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Rhodium-diphosphine catalysts for the hydroformylation of styrene: the influence of the excess of ligand and the chelate ring size on the reaction selectivity

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Abstract

This study discusses the hydroformylation of styrene using rhodium systems containing four structurally related diphosphines: 1,2-bis(diphenylphosphine)ethane **1** (dppe), 1,3-bis(diphenylphosphine)propane **2** (dppp), (*R,R*)-2,3-bis(diphenylphosphine)butane **3** (chiraphos) and (*S,S*)-2,4-bis(diphenylphosphine)pentane **4** (bdpp). A systematic analysis of the effect of the pressure, temperature and the ligand to metal molar ratio for these catalytic systems shows that the five- and six-membered ring chelating diphosphines behave different. The regio- and enantioselectivity observed provide evidence of the catalytic species involved in the process. By analyzing the selectivity of the catalytic systems formed by mixing $PEtPh_2$ and the chiral diphosphine ligands, we propose a model describing the equilibria among the catalytic species.

Keywords: Rhodium; Hydroformylation; Asymmetric catalysis; Diphosphine; Styrene, chelate; Ring size

1. Introduction

The control of the reactivity and selectivity in transition metal catalyzed reactions by the use of chelating diphosphane ligands is well documented [1,2]. Hydroformylation is one of the most extensively studied homogeneous catalytic processes [3]. In this reaction, the regioselective production of linear aldehydes remains as a focus for academic and industrial research. In this context, the use of rhodium catalysts modified by chelating diphosphines was first reported 15 years ago [4,5], but it was only recently that some specially designed ligands were shown to substantially improve the selectivity in the hydroformylation of 1-alkenes [6–11]. Casey developed the natural bite angle model

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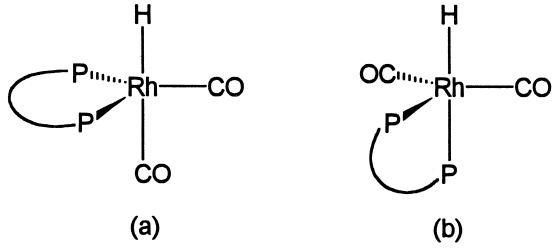
[12], which is a useful tool for correlating the selectivity produced by rhodium-diphosphane catalysts with the geometry of the ligands. In this approach, the regioselectivity depends on the stereochemistry of the trigonal bipyramidal complex, commonly accepted as the catalytic species formed by rhodium precursors and diphosphines under hydroformylation conditions. Thus, chelating P-donor ligands with a natural bite angle of nearly 120°, which are suitable for bis-equatorial chelation (a), yield higher normal to branched ratios than electronically comparable ligands with bite angles around 90°, which coordinate in an equatorial–axial fashion (b) [13].



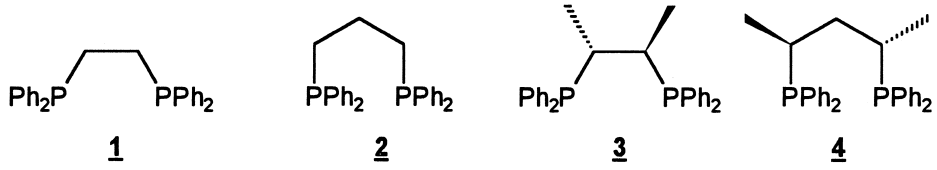
Nevertheless, a satisfactory explanation for the correlation between the catalytic results and the geometry imposed by the ligands has yet to be provided [14].

Deuteroformylation was first reported by Lazzaroni et al. [15] as a means to analyze the regioselectivity of styrene hydroformylation. He and other authors have shown that the regioselectivity in different catalytic systems can be explained by considering the relative rates of the two possible insertions of the olefin into the Rh–H, which lead to the two Rh-alkyl isomeric intermediates, as well as the rates of the β-elimination of these species [16,17].

