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In situ study of diphosphine rhodium systems in asymmetric hydroformylation of styrene

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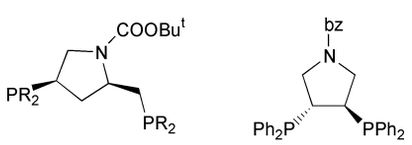
HPNMR and *in situ* HPIR (HP = High Pressure) spectroscopic techniques were used to study the species present in the hydroformylation of styrene by rhodium disphosphine systems. Rhodium precursors with BDPP [(2*S*,4*S*)-bis(diphenylphosphino)pentane] and CHIRAPHOS [(2*R*,3*R*)-bis(diphenylphosphino)butane] as the chiral ligands (P–P) were used. The species observed were compared in order to find a relation between the structures and the enantiomeric excesses obtained for both chiral diphosphines. The effect of the P–P : [Rh] molar ratio and the addition of a monophosphine on the enantiomeric excess were studied. It has been found that oxidation of the coordinated chiral diphosphine leads to formation of rhodium species more active but less regio- and enantioselective.

Introduction

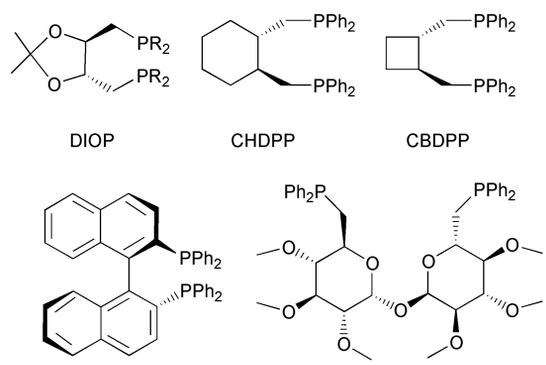
Diphosphines are among the most efficient chiral ligands in homogeneous catalysis.[1] Many chiral diphosphines have been used as ligands in rhodium systems for the asymmetric hydroformylation of styrene,[2,3] although the enantioselectivities achieved by the rhodium diphosphite,[4,5] diphosphinite[6] or phosphine–phosphite[7] systems have not been equalled by diphosphine systems.

In general rhodium systems with C_2-symmetric chiral diphosphines have been most studied in the rhodium catalysed asymmetric hydroformylation of styrene, although C_1-symmetric diphosphines such as BPPM[8] have also been studied and an enantiomeric excess (ee) of 14% has been reported. For [Rh]/DEGUPHOS systems[9] enantioselective discrimination was nearly nil (Scheme 1). For rhodium systems with C_2-symmetric diphosphines such as DIOP and related ligands enantiomeric excesses below 25% were obtained in the hydroformylation of styrene.[10,11] The highest enantiomeric excesses have been reported for rhodium systems with CHDPP and CBDPP and their dibenzophosphole derivatives (27%).[12] In the case of the [Rh]/BINAP system 7%[8] and 25% ee[11] have been reported. Diphosphines such as TREDIP[13] afford very low enantioselectivities in this reaction (Scheme 2). Nevertheless, the use of rhodium systems with a structurally simple diphosphine such as BDPP provides enantiomeric excesses up to 60% and a regioselectivity for 2-phenylpropanal (2-PP) of 95% at 30 bar CO/H_2 and 40 °C. A similar chiral diphosphine, CHIRAPHOS, gives enantioselectivities between 15 and 28%,[14,15] significantly lower than those of BDPP (Scheme 3).



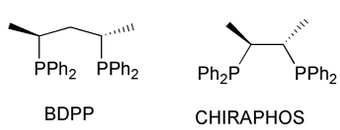
BPPM DEGUPHOS

Scheme 1 R = Biphenyl-2,2′-diyl.



DIOP CHDPP CBDPP BINAP TREDIP

Scheme 2 R = Ph.



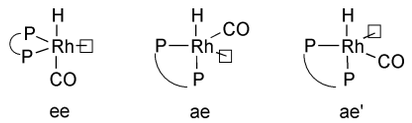
BDPP CHIRAPHOS

Scheme 3

It is still not known how ligand structures control the stereodifferentiation in the hydroformylation reaction so that the performance of new ligands can be predicted. According to the Wilkinson mechanism for the hydroformylation of 1-alkenes the regioselectivity is determined in the step that converts a five-coordinate [RhH(CO)L_2(alkene)] into either a linear or branched four-coordinate rhodium alkyl species [Rh(CO)L_2(alkyl)]. Depending on the conditions, this step can be irreversible. The structure of the alkene complex and the migratory insertion are therefore thought to play crucial roles in controlling regioselectivity.[16] However, unlike the [RhH(CO)$_2L_2$] species which has been reported for several systems as resting state,[5a,7d,17] the [RhH(CO)L_2(alkene)] intermediate has not been observed directly.

Alkene insertion reactions have early transition states and they are therefore assumed to have an approximately trigonal-

bipyramidal geometry.[18,19] Within this geometry type, an apical–equatorial (ae) coordination and an equatorial–equatorial (ee) coordination mode are available for C_2-symmetric diphosphine ligands (Scheme 4). In recent years,



Scheme 4

several studies have observed a correlation between the regioselectivity of the rhodium hydroformylation and the ae : ee isomer ratio.[16] However more detailed studies show that the structure of the saturated $[RhH(CO)_2L_2]$ complex has only some circumstantial relevance to the selectivity.[20]

It should be noted that intermediates with phosphorus ligands that coordinate in an equatorial–equatorial fashion give rise to only one vacant equatorial position with the chelate phosphorus ligand coordinated in the same plane and this in turn means that the substrate and ligand interact effectively. The highest enantiomeric excesses for C_2-symmetric diphosphite ligands are indeed obtained with the relatively stable $[RhH(CO)_2L_2]$ complexes in which the phosphorus-donor atoms coordinate equatorially to rhodium.[5] On the other hand, coordination in an apical–equatorial manner is assumed to give rise to two competing intermediate species ae and ae′ which probably lead to products with opposite absolute configurations (Scheme 4).[5,19] Therefore, a chiral ligand has to compensate for this "natural" cancellation by suitable backbone interactions, apparently this is the case for BINAPHOS {[2-(diphenylphosphino)-1,1′-binaphthalene-2′-yl][1,1′-binaphthalene-2,2′-diyl]phosphite}.[7,21]

Variable-temperature NMR and HPIR studies[22] have shown that BDPP coordinates in an apical–equatorial fashion, in accord with the calculated bite angle of 91°,[23] while a fast exchange of the two phosphine groups occurs. Other chiral diphosphines[8–13] have a wider bite angle and, especially for more flexible ligands, both equatorial–equatorial and apical–equatorial intermediates may form. The occurrence of several species does not seem to be a good starting point for obtaining high enantiomeric excesses.

