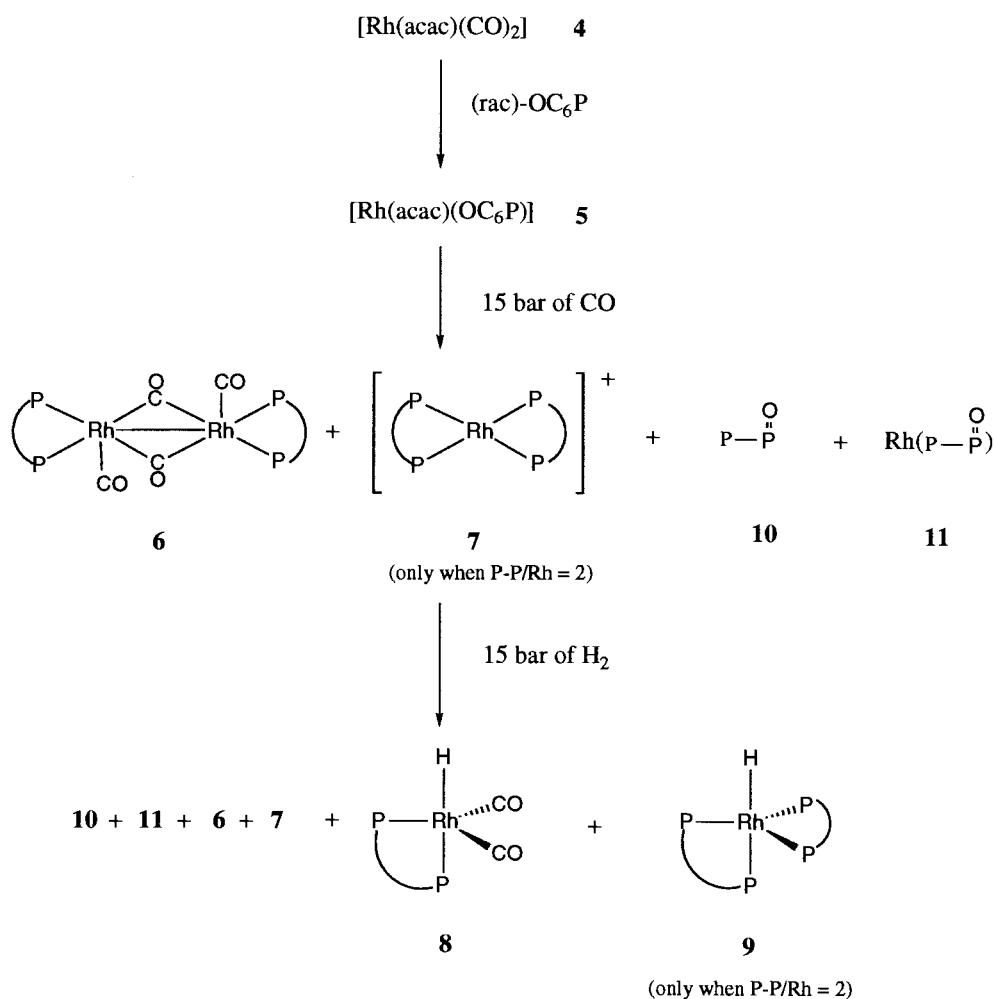
<sup>31</sup>P{<sup>1</sup>H}- and <sup>1</sup>H-NMR data of the species formed in the reaction of [Rh(acac)(CO)<sub>2</sub>]/*rac*-OC<sub>*n*</sub>P with CO/H<sub>2</sub>.

Compound	<sup>31</sup> P{ <sup>1</sup> H}-NMR		<sup>1</sup> H-NMR			<i>P</i> (atm)	
	δ (ppm)	<sup>1</sup> <i>J</i> <sub>Rh-P</sub> (Hz)	δ (ppm)	<sup>1</sup> <i>J</i> <sub>H-Rh</sub> (Hz)	<sup>2</sup> <i>J</i> <sub>H-P</sub> (Hz)	H <sub>2</sub>	CO
<b>5</b> <sup>a</sup>	65.27 66.82	117.8 119.7					
<b>6</b>	42.29 <sup>c</sup> 42.37 <sup>c</sup>	142.2 140.1				15	15
<b>7</b>	56.11 <sup>c</sup>	119.0					15
<b>8</b> <sup>b</sup>	52.94 53.34	117.2 115.4	-8.52	8.4	56.4	15	15
<b>9</b>	50.73	144.0	-10.51 <sup>c</sup>			15	15

<sup>a</sup> *J*<sub>P-P</sub> = 51.3.