Asymmetric hydroformylation is a potentially powerful process for the synthesis of a number of pharmacologically important compounds and different chiral building blocks [18]. Chiral P-donor ligands have been extensively used with Rh and Pt catalyst precursors for this reaction [19,20]. In the enantioselective hydroformylation of 1-alkenes, the branched aldehyde is the valuable product. Rhodium complexes of chiral diphosphites, which coordinates the metal in equatorial–equatorial positions, have been used in the asymmetric hydroformylation of styrene. Surprisingly, these catalysts yield high branched regioselectivity, and good enantioselectivity [21–24]. However, by using the rhodium catalyst with the phosphine-phosphito ligand (*R*,*S*)-binaphos, which coordinates the metal in an axial–equatorial form [25], the best results have so far been obtained in enantioselective hydroformylation of a variety of olefins [26]. It has also been reported that the modifications on the electronic effects on the substituents of the P atoms considerably influences both the regio- [27,28] and enantioselectivity [29] of the hydroformylation reaction catalyzed by rhodium-diphosphines. Finally, it has recently been reported that for the rhodium catalyst containing the chiral 2,4-bis(diphenylphosphino)pentane (bdpp) ligand the enantioselectivity heavily depends on the ligand to metal molar ratio [30]. This result indicates that equilibria among catalytically active species or intermediates must be taken into account in the case of rhodium-diphosphine catalysts, as is currently accepted in the case of P-donor monodentate co-catalysts.

To sum up, despite the progress made in the field of Rh-diphosphine hydroformylation catalysts, there as yet no real understanding of the intimate control of the regio- and enantioselectivity of the reaction. Although it is clear that it is a combination of electronic and steric factors of all the active species present under reaction conditions which determines the overall selectivity of the reaction, the models available for predicting or even explaining the behavior of the catalytic systems have only a

limited applicability. We believe that systematic studies on the effect that different parameters have on the selectivity of the reaction can help to rationalize the plethora of results accumulated for this reaction in the last 25 years. Along these lines, we report here the results of hydroformylation of styrene using four structurally related diphosphines with a C_2 axis: 1,2-bis(diphenylphosphine)ethane **1** (dppe), 1,3-bis(diphenylphosphine) propane **2** (dppp), (*R*,*R*)-2,3-bis(diphenylphosphine)butane **3** (chiraphos), and (*S*,*S*)-2,4-bis(diphenylphosphine)pentane **4** (bdpp).



1 **2** **3** **4**

Ligands **1** and **3** form five-member chelating rings, while **2** and **4** are six-member chelating ligands. Since they all have natural bite angles of nearly 90°, they would coordinate rhodium in equatorial–axial form. We studied the effect of three reaction parameters: pressure, temperature, and the ligand/metal molar ratio for each catalytic system. We also analyze the correlation between these results, the size of the chelating ring and the presence of stereogenic centers on the ligands.

2. Experimental

2.1. General methods

All the solutions were handled by standard Schlenk techniques, under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. Phosphines were of commercial origin, and they were used as supplied. The complex $[Rh_2(\mu\text{-OMe})_2(cod)_2]$ (cod = 1,5-cyclooctadiene) was prepared as previously reported [31]. Reaction conversions and regioselectivities were measured by gas chromatography in a Hewlett-Packard 5890A with an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) (25 m × 0.2 mm Ø) column. A chiral column FS-cyclodex β-I/P (50 m × 0.25 mm Ø) was used to determine the enantiomeric excess.

2.2. Catalysis

Hydroformylation experiments were carried out in a home-made autoclave with magnetic stirring. To prevent direct contact with the stainless steel, the catalytic solution was kept in a glass vessel, and the autoclave cap was Teflon-covered. Constant temperature was controlled by a preheated water bath circulating through an external autoclave jacket.

2.2.1. Standard hydroformylation experiment

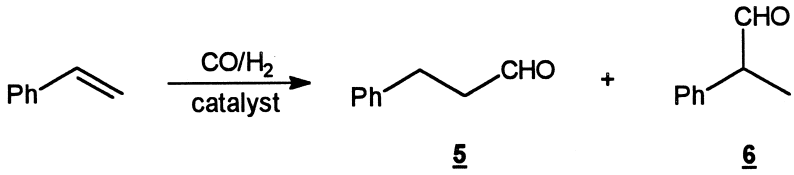
The catalyst precursor $[Rh_2(\mu\text{-OMe})_2(cod)_2]$ (0.0125 mmol), the diphosphine in the desired molar ratio, and styrene (10 mmol) were dissolved in 15 ml of toluene. The solution was transferred into the evacuated autoclave, which was then pressurized with syn-gas to about 80% of the reaction pressure. The pre-heated water circuit was connected to the autoclave jacket. When thermal equilibrium was reached (5–10 min), more gas mixture was introduced until the working pressure was achieved. At

the end of the reaction, the autoclave was cooled to room temperature and depressurized. Samples were analyzed by gas chromatography. Enantiomeric excesses were measured by GC using a chiral column after the aldehydes had been transformed into the carboxylic acids or alcohols, following described procedures [32].