Previous studies of the [Rh]/BDPP system have found that the enantiomeric excess depends heavily on the ligand : rhodium molar ratio at fixed rhodium concentrations. At P–P : [Rh] ratios of 1 and 2 : 1, the enantiomeric excesses are 1 and 58%, respectively.[11] Adding a monophosphine such as $PEtPh_2$ to the catalytic rhodium system increases the enantioselectivity in the same way that adding an excess of BDPP does.

In this paper we present *in situ* HPIR and HPNMR experiments using BDPP and CHIRAPHOS in order to compare the species present. We also study the effect of the excess of chiral diphosphine in the enantioselective catalysis, together with the role of addition of monophosphine.

Results

Comparison of BDPP/CHIRAPHOS

In situ HPIR and HPNMR experiments have revealed the solution structures of the dominant species present during styrene hydroformylation using the rhodium precursor $[Rh(\mu\text{-}OMe)(COD)]_2$ and BDPP.[22] We reproduced these results working under different conditions. HPIR experiments were carried out at 8 and 30 bar, 80 °C and $[Rh] = 1.67 \times 10^{-3}$ M with BDPP : Rh = 1 : 1 in cyclohexane and only one species, the apical–equatorial hydride $[RhH(CO)_2(BDPP)]$ **4a**, was present during the hydroformylation of styrene.[22] No rhodium dinuclear species $[Rh(CO)_2(BDPP)]_2$ **5a** was observed under these conditions, but the presence of traces of it could not be disregarded.

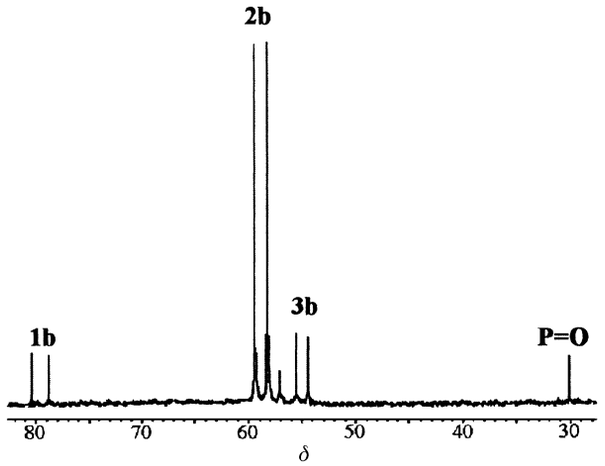
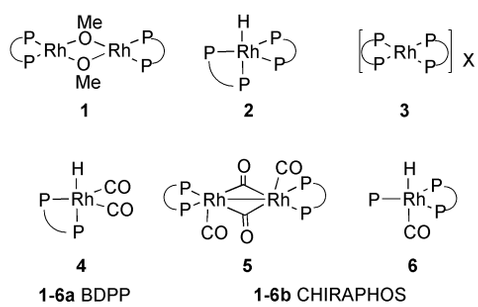


Fig. 1 $^{31}P\text{-}\{^1H\}$ NMR spectrum for the reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with CHIRAPHOS under hydroformylation conditions at room temperature.

HPNMR experiments were also performed at 20 bar H_2, 4 bar CO and [Rh] = 0.024 M. A higher H_2 pressure was used to prevent the formation of dinuclear species since the equilibrium between mono- and di-nuclear species depends on the pressure.[22] These experiments showed that additional species were present in the HPNMR experiments in comparison with the *in situ* HPIR experiment (Scheme 5). The solutions in the



Scheme 5

HPNMR experiments were more concentrated than those in the HPIR experiments so that the signal-to-noise ratio would be satisfactory. In the HPNMR experiments species **1a**, **2a**, **3a** and **6a** were present under CO/H_2 pressure before heating, but only **4a** and **5a** were in equilibrium after heating.

We performed the HPIR and HPNMR study under the same conditions for the CHIRAPHOS diphosphine in order to compare both systems. The IR spectra were recorded for the $[Rh(\mu\text{-}OMe)(COD)]_2$: CHIRAPHOS system (CHIRAPHOS : Rh = 1 : 1) in an HPIR autoclave under hydroformylation conditions (8 and 30 bar and 80 °C). There were two absorptions in the terminal carbonyl region (2000 and 1961 cm^{-1}), which were attributed to the hydride complex $[RhH(CO)_2(CHIRAPHOS)]$ **4b** with the diphosphine in the apical–equatorial position. No equatorial–equatorial isomer was observed, consistent with the calculated natural bite angle of 85° [see Fig. 5(a)].[23] The substrate was then added and an infrared spectrum was recorded every 10 minutes to collect information about the intermediates present throughout the process. During the hydroformylation of styrene at 8 and 30 bar ($CO : H_2 = 1 : 1$), the hydride complex **4b** was the only species observed.