<sup>b</sup> *J*<sub>P-P</sub> = 50.1.

<sup>c</sup> Broad.



Scheme 1. Intermediate species formed in the reaction of [Rh(acac)(CO)<sub>2</sub>] with *rac*-OC<sub>6</sub>P under hydroformylation conditions.

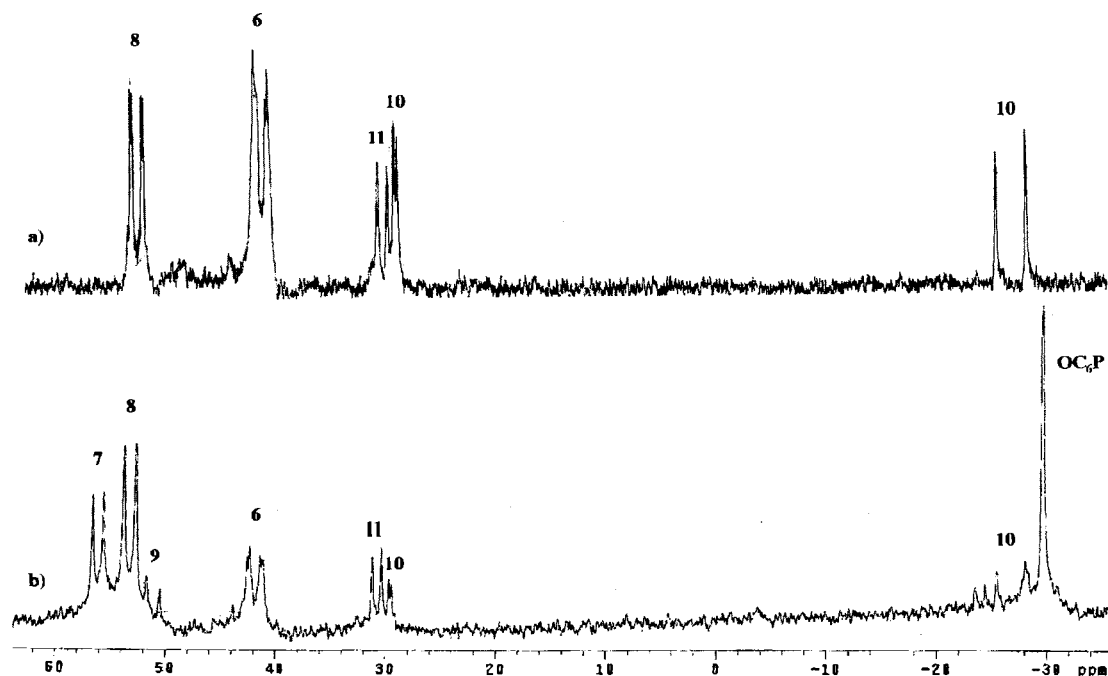


Fig. 2.  $^{31}\text{P}\{^1\text{H}\}$ -HPNMR spectrum of reaction of  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{rac-OC}_6\text{P}$  with  $\text{CO}$  and  $\text{H}_2$ : (a)  $\text{P-P/Rh} = 1$ ; (b)  $\text{P-P/Rh} = 2$ .

systems, the intermediate species are modified by the diphosphine ligand, as HPNMR studies under hydroformylation conditions showed (see below).

We studied the effect of increasing the P–P/Rh ratio to two and the  $\text{CO}/\text{H}_2$  pressure to 75 bar. Interestingly, the excess of the diphosphine ligand (entries 6–9) produces higher conversions in all cases except for the (*S*)- $\text{OC}_4\text{P}$  ligand, where conversion is similar (entries 2 and 7). For the *rac-OC*<sub>5</sub>P, 18% of hydrogenation to ethylbenzene was observed (entry 8). As far as regioselectivity is concerned, an excess of ligand, P–P/Rh = 2, produces higher regioselectivity in 2-phenylpropanal, as previously seen for other rhodium diphosphine systems (diphosphine = dppe, dppp, chiraphos, bdpp) [12].