3. Results

3.1. The influence of the nature of the diphosphine and the reaction conditions on the regioselectivity

The hydroformylation of styrene yields two isomeric aldehydes, 3-phenylpropanal **5**, and 2-phenylpropanal **6**:



5 **6**

In the second compound, a stereogenic center was created, so that the enantioselectivity of the reaction could be controlled by using chiral ligands, such as **3** and **4**.

The catalytic solutions were prepared by dissolving the appropriate amounts of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ and the corresponding diphosphine in toluene. Under syn-gas, the mixture forms rhodium hydrido carbonyl diphosphine complexes, as has been recently demonstrated for the case of ligand **4** [33].

The results of the hydroformylation of styrene with the rhodium catalysts of ligands **1**–**4** are collected in Tables 1–4, respectively. At least two samples were taken at different times along each experiment, and the conversion and selectivity were determined. Since the selectivity measured was independent of the reaction time, within the experimental error, it can be inferred that the catalytically active species did not evolve during the reaction. The selectivity was explored at two different pressures and temperatures. Thus, four different experiments were carried out for each ligand at different ligand to metal molar ratios. As expected, for rhodium phosphine catalysts the chemoselec-

Table 1
Hydroformylation of styrene with rhodium-**1** catalytic system[a]

Entry	*P* (bar)	*T* (°C)	[**1**]/[Rh][b]	Con. (%)[c]	*t* (h)	Ald. (%)[d]	Bra. (%)[e]
1	8	65	1.25	28	7	99	72
2	8	65	2	14	7	99	65
3	8	80	1.25	> 99	7	> 99	67
4	8	80	2	98	11	> 99	63
5	30	65	1.25	83	18	96	90
6	30	65	2	85	18	94	90
7	30	80	1.25	99	12	99	87
8	30	80	2	97	7	99	86

[a]Reaction conditions: 10 mmol of styrene, and 0.0125 mmol of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 15 ml of toluene. $P(CO) = P(H_2)$. [b]Ligand to metal molar ratio. [c]Converted olefin as percent of the initial amount. [d]Percent of aldehydes relative to the olefin converted. [e]Branched aldehyde **6** relative to the total amount of aldehyde formed.

Table 2
Hydroformylation of styrene with rhodium-**2** catalytic system[a]

Entry	*P* (bar)	*T* (°C)	[**2**]/[Rh][b]	Con. (%)[c]	*t* (h)	Ald. (%)[d]	Bra. (%)[e]
9	8	65	1.25	99	12	99	83
10	8	65	2	43	7	99	90
11	8	80	1.25	> 99	7	> 99	59
12	8	80	2	99	5	> 99	63
13	30	65	1.25	94	7	99	91
14	30	65	2	66	7	97	91
15	30	80	1.25	99	7	99	81
16	30	80	2	99	12	99	88

[a]Reaction conditions: 10 mmol of styrene, and 0.0125 mmol of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 15 ml of toluene. $P(CO) = P(H_2)$.[b]Ligand to metal molar ratio. [c]Converted olefin as percent of the initial amount. [d]Percent of aldehydes relative to the olefin converted. [e]Branched aldehyde **6** relative to the total amount of aldehyde formed.