The HPNMR spectroscopic study was performed at 20 bar H_2, 4 bar CO, [Rh] = 0.024 M, room temperature and a CHIRAPHOS : Rh ratio of 1 : 1 (Fig. 1). The $^{31}P\text{-}\{^1H\}$ NMR spectrum of the solution had three doublets at δ 79.4 ($^1J_{Rh\text{-}P} = 195$), 58.7 (142) and 54.9 (132 Hz) (Table 1). The resonance of the oxidized phosphine is at δ 30. The ^1H NMR spectrum shows a broad quintet of doublets at δ −10.4. This

Table 1 ^{31}P-{^{1}H} and ^{1}H NMR data of the species formed in the reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with CHIRAPHOS under hydroformylation conditions

	^{31}P-{^{1}H}		^{1}H		
Complex	δ	$^{1}J_{Rh\text{-}P}$/Hz	δ	$^{1}J_{H\text{-}Rh}$/Hz	$^{2}J_{P\text{-}H}$/Hz
1b	79.4	195			
2b	58.7	142	−10.4	12	17
3b	54.9	132			
4b	61.7	115	−8.7	10	60
5b	43.9	138			

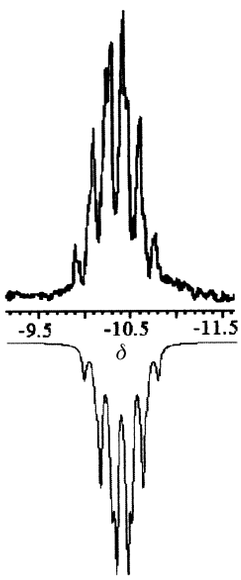


Fig. 2 Hydride region of the ^{1}H NMR spectrum for the reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with CHIRAPHOS under hydroformylation conditions. Top: experimental spectrum. Bottom: spectrum simulated with the coupling constants in Table 1.

pattern is due to coupling of the hydride nucleus with four (time-averaged) equivalent phosphorus atoms and the rhodium nucleus with coupling constants $^{1}J_{Rh\text{-}H} = 12$, $^{2}J_{P\text{-}H} = 17$ Hz (Fig. 2).[22]

In accordance with the literature,[24] the doublet at δ 79.4 is attributed to the dinuclear rhodium complex **1b**, which retains the methoxy bridges and contains one diphosphine coordinated to each rhodium atom. The doublet at δ 58.7 and the hydride observed in the ^{1}H NMR was attributed to the mononuclear rhodium complex **2b**, which has four equivalent phosphorus atoms with a time-averaged coupling constant.[25] The doublet at δ 54.9 was attributed to a square-planar rhodium complex **3b** with two CHIRAPHOS ligands coordinating to the metal (Scheme 5).[26] Related species **1a**, **2a** and **3a** have been characterized before for the BDPP system. The small signal present at δ 57 could not be assigned.

When the temperature was increased to 80 °C four doublets were observed in the ^{31}P-{^{1}H} NMR spectrum. Those at δ 58.9 and 55.5 were attributed to complexes **2b** and **3b** respectively, and two new doublets were observed at δ 61.7 ($^{1}J_{Rh\text{-}P} = 115$) and 43.9 (138 Hz) (Fig. 3). The ^{1}H NMR of this solution revealed a double triplet in the hydride region at δ −8.7 ($^{1}J_{Rh\text{-}H} = 10$, $^{2}J_{P\text{-}H} = 60$ Hz), which is indicative of the presence of time-averaged equivalent phosphorus nuclei, together with the broad quintet of doublets at δ −10.4 assigned to complex **2b** (Table 1).

In agreement with the literature,[22] we assigned the doublet at δ 61.7 and the hydride to the mononuclear rhodium complex **4b** (Scheme 5), in which one diphosphine of complex **2b** had been displaced by two CO molecules. Complex **4b** has a trigonal-bipyramidal geometry and the CHIRAPHOS is apically

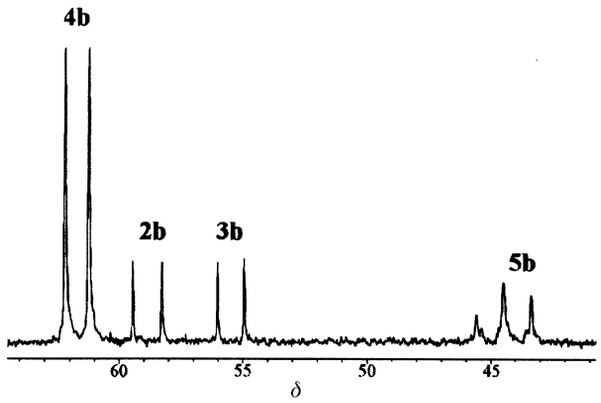


Fig. 3 ^{31}P-{^{1}H} NMR spectrum for the reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with CHIRAPHOS under hydroformylation conditions at 80 °C.

equatorially coordinated to the rhodium center. In the present case the intermediate phosphorus–hydride coupling constant ($^{2}J_{P\text{-}H} = 60$ Hz) suggests that there is a time-averaged *cis-trans* relationship between the phosphorus and hydride nuclei.[5,14,27] As is the case with BDPP,[22] a fast apical–equatorial exchange of the phosphorus atoms resulted in an averaged coupling constant ($^{1}J_{Rh\text{-}P} = 115$ Hz) and it was impossible to observe the distinct P_{ap}–H and P_{eq}–H coupling constants, not even in experiments at low temperatures. The magnitude of the averaged value indicates that the compound has a purely apical–equatorial structure and that equatorial–equatorial isomers are not involved in the fast equilibrium.

The doublet at δ 43.9 was assigned to the carbonyl diphosphine dimer $[Rh(CO)_2(CHIRAPHOS)]_2$ **5b**, which has a Rh–Rh bond and two CO groups bridging the metal atoms.[28] The small signal present at δ 46 could correspond to another dinuclear species.

When the system was cooled to room temperature the same species were present. The major compounds were **4b** and **5b**, and the minor ones **2b** and **3b**. When BDPP was used at the same concentrations only complexes **4a** and **5a** were present after heating. The relative stabilities of the species are different for BDPP and CHIRAPHOS; **2b** and **3b** are favoured in the case of CHIRAPHOS.