With respect to the effect of the  $\text{CO}/\text{H}_2$  pressure, both conversions to aldehydes and regioselectivity in 2-phenylpropanal increased at higher pressure (75 bar) (entries 10–13). This is well known for rhodium systems in the hydroformylation of styrene [12b,13]. Only for (*S*)- $\text{OC}_4\text{P}$  diphosphine is the regioselectivity the same at 30 and 75 bar (entries 2 and 11)

At 30 bar, the percentage enantiomeric excess (*ee*%) was low (about 10%) for the precursor containing the most rigid (*S*)- $\text{OC}_2\text{P}$  diphosphine and there was practically no enantioselectivity for the other diphosphines.

### 2.3. Solution structure of the species formed during the reaction of $[\text{Rh}(\text{acac})(\text{CO})_2]$ with *rac-OC*<sub>6</sub>P under hydroformylation conditions

To find out the intermediate species formed during the

hydroformylation process, we made a spectroscopic study of the solution that resulted from adding: (a) 15 bar of  $\text{CO}$ ; and (b) 15 bar of  $\text{H}_2$  (30 bar of  $\text{CO}/\text{H}_2$ ) to solutions of  $\text{Rh}(\text{acac})(\text{CO})_2/\text{rac-OC}_6\text{P}$  (P–P/Rh = 1 and P–P/Rh = 2) in toluene-*d*<sub>8</sub>.

The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of solutions of  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{rac-OC}_6\text{P}$  (P–P/Rh = 1 and P–P/Rh = 2) showed two doublets of doublets at 65.27 and 66.82 ppm (Table 3) (AB part of an ABX spectrum) attributed to the mononuclear rhodium complex **5** (Scheme 1).

#### 2.3.1. 15 bar of $\text{CO}$

When P–P/Rh = 1, the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the solution showed two broad doublets at 42.29 and 42.37 ppm assigned to complex **6** (Scheme 1, Table 3). This type of signal was previously assigned to carbonyl diphosphine dimers  $[\text{Rh}(\text{CO})_2(\text{diphosphine})]_2$  (diphosphine = dppe, dppp, diop, bdpp) [14] and  $[\text{Rh}_2(\text{CO})_{8-x}\text{L}_x]$  ( $x = 0-2$ , L = phosphite) [15] which have a Rh–Rh bond and two CO groups bridging the metal atoms. The fact that there were only two broad doublets for this AA'A''A'''XX' spin system proves either the fast equilibration of several isomers or, possibly, the predominance of a highly symmetrical species. There was also a set of signals centered at 30 and –27 ppm, which could be attributed to **10**, formed by partial oxidation of the free diphosphine, and a group of signals at 31 ppm which were attributed to rhodium complexes **11** derived from **10**.

With P–P/Rh = 2, a broad doublet at 56.11 ppm ( $^1J_{\text{P-Rh}} = 119$  Hz) appears. This is attributed to a square

planar cationic rhodium complex **7** (Scheme 1) with two diphosphines coordinated to the metal center. Related compounds have previously been reported,  $[\text{Rh}(\text{L-L})_2]^+$  ( $\text{L-L} = \text{dppe}$ ,  $\text{dppp}$ ,  $\text{bdpp}$ ), which show similar rhodium–phosphorus coupling constants [14b,16].

### 2.3.2. 15 bar of CO and 15 bar of H<sub>2</sub>

When the solution was pressurized at r.t. with 15 bar of H<sub>2</sub> (30 bar of CO/H<sub>2</sub>), after a few minutes, the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum, at 65°C, showed two new doublets of doublets at 52.94 and 53.34 ppm (AB part of and ABX system), attributed to mononuclear hydride–rhodium complex **8** (Scheme 1, Figs. 2 and 3). The

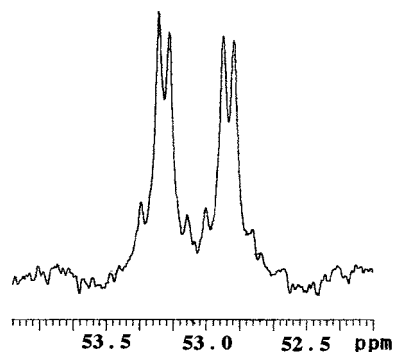


Fig. 3.  $^{31}\text{P}\{^1\text{H}\}$ -HPNMR spectrum of compound **8**.