Table 3
Hydroformylation of styrene with rhodium-**3** catalytic system[a]

Entry	*P* (bar)	*T* (°C)	[**3**]/[Rh][b]	Con. (%)[c]	*t* (h)	Ald. (%)[d]	Bra. (%)[e]	ee (%)[f]
17	8	65	1.25	30	24	> 99	96	25
18	8	65	2	32	29	> 99	97	20
19	8	65	6	17	24	> 99	96	15
20	8	80	1.25	98	7	> 99	85	15
21	8	80	2	> 99	5	> 99	71	15
22	30	65	1.25	82	20	> 99	97	25
23	30	65	2	67	22	> 99	98	28
24	30	80	1.25	96	20	> 99	92	20
25	30	80	2	100	22	> 99	95	21

[a]Reaction conditions: 10 mmol of styrene, and 0.0125 mmol of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 15 ml of toluene. $P(CO) = P(H_2)$. [b]Ligand to metal molar ratio. [c]Converted olefin as percent of the initial amount. [d]Percent of aldehydes relative to the olefin converted. [e]Branched aldehyde **6** relative to the total amount of aldehyde formed. [f]Enantiomeric excess of the *R* isomer.

Table 4
Hydroformylation of styrene with rhodium-**4** catalytic system[a]

Entry	*P* (bar)	*T* (°C)	[**4**]/[Rh][b]	Con. (%)[c]	*t* (h)	Ald. (%)[d]	Bra. (%)[e]	ee (%)[f]
26	8	65	1	–	–	> 99	83	3
27	8	65	1.25	73	16	> 99	84	6
28	8	65	2	33	20	> 99	95	43
29	8	80	1	93	9	> 99	78	1
30	8	80	1.25	76	8	> 99	74	7
31	8	80	2	76	11	> 99	79	51
32	30	65	1	78	5	> 99	90	14
33	30	65	1.25	23	7	> 99	95	20
34	30	65	2	25	7	> 99	96	55
35	30	80	1	90	7	> 99	88	5
36	30	80	1.25	69	7	> 99	89	6
37	30	80	2	45	8	> 99	94	58
38	30	80	6	71	20	> 99	94	54
39[g]	30	80	6	100	8	> 99	94	50

[a]Reaction conditions: 10 mmol of styrene, and 0.0125 mmol of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 15 ml of toluene. $P(CO) = P(H_2)$, except when indicated. [b]Ligand to metal molar ratio. [c]Converted olefin as percent of the initial amount. [d]Percent of aldehydes relative to the olefin converted. [e]Branched aldehyde **6** relative to the total amount of aldehyde formed. [f]Enantiomeric excess of the *S* isomer. [g]$P(H_2)/P(CO) = 6$.

tivity in aldehydes was very high (> 99%) in almost all the experiments. Only in the case of the non-chiral ligands **1** and **2**, and working at 30 bar and 65°, was the chemoselectivity slightly lower (> 94%).

Fig. 1 represents, in a visual form, the regioselectivity measured for catalysts containing ligands **1**–**4**, in selected reaction conditions. Regardless of the excess of ligand used, the four diphosphines showed that the regioselectivity depended to the same extent on the pressure and temperature: the amount of the branched aldehyde **6** increased when the pressure was raised and/or when the temperature was reduced. The same behavior was previously observed for the hydroformylation of styrene with the unmodified Rh catalyst, $[RhH(CO)_4]$ [34]. Indeed Lazzaroni reported that, in the last case, the branched Rh-alkyl intermediate forms faster than the linear isomer intermediate. However, the first process was shown to be reversible through β-elimination, while the second is irreversible and can only evolve to the linear aldehyde. The β-elimination of the branched Rh-alkyl intermediate significantly increases with temperature, thus forming more linear Rh-alkyl complex and raising the selectivity in linear aldehyde. On the other hand, if the pressure increases, or more specifically the CO pressure, the β-elimination is reduced, since the rate of alkyl migration to the CO (the so-called CO insertion) increases. Thus the percentage of branched aldehyde raises [35]. This mechanism may also be responsible for the behavior observed for the catalytic species formed with ligands **1**–**4**.