Effect of the P–P : [Rh] ratio on the enantiomeric excess

It was found that the P–P : [Rh] molar ratio affected BDPP and CHIRAPHOS in different ways. We have previously reported that the enantiomeric excess for the $[Rh(\mu\text{-}OMe)(COD)]_2$/BDPP system is dependent on the P–P : [Rh] molar ratio under different pressures and temperatures (Table 2, entries 1–4).[11,15] However, in this work we found that, when experimental conditions were carefully controlled and the styrene was deoxygenated to prevent diphosphine oxidation, enantiomeric excesses were as high as 43% for a P–P : [Rh] ratio of only 1 : 1 (Table 2, entries 5, 6).

Therefore, no excess of diphosphine was required to achieve enantiomeric excesses between 40 and 50% (Table 2, entry 5). The enantiomeric excess obtained using P–P : [Rh] = 1 : 1 (43%) was not as high as the one obtained using P–P : [Rh] = 2 : 1, because minor pathways leading to oxidation could not totally be prevented.

It is well known that phosphines are more prone to oxidation than phosphites. Oxidation of diphosphines could lead to species in which the diphosphine is partially oxidized and can coordinate as monodentate. These monooxidized diphosphines have been synthetized[29] and found to be more active in the hydroformylation of styrene.[30]

It should be pointed out that, when oxidation was avoided, the regioselectivity was maintained at 94/6. When oxygen was present in the system, however, the regioselectivity was lower

Table 2 Hydroformylation of styrene with the $[Rh(\mu\text{-}OMe)(COD)]_2$/BDPP system[a]

Run	*P*/bar	*T*/°C	P–P : [Rh]	*t*/h	% Conversion	% 2-PP/3-PP[d]	% ee
1[b]	5	65	1 : 1	7	88	77/23	1
2[b]	5	65	2 : 1	7	90	94/6	53
3[c]	30	80	1 : 1	7	99	88/12	5
4[c]	30	80	2 : 1	8	99	94/6	58
5	8	80	1 : 1	5	94	91/9	43
6	8	80	2 : 1	8	89	94/6	51

[a] Conditions: 0.0125 mmol $[Rh(\mu\text{-}OMe)(COD)]_2$, in 15 mL of toluene, $P(CO) = P(H_2)$. [b] Experiments previously reported.[11] [c] Experiments previously reported.[15] [d] 2-PP and 3-PP are 2- and 3-phenylpropanal.

Table 3 Hydroformylation of styrene with the $[Rh(\mu\text{-}OMe)(COD)]_2$/CHIRAPHOS system[a]

Run	*P*/bar	*T*/°C	P–P : [Rh]	*t*/h	% Conversion	% 2-PP/3-PP	% ee
7[b]	30	80	1 : 1	20	99	92/8	20
8[b]	30	80	2 : 1	22	99	95/5	21
9	8	80	1 : 1	13	96	93/7	24

[a] Conditions: 0.0125 mmol $[Rh(\mu\text{-}OMe)(COD)]_2$, in 15 mL of toluene, $P(CO) = P(H_2)$. [b] Experiments previously reported.[15]

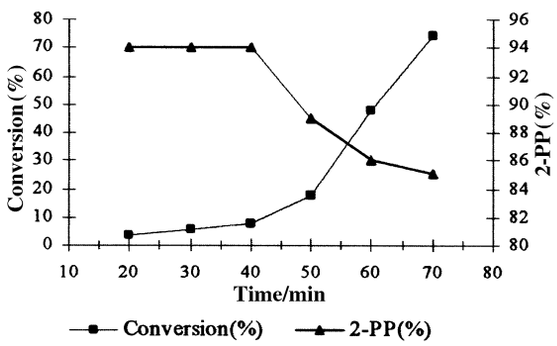


Fig. 4 Conversion and regioselectivity with time in the presence of oxygen using the BDPP/[Rh] system.

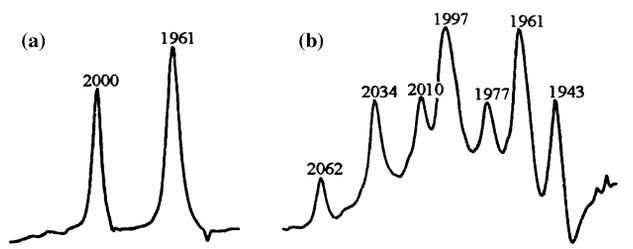


Fig. 5 HPIR spectra: (a) reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with CHIRAPHOS and styrene under hydroformylation conditions at 30 bar; (b) reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with CHIRAPHOS and styrene at 30 bar in the presence of oxygen.

than that obtained using the non-oxidized systems. With this in mind, several catalytic experiments were carried out while taking samples and measuring the conversion and regioselectivity over time. Using BDPP : [Rh] = 2 : 1 without deoxygenation of styrene, the regioselectivity was constant and the conversion was linear during the initial 40 minutes. However, after 40 minutes some diphosphine could be oxidized and coordinated to the rhodium centre as monodentate, increasing significantly the activity of the system and decreasing the regioselectivity to 2-PP/3-PP = 85/15 (Fig. 4). In the same way, the regioselectivity with the $[Rh]/PEtPh_2$ system in the hydroformylation of styrene under the same conditions[9] was in the range of 2-PP/3-PP = 80/20. Furthermore, the rate observed for the catalyst modified with the monophosphine[9] was a value between 4 and 10 times higher than for the ligand BDPP.