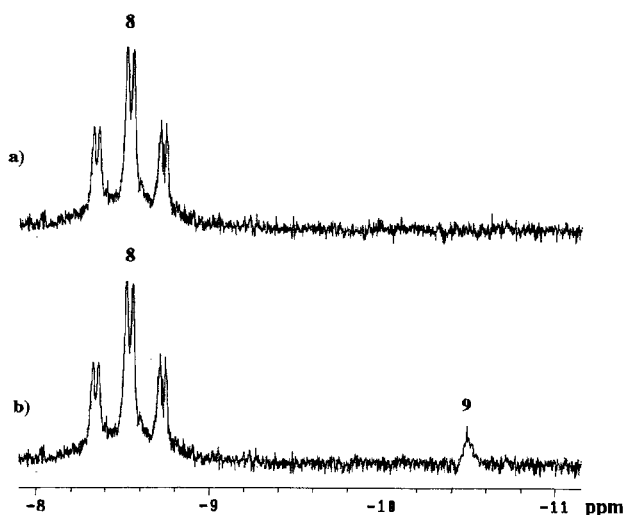
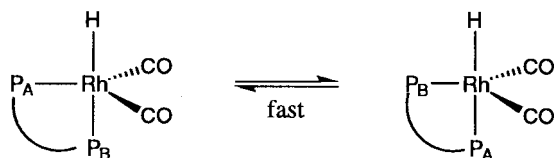


Fig. 4.  $^1\text{H}$ -HPNMR spectrum of reaction of  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{rac-OC}_6\text{P}$  with CO and H<sub>2</sub> in the high-field region: (a)  $\text{P-P/Rh} = 1$ ; (b)  $\text{P-P/Rh} = 2$ .



Scheme 2. Equatorial–axial phosphorus exchange.

$^1\text{H}$ -NMR of this solution revealed a doublet pseudo triplet in the hydride region (Table 3, Fig. 4), indicative of the coupling of a hydride with the rhodium and two almost equivalent phosphorus nuclei. Phosphorus–hydride coupling constants observed ( $^2J_{\text{H-P}} = 56.4\text{ Hz}$ ) are in agreement with a time-averaged *cis*, *trans* relationship between the phosphorus and hydride nuclei [14b]. A fast equatorial–axial exchange of the phosphorus atoms results in averaged rhodium–phosphorus coupling constants of 117.2 and 115.4 Hz (Scheme 2).

After 90 min, with  $\text{P-P/Rh} = 2$ , there was a new broad doublet in the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum at 50.73 ppm ( $^1J_{\text{Rh-P}} = 144\text{ Hz}$ ) (Fig. 2(b)). The  $^1\text{H}$ -NMR spectrum also revealed a new broad signal in the hydride region at  $-10.5\text{ ppm}$  (Fig. 4(b)). This new phosphorus–hydride–rhodium complex could be attributed to the mononuclear rhodium complex **9** (Scheme 1) since the spectroscopic data agree well with those previously reported for compounds  $[\text{HRh}(\text{L-L})_2]$ , where  $\text{L-L} = \text{dppe}$  ( $^1J_{\text{Rh-P}} = 142.5\text{ Hz}$ ),  $\text{dppp}$  ( $^1J_{\text{Rh-P}} = 141.8\text{ Hz}$ ),  $\text{diop}$  ( $^1J_{\text{Rh-P}} = 146\text{ Hz}$ ) and  $\text{bdpp}$  ( $^1J_{\text{Rh-P}} = 141\text{ Hz}$ ) [14b,16c].

It is important to note that the amount of species **8** increased with respect to the others in solution when an excess of diphosphine was used (estimated proportion of species  $\mathbf{8/11} = 1.3$  and  $\mathbf{8/6} = 0.7$  for  $\text{P-P/Rh} = 1$ ;  $\mathbf{8/11} = 2.2$  and  $\mathbf{8/6} = 1.7$  for  $\text{P-P/Rh} = 2$ ) (Fig. 2).

In summary, this study reveals several species under hydroformylation conditions (Scheme 1). Several papers have described type **8** species as being responsible for the catalytic activity [8a,14b]. The partial oxidation of the diphosphine ligand causes the formation of species **11**, where the P–P ligand is bound in monodentate fashion. This species could evolve into monodentate species [14b,17], which are known to be active and less regioselective than the corresponding chelate species in the hydroformylation of styrene. On the other hand the dinuclear inactive species **6**, which has been described to be in equilibrium with the pentacoordinated species **8** [14b], is also present. Species with two diphosphines coordinated to the rhodium center **7** and **9**, have been observed when  $\text{P-P/Rh} = 2$ . As far as we know, these species are inactive under hydroformylation conditions.

How a change in the  $\text{P-P/Rh}$  ratio from one to two affects conversion and regioselectivity in the hydroformylation experiments may now be explained by the increased concentration of species **8** when excess diphosphine is added.