The selectivity obtained with the chiral ligands **3** and **4** in branched isomer **6** was always higher than the values for the corresponding non-chiral ligands, **1** and **2**, respectively, in the same reaction conditions. Therefore, the presence of two methyl substituents in the backbone of the chiral ligands

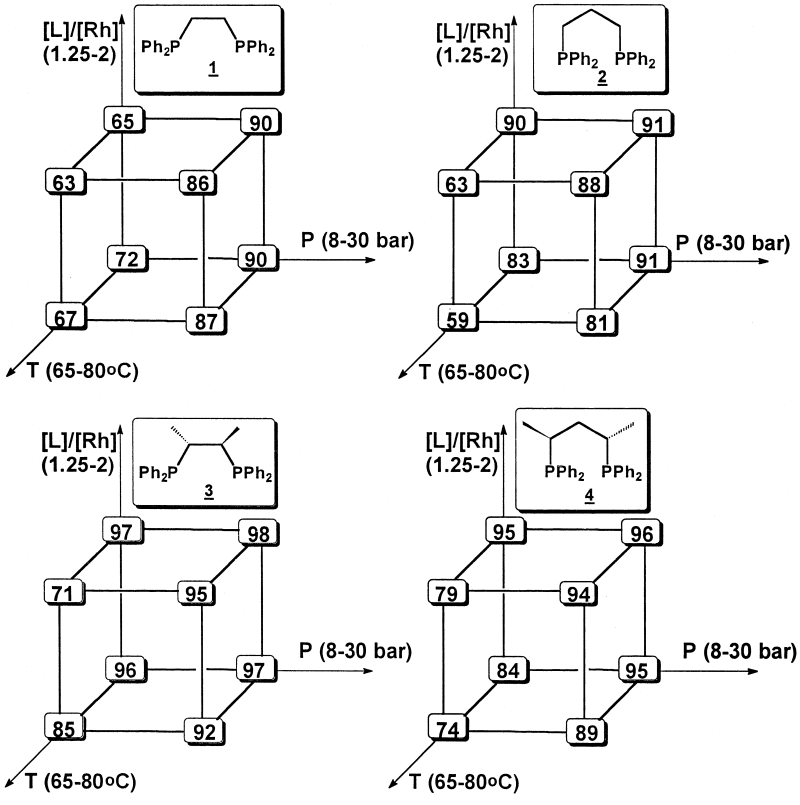


Fig. 1. Percent of branched aldehyde **6** (number in the boxes) for rhodium catalysts formed with ligands **1**–**4** at selected reaction conditions.

enhances the output of the branched aldehyde quite considerably. It is not clear if this enhancement is related to the discrimination in the rates of formation of the Rh-alkyl intermediates or to the rates of β-elimination. Ligand **3** yields the best regioselectivity: at 65°C, more than 95% of branched aldehyde was obtained at all pressures and ligand to metal molar ratios studied. Fig. 2 shows the dependence of the regioselectivity on the ligand to metal molar ratio.

In most of the reaction conditions used, for the five-member chelating ligands **1** and **3**, less branched aldehyde **6** was obtained when the high ligand to metal molar ratio was used. On the contrary, for six-member chelating ring ligands **2** and **4**, the highest yield in **6** was obtained at the largest ligand/metal ratio used. It is also worth noting, that, at 8 bar, for all the diphosphines, the regioselectivity heavily depends on the ligand to metal molar ratio, but that it is nearly independent in the experiments carried out at 30 bar and 65°C.

3.2. The influence of the nature of the diphosphine and the reaction conditions on the enantioselectivity

Fig. 3 shows two different behaviors for chiral ligands **3** and **4** with respect to the enantioselectivity. In case of ligand **3**, no significant change was observed when the ligand to rhodium molar ratio was increased. Only at 8 bar and 65°C there was a slight drop in the enantiomeric excess (ee), when