When the experiment with BDPP/[Rh] was carried out in the absence of oxygen the conversion was found to be linearly proportional with time and the regioselectivity constant at 94/6. The same behavior was observed with an excess of diphosphine (P–P : [Rh] = 3 : 1) without deoxygenation of the styrene. This suggests that as long as a considerable amount of non-oxidized diphosphine is present, no coordination of the monooxidized diphosphine takes place because of the stability of the rhodium–diphosphine chelate. The fact that regioselectivities lower than 2-PP/3-PP = 80/20 are not observed rules out the presence of rhodium carbonyl species that will lead to lower regioselectivities under these conditions.[3]

Surprisingly, in the case of the $[Rh(\mu\text{-}OMe)(COD)]_2$/CHIRAPHOS system, there was no significant change in the enantiomeric excess[15] when the ligand to rhodium molar ratio was increased (Table 3, entries 7, 8). For the different conditions used, the regio- and enantio-selectivity of the system did not depend on P–P : [Rh] ratio (Table 3, entry 9). The different stabilities of the CHIRAPHOS/BDPP species present may account for these results. Since the chelate CHIRAPHOS complexes are more stable, the formation of species with monocoordinated diphosphine could be disfavoured.

In order to obtain more information about the effects of oxidation of the diphosphine, HPIR *in situ* experiments were carried out with the $[Rh(\mu\text{-}OMe)(COD)]_2$/CHIRAPHOS system during the hydroformylation of styrene in the absence of oxygen at 30 bar CO/H_2 and 80 °C. The two absorptions of the hydride complex $[RhH(CO)_2(CHIRAPHOS)]$ **4b** were observed at 2000 and 1961 cm^{-1} (Fig. 5a). When the same spectrum was recorded after exposure of the solution to the air there were new absorptions at 2034, 1997, 1977 and 1943 cm^{-1} which were attributed to monooxidation of the diphosphine giving rise to two monocoordinated diphosphines in apical–equatorial (1997 and 1943 cm^{-1}) and equatorial–equatorial (2034 and 1977 cm^{-1}) positions. These absorptions were assigned by comparison with the HPIR spectra of $[RhH(CO)_2(PEtPh_2)_2]$ (Fig. 6a).

Effect of adding a monophosphine on the enantiomeric excess

A previous series of experiments had been carried out using the chiral diphosphines BDPP and CHIRAPHOS with added $PEtPh_2$ in the hydroformylation of styrene.[15] The diphosphine : rhodium molar ratio was low, P–P : [Rh] = 1 : 1, and non-chiral monodentate phosphine was added. This monophosphine was chosen to simulate the electronic and steric properties of the additional BDPP coordinating as a monodentate ligand, but it lacks an asymmetric carbon (Table 4).

The results at 8 bar (Table 4, entries 10,11) showed that $PEtPh_2$ considerably improves the regio- and enantio-

Table 4 Hydroformylation of styrene with the $[Rh(\mu\text{-}OMe)(COD)]_2$/BDPP/$PEtPh_2$ system[a]

Run	*P*/bar	*T*/°C	BDPP : [Rh]	$PEtPh_2$: [Rh]	*t*/h	% Conversion	% 2-PP/3-PP	% ee
10[b]	8	80	1 : 1	—	8	76	74/26	7
11[b]	8	80	1 : 1	2 : 1	8	97	88/12	56
12[b]	30	80	1 : 1	—	7	69	89/11	6
13[b]	30	80	1 : 1	2 : 1	10	99	91/9	4
14[b]	30	80	2 : 1	—	8	45	94/6	58

[a] Conditions: 0.0125 mmol $[Rh(\mu\text{-}OMe)(COD)]_2$, in 15 mL of toluene, $P(CO) = P(H_2)$. [b] Experiments previously reported.[15]

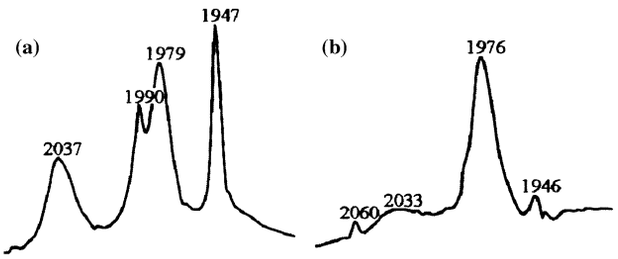


Fig. 6 HPIR spectra: (a) reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with $2PEtPh_2$ and styrene under hydroformylation conditions; (b) reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with $4PEtPh_2$ and styrene under hydroformylation conditions.

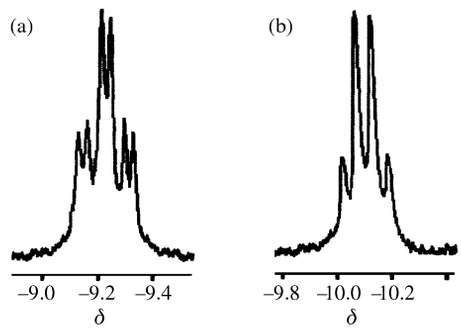


Fig. 7 Hydride region of the ^1H NMR spectra for the reaction of $[Rh(\mu\text{-}OMe)(COD)]_2$ with $PEtPh_2$ under hydroformylation conditions.

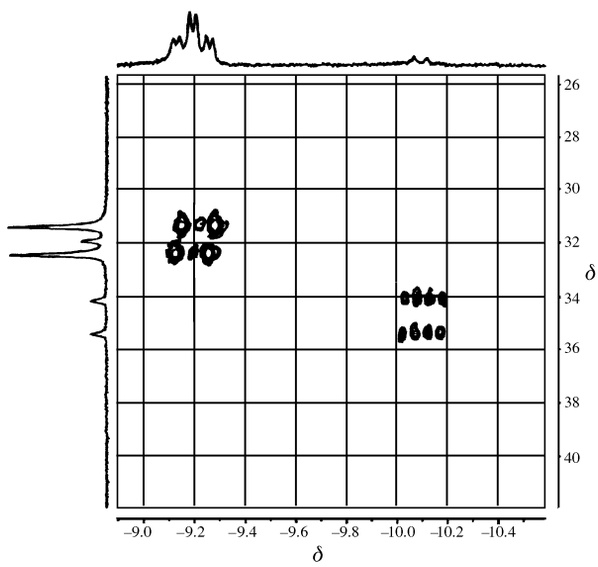
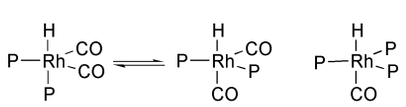