## 3. Experimental

### 3.1. General comments

All the rhodium complexes were synthesized using standard Schlenk techniques under argon atmosphere. The complexes  $[\text{Rh}(\text{cod})_2]\text{BF}_4$  [18],  $[\text{Rh}(\text{acac})(\text{CO})_2]$  [11]

and the diphosphine ligands [3] were prepared by previously described methods. Solvents were purified by standard procedures. All other reagents were used as commercially available. Elemental analyses were performed on a Carlo–Erba EA-1108 instrument.  $^1\text{H}$ -,  $^{13}\text{C}\{^1\text{H}\}$ - and  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Chemical shifts are relative to  $\text{SiMe}_4$  ( $^1\text{H}$  and  $^{13}\text{C}$ ) as internal standard or  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ) as external standard. All assignments in NMR spectra were determined by COSY and HETCOR spectra. A VG-Autospect equipment was used for fast atom bombardment (FAB) mass spectral analyses. The matrix was *m*-nitrobenzylalcohol. Gas chromatographic analyses were run on a Hewlett–Packard HP 5890A instrument (split/splitless injector, J&W Scientific, Ultra-2 25 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 150 kPa He, F.I.D. detector) equipped with a Hewlett–Packard HP 3396 series II integrator. Enantiomeric excesses were measured after oxidation of the aldehydes to the corresponding carboxylic acids on a Hewlett–Packard HP 5890A gas chromatograph (split/splitless injector, J&W Scientific, FS-Cyclodex  $\beta$ -I/P 50 m column, internal diameter 0.2 mm, film thickness 0.33 mm, carrier gas: 100 kPa He, F.I.D. detector). Absolute configuration was determined by comparing the retention times with optically pure (*S*)-(+)-2-phenylpropionic and (*R*)-(–)-2-phenylpropionic acids. Hydroformylation reactions were carried out in a home-made 100 ml stainless steel autoclave.

### 3.2. Preparation of rhodium complexes

Diphosphine ligand (0.1 mmol) was added to a solution of  $[\text{Rh}(\text{cod})_2]\text{BF}_4$  (40.5 mg, 0.1 mmol) in 2 ml of dichloromethane. After 10 min, the desired products were obtained by precipitation with diethyl ether.

#### 3.2.1. $[\text{Rh}(\text{COD})(\text{OC}_4\text{P})]\text{BF}_4$ (1)

Yield: 79 mg (80%, yellow solid). Elemental analysis. Found (%): C, 65.53; H, 5.43. Anal. Calc. (%) for  $\text{RhC}_{54}\text{H}_{54}\text{O}_2\text{P}_2\text{BF}_4$ : C, 65.74; H, 5.52. FAB-MS:  $m/z$ : 899  $[\text{M}^+]$ .  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ ),  $\delta$ (ppm): 54.32 (dd, 1P,  $J_{\text{P-P}} = 26.72$  Hz,  $J_{\text{P-Rh}} = 150.55$  Hz), 55.40 (dd, 1P,  $J_{\text{P-P}} = 26.72$  Hz,  $J_{\text{P-Rh}} = 148.57$  Hz).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ),  $\delta$ (ppm): 1.10–1.90 (m, 10H,  $\text{CH}_2$ ,  $\text{CH}_2$  cod), 2.00–2.90 (m, 10H,  $\text{CH}_2$ ,  $\text{CH}_2$  cod), 3.60–4.10 (m, 4H,  $\text{CH}_2\text{-O}$ ), 4.82 (m, H,  $\text{CH=}$ ), 4.89 (m, H,  $\text{CH=}$ ), 5.16 (m, 1H,  $\text{CH=}$ ), 5.24 (m, 1H,  $\text{CH=}$ ), 7.05–8.00 (m, 26H, Ar).