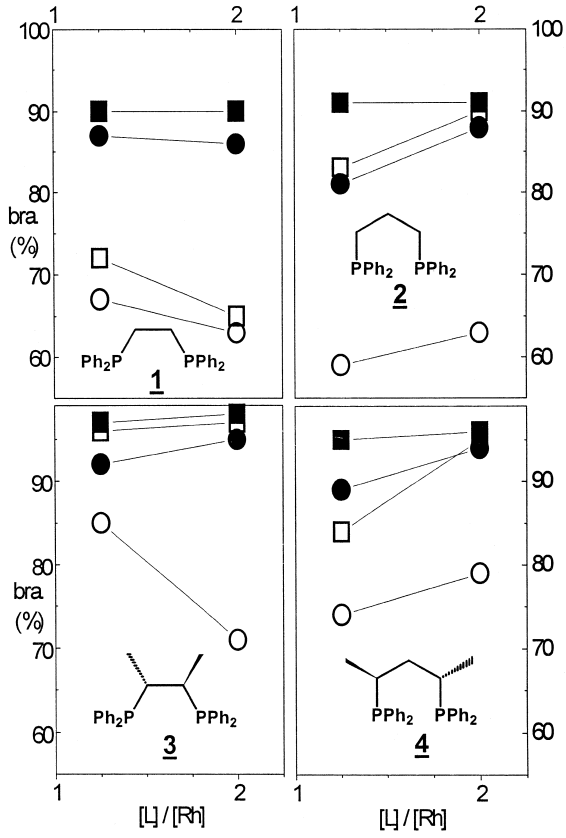


Fig. 2. Regioselectivity in percent of branched aldehyde **6** versus the ligand to rhodium molar ratio for ligands **1**–**4**. Symbols: ○ (80°C, 8 bar); □(65°C, 8 bar); ● (80°C, 30 bar); ■ (65°C, 30 bar).

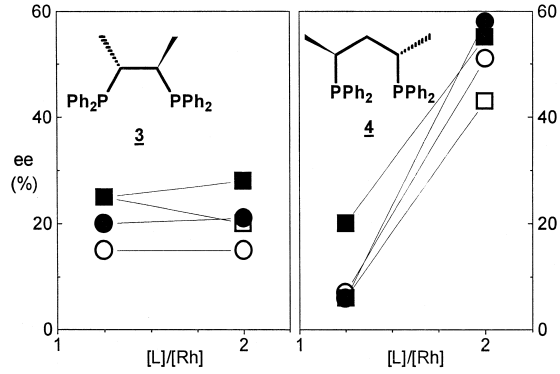


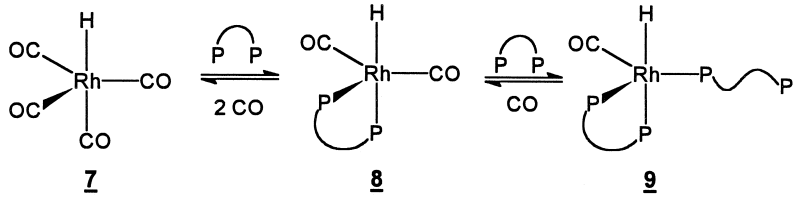
Fig. 3. Enantiomeric excess (%) of the branced aldehyde **6** versus the ligand to rhodium molar ratio for ligands **3** and **4**. Symbols: ○ (80°C, 8 bar); □ (65°C, 8 bar); ● (80°C, 30 bar); ■ (65°C, 30 bar).

[**3**]/[Rh] was raised from 1.25 to 6. In fact, the ee measured when using ligand **3** only ranges between 15 and 28%. On the other hand, the enantioselectivity of the catalytic system formed with ligand **4** heavily depended on the ligand/rhodium molar ratio, as has already been reported [30]. Thus, at [**4**]/[Rh] ≤ 1.25 the ee were less than 10% (except at 30 bar and 65°C, for which it was 20%), while at [**4**]/[Rh] ≥ 2 values around 50% ee were achieved. Finally, there are no clear correlations between the effect of the pressure and temperature and the enantioselectivity measured for these catalysts.

4. Discussion

The regio- and enantioselectivity of five- and six-membered ring ligands both depends on the ligand/metal molar ratio but in a different way. In the case of ligands **1** and **3**, both selectivities decrease when an excess of diphosphine is added, while the reverse is true for ligands **2** and **4**. It is also noticeable that the overall effect of the ligand to metal molar ratio on the selectivity is more pronounced in **4** than in **3**.

According to previous reports, the following scheme could describe the equilibria among the species formed by rhodium-diphosphine catalysts in the presence of syn-gas [4,5,14,33].



This scheme is simplified and does not include species such as $[Rh_2(CO)_2(\mu\text{-}CO)_2(PP)_2]$ (PP = diphosphine) which also exist in equilibrium [33,36].