Fig. 8 Section of the $^{31}P/^1H$ correlation spectrum of the $[Rh(\mu\text{-}OMe)(COD)]_2$/$PEtPh_2$ system.

selectivity.[15] The values of both parameters were close to the ones achieved at BDPP : [Rh] = 2 : 1. These results suggested that species such as [RhH(CO)(BDPP)($PEtPh_2$)] were formed. In the experiments carried out at 30 bar the presence of the monophosphine ligand does not affect the enantioselectivity (Table 4, entries 12–14). This was thought to be because CO could not be substituted by monophosphine at high pressure.[15]

For the system [Rh]/CHIRAPHOS/$PEtPh_2$ the enantioselectivity has not previously been observed to increase after the addition of monophosphine.[15]

In an attempt to identify the species formed under hydroformylation conditions in the presence of the monophosphine, HPNMR and HPIR experiments were performed on the [Rh]/$PEtPh_2$ system and the species present compared with those present in the [Rh]/BDPP/$PEtPh_2$ system. The $[Rh(\mu\text{-}OMe)(COD)]_2$/$PEtPh_2$ system has previously been studied through HPNMR experiments.[9] We present here a study of the hydroformylation reaction in an *in situ* HPIR autoclave at 8 bar CO/H_2, 80 °C and [Rh] = 1.67×10^{-3} M with and without styrene. For $PEtPh_2$: [Rh] = 2 : 1, the IR spectrum revealed carbonyl absorptions at 2037, 1990, 1979 and 1947 cm^{-1} (Fig. 6a). These absorptions were assigned to the mononuclear hydrido complex **7** with the two isomers in dynamic equilibrium, apical–equatorial **7**ae (1990 and 1947 cm^{-1}) and equatorial–equatorial **7**ee (2037 and 1979 cm^{-1}) (Scheme 6). The assignment was



Scheme 6

made in accordance with previous H/D exchange HPIR experiments with diphosphines.[20]

When the $PEtPh_2$: [Rh] ratio was increased to 4 : 1 at fixed rhodium concentrations there was one major carbonyl absorption at 1976 cm^{-1} (Fig. 6b). It was assigned to [RhH-($PEtPh_2$)$_3$(CO)] **8** which contained CO coordinated in the apical position in the hydride complex with the three monophosphines in equatorial positions (Scheme 6). The rhodium complex **7** with two coordinated monophosphines was still present as a minor compound.

We also performed an HPNMR study of the $[Rh(\mu\text{-}OMe)(COD)]_2$/$PEtPh_2$ system under the conditions used in this work for diphosphines. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of a solution of $[Rh(\mu\text{-}OMe)(COD)]_2$ with 4 equivalents of $PEtPh_2$ at room temperature, 20 bar H_2, 4 bar CO and [Rh] = 0.024 M shows two doublets at δ 50.9 ($^1J_{Rh\text{-}P} = 184$) and 34.5 (150 Hz). The ^1H NMR spectrum shows a broad signal in the hydride region (δ −10.1). When the system was heated a new doublet appeared in the ^{31}P NMR spectra at δ 31.9 ($^1J_{Rh\text{-}P} = 131$ Hz). A double triplet was also observed in the hydride region of the ^1H NMR spectra at δ −9.4 ($^1J_{Rh\text{-}H} = 7$, $^2J_{P\text{-}H} = 15$ Hz) (Fig. 7a). The doublet at δ 50.9 must be attributed to the dinuclear rhodium complex $[Rh(\mu\text{-}OMe)(PEtPh_2)_2]_2$, which maintains the methoxy bridge, like the doublet previously characterized for CHIRAPHOS (complex **1b**).

By means of a $^{31}P/^1H$ correlation experiment at −20 °C, 20 bar H_2, 4 bar CO, [Rh] = 0.024 M and $PEtPh_2$: [Rh] = 8 : 1 (Fig. 8), we were able to correlate the hydrides with the $^{31}P\text{-}\{^1H\}$ NMR doublets (Table 5). The ^{31}P NMR doublet at δ 31.9 and the ^1H NMR double triplet at δ −9.4 were assigned to the mononuclear rhodium complex **7** in which the hydride is coupled with the rhodium and with two degenerate phosphorus

nuclei as has previously been reported.[9] The doublet at δ 34.5 and the hydride observed at δ −10.1 were attributed to the mononuclear rhodium complex **8** with three monophosphines coordinated to the rhodium center. Further evidence was obtained by bubbling hydrogen through a solution of complex **7**, which led to the displacement of one molecule of CO. A quartet appeared in the hydride region of the ^{1}H NMR spectra at δ −10.1 ($^2J_{P\text{-}H}$ = 15 Hz) (Fig. 7b), because of coupling of the hydride with three equivalent phosphorus atoms. The Rh–H coupling is very small and could not be observed.

The mixed system [Rh(μ-OMe)(COD)]$_2$/BDPP/PEtPh$_2$ was studied by HPIR and HPNMR to obtain information about the species formed under these conditions. The only species observed in the HPIR experiments under hydroformylation conditions in the absence of oxygen at 8 and 30 bar CO/H$_2$ and 80 °C was the rhodium hydride complex [RhH(CO)$_2$(BDPP)] **4a** described previously.[22] No other species containing monophosphine or mixed BDPP/PEtPh$_2$ were observed.

Substrate was then added and the hydroformylation reaction monitored by *in situ* IR spectroscopy. The rhodium hydride complex **4a** was fully retained throughout the reaction and no other species was observed. The regioselectivity and the enantiomeric excess were measured at the end of the HPIR experiments (Table 6). These results are reliable since the conditions and concentrations of the reagents are identical to those of catalytic experiments in the standard autoclaves. The results were the same as for the [Rh]/BDPP system at 8 and 30 bar (Table 2, entries 4,6), although no excess of diphosphine was used (Table 6, entries 15,17). Even when the PEtPh$_2$: [Rh] molar ratio was 4 : 1, no change was observed in the regio- or the enantioselectivity with respect to the rhodium system without PEtPh$_2$ (Table 6, entry 16).