#### 3.2.2. $[\text{Rh}(\text{COD})(\text{OC}_5\text{P})]\text{BF}_4$ (2)

Yield: 87 mg (86%, yellow solid). Elemental analysis. Found (%): C, 67.01; H, 5.61. Anal. Calc. (%) for  $\text{RhC}_{56}\text{H}_{58}\text{O}_2\text{P}_2\text{BF}_4$ : C, 66.29; H, 5.76. FAB-MS:  $m/z$ : 927  $[\text{M}^+]$ .  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ ),  $\delta$ (ppm): 54.92 (dd, 1P,  $J_{\text{P-P}} = 27.02$  Hz,  $J_{\text{P-Rh}} = 149.37$  Hz), 56.20 (dd, 1P,

$J_{\text{P-P}} = 27.02$  Hz,  $J_{\text{P-Rh}} = 149.99$  Hz).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ),  $\delta$ (ppm): 1.10–1.70 (m, 8H,  $\text{CH}_2$ ), 1.80–2.10 (m, 4H,  $\text{CH}_2$  cod), 2.10–2.80 (m, 12H,  $\text{CH}_2$ ,  $\text{CH}_2$  cod), 3.80–4.00 (m, 4H,  $\text{CH}_2\text{-O}$ ), 4.91 (m, 2H,  $\text{CH=}$ ), 5.23 (m, 1H,  $\text{CH=}$ ), 5.42 (m, 1H,  $\text{CH=}$ ), 7.05–8.00 (m, 26H, Ar).

#### 3.2.3. $[\text{Rh}(\text{COD})(\text{OC}_6\text{P})]\text{BF}_4$ (3)

Yield 85 mg (81%, yellow solid). Elemental analysis. Found (%): C, 66.59; H, 6.18. Anal. Calc. (%) for  $\text{RhC}_{58}\text{H}_{62}\text{O}_2\text{P}_2\text{BF}_4$ : C, 66.80; H, 5.99. FAB-MS:  $m/z$ : 955  $[\text{M}^+]$ .  $^{31}\text{P}$ -NMR ( $\text{CDCl}_3$ ),  $\delta$ (ppm): 55.14 (dd, 1P,  $J_{\text{P-P}} = 27.02$  Hz,  $J_{\text{P-Rh}} = 149.26$  Hz), 55.39 (dd, 1P,  $J_{\text{P-P}} = 27.02$  Hz,  $J_{\text{P-Rh}} = 150.58$  Hz).  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ),  $\delta$ (ppm): 1.10–1.20 (m, 4H,  $\text{CH}_2$ ), 1.20–1.70 (m, 10H,  $\text{CH}_2$ ), 1.80–2.10 (m, 4H,  $\text{CH}_2$  cod), 2.20–2.70 (m, 10H,  $\text{CH}_2$ ,  $\text{CH}_2$  cod), 3.70–4.10 (m, 4H,  $\text{CH}_2\text{-O}$ ), 4.82 (m, 2H,  $\text{CH=}$ ), 5.43 (m, 2H,  $\text{CH=}$ ), 7.00–8.00 (m, 26H, Ar).

### 3.3. Hydroformylation of styrene

The autoclave was purged three times with CO. The solution was formed from  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.015 mmol), diphosphine and substrate (10.2 mmol) in toluene (7.5 ml). After pressurizing to the desired pressure with *syn* gas and heating the autoclave to the reaction temperature, the reaction mixture was stirred. During the reaction several samples were taken from the autoclave. After the desired reaction time, the autoclave was cooled to r.t. and depressurized. The reaction mixture was analysed by gas chromatography.

The aldehydes obtained from the hydroformylation were oxidized to carboxylic acids to determine the enantioselective excess. A small portion of the hydroformylation reaction mixture (2 ml) was added to the solution prepared from 10 ml of a potassium permanganate 1 M solution and 10 ml of a potassium dihydrogenphosphate 1.25 M solution. After 1 h of agitation, 5 ml of a saturated solution of sodium sulfite was added. Diluted hydrochloric acid was then added until the brown precipitate of manganese(IV) oxide disappeared. The acids formed were extracted with diethyl ether ( $3 \times 10$  ml) and the organic phase was concentrated to dryness. A 2 M solution of sodium hydroxide (10 ml) was then added. After washing the solution with diethyl ether, 10 ml of concentrated hydrochloric acid was added and the product was extracted with diethyl ether ( $3 \times 10$  ml). The carboxylic acids were obtained after washing the etheric phase with water, drying it with magnesium sulfate and evaporating it to dryness.

### 3.4. In situ HPNMR experiments

In a typical experiment a sapphire tube ( $\varnothing = 10$  mm) was filled under argon with a solution of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.030 mmol) and diphosphine ligand

(molar ratio P–P/Rh = 1 or 2) in toluene- $d_8$  (1.5 ml). The HPNMR tube was purged twice with CO and pressurized to the appropriate pressure of CO/H<sub>2</sub>. After a reaction time of 15 h with constant shaking at r.t., the solution was analysed at the appropriate temperature.

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