In the reaction conditions used, it is unlikely that species **7** is involved in the catalytic process. Typical values for the regioselectivity in branched aldehyde, in the hydroformylation of styrene catalyzed by $[RhH(CO)_4]$, range from 61% (at 30 bar and 65°C) to 43% (at 8 bar and 80°C) [37], far below the regioselectivity achieved in these reaction conditions, with catalysts made up of ligands **3**

and **4**. Furthermore, at 8 bar the rate of the reactions catalyzed by **7** is significantly lower than when rhodium-diphosphines are used, so, even if **7** is present in the reaction solution at whatever concentration, its contribution to the selectivity of the reaction must be very low. Consequently, the simplest way to explain the dependence on the selectivity of the ligand to metal molar ratio is to consider an equilibrium between species **8** and **9**. Species with the structure of **8** are well established as one of the resident states of the metal in rhodium/P-donor catalytic systems. Moreover, this species was spectroscopically characterized under hydroformylation conditions in the case of ligand **4** [33]. The species type **9** have been less studied. They were first characterized and also thought to be behind the improvement in selectivity in the pioneering work with rhodium-diphosphine catalysts [4,5]. Furthermore, species **9** has been spectroscopically detected in the case of ligand **4** [33].

The higher ee achieved when [4]/[Rh] was raised cannot be attributed to the additional chiral information on the ligand coordinating in a monodentate way, since it is known that chiral monodentate phosphines yield meaningless ee in asymmetric hydroformylation.

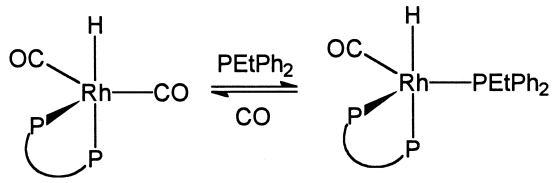
4.1. The influence of the addition of $PEtPh_2$ on the enantioselectivity

In order to further investigate these catalytic systems, a series of experiments were carried out using the chiral diphosphines plus $PEtPh_2$. A low ligand to metal molar ratio, [**4**]/[Rh] = 1.25, was used, and the non-chiral monodentate phosphine was added. This phosphine was chosen to simulate the electronic properties and steric hindrance of **4** coordinating as a monodentate ligand, but without the presence of any asymmetric carbon. Table 5 collects the results of these experiments, together with selected experiments of Table 4, which are included for comparative purposes. The results at 8 bar (entries 40 and 41), clearly show that $PEtPh_2$ causes a remarkable improvement in the regio and enantioselectivity. The values of both parameters reached values close to the ones achieved at [**4**]/[Rh] = 2. As in the case of the results obtained with an excess of ligand **4**, these results also suggest the formation of a species like **10**, structurally related to **9**. Species type **10** has been spectroscopically characterized [4,5,13].

Table 5
Hydroformylation of styrene with rhodium-**4**-$PEtPh_2$ catalytic system[a]

Entry	*P* (bar)	*T* (°C)	[**4**]/[Rh][b]	[$PEtPh_2$]/[Rh]	Con. (%)[c]	*t* (h)	Bra. (%)[d]	ee (%)[e]
27	8	65	1.25	0	73	16	84	6
40	8	65	1.25	2	45	5	92	23
28	8	65	2	0	33	20	95	43
30	8	80	1.25	0	76	8	74	7
41	8	80	1.25	2	97	8	88	56
31	8	80	2	0	76	11	79	51
33	30	65	1.25	0	23	7	95	20
42	30	65	1.25	2	51	4	91	2
34	30	65	2	0	25	7	96	55
36	30	80	1.25	0	69	7	89	6
43	30	80	1.25	2	99	10	91	4
37	30	80	2	0	45	8	94	58

[a]Reaction conditions: 10 mmol of styrene, and 0.0125 mmol of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ in 15 ml of toluene. $P(CO) = P(H_2)$. [b]Ligand to metal molar ratio. [c]Converted olefin as percent of the initial amount. Chemoselectivity was higher than 99%. [d]Branched aldehyde **6** relative to the total amount of aldehyde formed. [e]Enantiomeric excess of the *S* isomer.



8 **10**

In the case of platinum catalysts, a beneficial effect on the enantioselectivity in the hydroformylation of styrene was reported when monophosphines (PPh_2Py or PBu_3) were added to the Pt–$SnCl_2$/**4** catalytic system [38]. Species [Pt(diphosphine)(monophosphine)Cl]$^+$ has been spectroscopically characterized in this case [39].