In ^{31}P-{^{1}H} HPNMR experiments of the [Rh(μ-OMe)(COD)]$_2$/BDPP/PEtPh$_2$ system at 20 bar H$_2$, 4 bar CO, [Rh] = 0.024 M and room temperature the following compounds were found: [Rh(μ-OMe)(BDPP)]$_2$ **1a**, [RhH(BDPP)$_2$] **2a** and [Rh(BDPP)$_2$]X **3a**, which have previously been characterized.[22] In addition, a new mixed hydride [RhH(CO)(BDPP)(PEtPh$_2$)] **6c** was observed as a multiplet at δ 51.8 and 36.9. This spectrum has a 16-line multiplet component that originates from a four-spin (1/2) system as has previously been observed for similar complexes such as [RhH(CO)(BDPP)(BDPP-*P*)][22,31] (Fig. 9). However, after the temperature was increased to reach hydroformylation conditions only the known species [RhH(CO)$_2$(BDPP)] **4a** and [Rh(CO)$_2$(BDPP)]$_2$ **5a** were observed. After these rhodium complexes were formed, variable temperature experiments were carried out and no other species were detected. Only the equilibrated species **4a** and **5a** were observed.

Table 5 ^{31}P-{^{1}H} and ^{1}H NMR data of species formed in the reaction of [Rh(μ-OMe)(COD)]$_2$ with PEtPh$_2$ under hydroformylation conditions

	^{31}P-{^{1}H}		^{1}H		
Complex	δ	$^1J_{Rh\text{-}P}$/Hz	δ	$^1J_{H\text{-}Rh}$/Hz	$^2J_{P\text{-}H}$/Hz
7	31.9	131	−9.4	7	15
8	34.5	150	−10.1	—	15

Discussion

In the hydroformylation of styrene using [Rh]/CHIRAPHOS systems the *in situ* HPIR experiments show that complex [RhH(CO)$_2$(CHIRAPHOS)] **4b**, which contains the diphosphine in the apical–equatorial position, is the only species observed as the resting state under 8 and 30 bar CO/H$_2$ and 80 °C (Fig. 5a). This species is analogous to the previously observed intermediate in the BDPP system. In the HPNMR experiments, however, the more concentrated solutions give rise to other species. A mixture of the complexes **4b**, **5b** (also observed for BDPP, **4a**, **5a**), **2b** and **3b** (not observed for BDPP after heating) was stable for CHIRAPHOS at high temperatures and pressures (Fig. 3).

Complexes **2b** and **3b** cannot be observed by HPIR techniques due to the absence of CO absorptions. Hydride **2b**, which contains two bidentate phosphines, is thought not to be a catalyst precursor in view of the steric hindrance that results even after dissociation of one of the arms of one of the bidentate ligands.

The main difference between the two ligands lies in the ring size that they form upon coordination; CHIRAPHOS forms a five-membered ring and BDPP a six-membered ring. Five-membered rings are more stable in transition metal complexes, although the natural bite angles of both ligands would seem small for the type of complexes to be expected. Therefore, in competition with CO, complex [RhH(CHIRAPHOS)$_2$] **2b** is relatively stable, while [RhH(BDPP)$_2$] **2a** is easily converted into complex **4a** or **5a**, as is observed in the HPNMR experiments.

While the experimental requirements for a hydroformylation reaction to be successful are usually not very stringent, some reaction always takes place, our experiments have shown that for the present study the exclusion of oxygen is extremely important. The ligands contain two alkyl substituents and therefore they are more sensitive to oxidation than triphenylphosphine. Furthermore, they are both bidentate ligands, and oxidation of only one phosphine destroys the necessary chelate ligand properties. The different stabilities of the five- and six-membered chelating rings may explain why BDPP and CHIRAPHOS behave differently towards oxidation. The six-membered ring complex is less stable and oxidation occurs when the chelate diphosphine is opened to form a monodentate

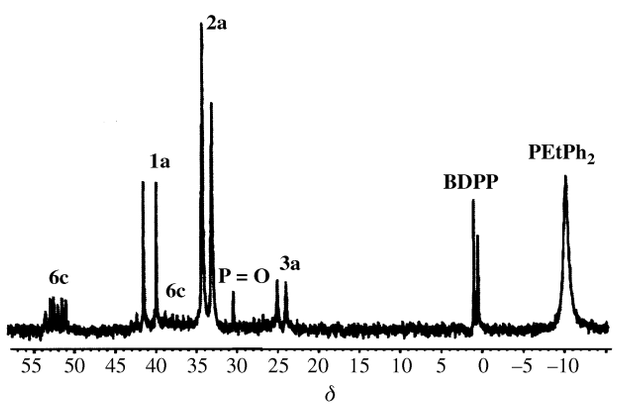


Fig. 9 ^{31}P-{^{1}H} NMR spectrum for the reaction of [Rh(μ-OMe)(COD)]$_2$ with BDPP and PEtPh$_2$ under hydroformylation conditions at room temperature.

Table 6 Hydroformylation of styrene with the [Rh(μ-OMe)(COD)]$_2$/BDPP/PEtPh$_2$ system[a]

Run	*P*/bar	*T*/°C	BDPP : [Rh]	PEtPh$_2$: [Rh]	*t*/h	% Conversion	% 2-PP/3-PP	% ee
15	8	80	1 : 1	2 : 1	15	100	93/7	49
16	8	80	1 : 1	4 : 1	14	99	92/8	47
17	30	80	1 : 1	2 : 1	5	52	93/7	47

[a] Conditions: 0.0125 mmol [Rh(μ-OMe)(COD)]$_2$, in 15 mL of cyclohexane, P(CO) = P(H$_2$).

species with a one-arm oxidized diphosphine. The species formed from the phosphine–phosphine oxide are more active and less regio- and enantio-selective.