In recent years, mechanistic studies in rhodium-diphosphine catalytic systems have focused on the pentacoordinate species $RhH(P_2)(CO)_2$, [13,23,25,33,40]. The next step, in the generally accepted dissociative mechanism, involves the dissociation of a CO and the formation of a four-coordinate intermediate in which the olefin is coordinated. The two consecutive steps, alkene coordination and hydride migration, are of particular importance in controlling the regio- and enantioselectivity of the reaction [13,14,16,17]. For species **9** or **10**, the dissociation of a CO, which would be followed by the coordination of the olefin to species containing one hydride and three phosphorous, could be controversial. However, the presence of a monophosphine during these two consecutive steps, alkene coordination and hydride migration, would have an effect on the regio- and enantioselectivity. Thus, in a broader approach, it could be considered that in presence of a excess of diphosphine or a monophosphine, species of the type $RhR(P_2)(CO)(P)$, R = hydride, alkyl or acyl, are present in equilibrium with species $RhR(P_2)(CO)_2$. These equilibria should have a substantial effect on the selectivity of the reaction.

It is important to note that, in the experiments carried out at 30 bar, the presence of the monophosphine ligand decreases the enantioselectivity (entries 42 and 43), while the regioselectivity is hardly modified. This can be explained considering that a high pressure the substitution of CO ligand by the phosphine is not feasible.

Table 6 summarizes the catalytic experiments carried out with ligand **3** in the presence of $PEtPh_2$. Interestingly, the adding the monophosphine to the catalytic mixture produced a significant drop in the enantioselectivity from 20% ee to nearly 0, both at low and high pressure (entries 44 and 45). These results, together with the fact that ee decreases when [**3**]/[Rh] increases (entries 17, 18 and 19

Table 6
Hydroformylation of styrene with rhodium-**3**-$PEtPh_2$ catalytic system[a]

Entry	*P* (bar)	*T* (°C)	[**3**]/[Rh][b]	[$PEtPh_2$]/[Rh]	Con. (%)[c]	*t* (h)	Bra. (%)[d]	ee (%)[e]
20	8	80	1.25	0	98	7	85	15
44	8	80	1.25	2	52	8	97	2
21	8	80	2	0	> 99	5	71	15
22	30	65	1.25	0	82	20	97	25
45	30	65	1.25	2	25	3	96	4
23	30	65	2	0	67	22	98	28

[a]Reaction conditions: 10 mmol of styrene, and 0.0125 mmol of [$Rh_2(\mu\text{-}OMe)_2(cod)_2$] in 15 ml of toluene. $P(CO) = P(H_2)$. [b]Ligand to metal molar ratio. [c]Converted olefin as percent of the initial amount. Chemoselectivity was higher than 99%. [d]Branched aldehyde **6** relative to the total amount of aldehyde formed. [e]Enantiomeric excess of the *R* isomer.

in Table 3), may be due to the dissociation of one of the arms of the chelate by the additional phosphorus ligand.

5. Conclusions

The catalytic systems generated by a rhodium precursor and ligands **1**–**4** produce different regio- and enantioselectivities depending on the nature of the ligand and the ligand/metal molar ratio used. In the case of ligands **1** and **3**, which form five-membered chelate ring, a high ligand concentration $[L]/[Rh] \geq 2$ decreases of the selectivity of the catalytic system. On the contrary, for **2** and **4**, which form six-membered rings, selectivities are higher at high ligand concentrations, $[L]/[Rh] \geq 2$. Enantioselectivities of up to 58% can be obtained in the hydroformylation of styrene using a appropiate excess of ligand **4**, $[\mathbf{4}]/[Rh] \geq 2$. The addition of $PEtPh_2$ to the catalytic rhodium system with $[\mathbf{4}]/[Rh] = 1.25$ increases the enantioselectivity in the same way as adding an excess of **4**. In the case of ligand **3**, however the enantioselectivities obtained are in the order of 20% and both, the excess of ligand and the addition of the monophoshine caused a drop in enantioselectivity. Further work is in progress to rationalize the different behavior of the five- and six-membered ring chelating ligands.

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