When $PEtPh_2$, with electronic and steric effects similar to BDPP, was added the rhodium hydride **4a** and the dinuclear species **5a** were the only species present after heating to reach hydroformylation conditions, despite the presence of a mixed-ligand hydride **6c** during room temperature HPNMR experiments (Fig. 9). It should also be taken into account that the high concentrations used in the HPNMR provide different species. In the HPIR experiments the concentrations of the reagents are identical to those in the catalytic experiments and $[RhH(CO)_2(BDPP)]$ **4a** is the only species observed responsible for hydroformylation in spite of an excess of monophosphine. In this case, and in the absence of oxygen, the activity, regioselectivity and enantiomeric excess were the same as the ones obtained without monophosphine (Table 6, entries 15–17).

Therefore, in the presence of mono- and di-phosphine, the rhodium center prefers to coordinate with the diphosphine because of the chelate stabilization. In the same way, in the presence of oxidized and non-oxidized diphosphine, the chelate formed with the non-oxidized diphosphine is preferred. This is why an enantiomeric excess between 40 and 60% can be obtained either by working with careful exclusion of oxygen or by adding an excess of a diphosphine or a monophosphine to prevent oxidation of the coordinated diphosphine or monocoordination of the oxidized diphosphine.

The fact that the apical–equatorial isomer **4a** was the only species responsible for the hydroformylation present in the case of BDPP may explain why the enantiomeric excesses obtained for BDPP (50–60%) were higher than those for DIOP and other diphosphines (see Introduction). In contrast, the enantiomeric excess was lower when CHIRAPHOS was used, although the only species present at the resting state is the same. The larger bite angle of BDPP leads to a larger, and therefore more efficient, ligand than CHIRAPHOS, which may lead in turn to a higher enantioselectivity. CHIRAPHOS has a smaller chelate ring and this may decrease the influence on the asymmetric induction for the only available apical–equatorial coordination modes and the "natural" cancellation of stereoselectivities cannot be overcome.

Conclusion

We can conclude that the $[RhH(CO)_2(P–P)]$ species are the resting state observed in the case of BDPP and CHIRAPHOS under hydroformylation conditions. The presence of a monophosphine or an excess of diphosphine does not result in formation of other species under hydroformylation conditions. Only the oxidation of the coordinated chiral diphosphine leads to formation of the mononuclear rhodium hydride species **7** and **8** described for monophosphines, with the chiral diphosphine monocoordinated. These species are more active and provide lower regioselectivity and no enantioselectivity.

The different behaviour of rhodium systems with BDPP and CHIRAPHOS diphosphines prior to oxidation can be explained by the stability of the five-membered ring formed with CHIRAPHOS and the rhodium centre. The different enantiomeric excess obtained for BDPP and CHIRAPHOS, in spite of the presence of only one apical–equatorial isomer in each case, may be due to the different enantioface discrimination.

Experimental

General comments

Rhodium complexes were synthesized using standard Schlenk techniques under a nitrogen or argon atmosphere. Solvents were dried, distilled and deoxygenated before use. Styrene was filtered over alumina and deoxygenated to remove the oxygen. All other reagents were commercial samples used as purchased.

^1H NMR (300 MHz, referenced to TMS) and ^{31}P-$\{^1H\}$ NMR spectra (121.5 MHz, referenced to external 85% H_3PO_4) were recorded on a Bruker AMX-300 spectrometer. Assignments in complex spectra were made by simulation with gNMR 3.5M software.[32]

Gas chromatography was performed on a Carlo Erba GC 6000 Vega series or an Interscience Mega 2 series apparatus (split/splitless injector, J & W Scientific, DB1 30 m column, film thickness 3.0 μm, carrier gas 70 kPa of He, flame ionization detector) equipped with a Hewlett Packard Data system (Chrom-Card). Enantiomeric excesses were measured after reduction of the aldehydes to the corresponding alcohols on a Carlo Erba Vega 6000 Gas Chromatograph Shimadzu C-R 5A integrator.

Standard hydroformylation experiments

A solution of the catalyst precursor (0.0125 mmol), the phosphorus compound (0.0150 mmol) and the substrate were placed in an evacuated autoclave. The gas mixture (CO/H_2) was introduced, the system heated and stirring initiated when thermal equilibrium was reached. Conversions and regioselectivities were determined by GC analysis of the crude samples. A sample of the reaction mixture was treated to reduce the aldehydes to alcohols. The final mixture was analysed by GC to determine the enantiomeric excess.

In situ HPIR experiments

The HPIR spectra were recorded using previously described equipment.[33] The rhodium complex $[Rh(\mu\text{-}OMe)(COD)]_2$ (0.0125 mmol) and the corresponding phosphorus ligand (0.0150 mmol) were dissolved in 15 mL of cyclohexane. This solvent was used due to the lack of absorptions in the range of CO stretching bands. The autoclave was closed and flushed several times with the corresponding gas. After the autoclave had been pressurized and the mixture heated, the autoclave was placed in the infrared spectrometer. While the sample was being stirred the infrared spectra were recorded. Hydroformylation studies were performed using the same equipment, and the substrate was taken from the reservoir and added to the reaction mixture by overpressure. Once this addition had been done, the reaction started, as was shown by a pressure drop, and the spectra were recorded. The final solution was analysed by GC.

In situ HPNMR experiments

The *in situ* HPNMR experiments were carried out in a sapphire tube (diameter = 10 mm). The rhodium complex $[Rh(\mu\text{-}OMe)(COD)]_2$ (0.018 mmol), the corresponding phosphorus ligand and styrene (0.045 mmol) were dissolved in toluene-d_8 (1.5 mL) under nitrogen, and the sapphire tube was closed. After pressurizing the mixture with H_2/CO, the tube was placed in the NMR spectrometer and the spectra were recorded.

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