ELSEVIER

Journal of Molecular Catalysis A: Chemical 184 (2002) 111–119

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Rhodium-catalysed asymmetric hydroformylation of vinylarenes with chiral *P*,*N*-ligands based on DIOP skeleton

Ali Aghmiz [a], Anna M. Masdeu-Bultó [a,*], Carmen Claver [a], Denis Sinou [b,1]

[a] *Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Pl. Imperial Tàrraco 1, 43005 Tarragona, Spain*
[b] *Laboratoire de Synthèse Asymétrique Associé au CNRS, CPE Lyon, Université Claude Bernard Lyon I, 43, Boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France*

Received 7 May 2000; accepted 28 November 2001

Abstract

Hydroformylation of vinylarenes is performed using rhodium precursors with various *P*,*N*-donor chiral 4-diphenylphosphanyl-1-(dialkylamino)butane ligands (**8a**–**d**) with DIOP backbone. The systems were active at mild conditions and the selectivity in aldehydes was total when mixtures of CO/H_2 at a ratio 1/1 were used. The maximum regioselectivity in the branched products was 95%. The highest ee was 23%. NMR studies under catalytic conditions showed that species with monodentate ligands were present in the catalytic solution. © 2002 Published by Elsevier Science B.V.

Keywords: Rhodium; Hydroformylation; *P*,*N*-ligands; Asymmetric catalysis

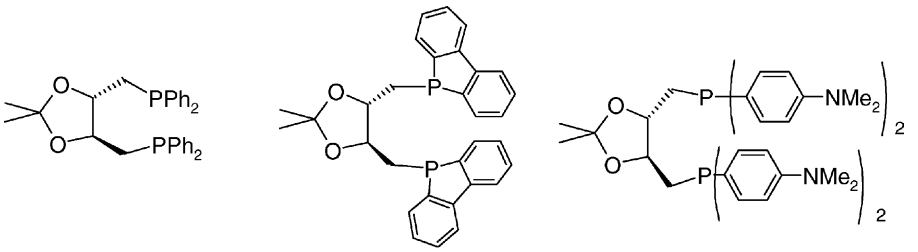
1. Introduction

Chiral diphosphines based on DIOP backbone [1] (**1**) (Fig. 1) have been widely applied in homogeneous catalysis. As these ligands are easy and cheap to prepare from tartaric acid, they have been often modified for different purposes. Since Rh/**1** systems were first used in the asymmetric hydroformylation of styrene derivatives [2], several substituents have been introduced into the phosphorus atom or into the dioxolan ring to improve optical induction or to allow the separation of the catalyst. For example, in the asymmetric hydroformylation of styrene using platinum complexes, the enantioselectivity obtained with the DIOP-based ligands increased from 26% ee with DIOP [3] to 64% ee with the dibenzophosphole derivative **2** [4] (Fig. 1). For the rhodium hydroformylation of vinyl acetate, the system with ligand **2** afforded an ee of 51%. By modifying the dioxolan moiety, **2** was attached to a 20% cross-linked polymer allowing to reuse the catalyst. By introducing an amino group into the diphenylphosphino moieties (**3**), the system became water soluble and the catalyst was recovered carrying out the reaction in a biphasic system [5].

Chiral non-C_2-symmetric *P*,*N*-donor heterobidentate ligands have afforded excellent stereochemical control in some homogeneous catalysis processes such as allylic substitution [6]. The presence of two different donor atoms can influence the stability and reactivity of the diastereomeric intermediates in the catalytic cycle. In this paper, we describe the application in the hydroformylation of alkenes of *P*,*N*-donor ligands with DIOP backbone.

* Corresponding author. Tel.: +34-977-559-572; fax: +34-977-559-563.
E-mail addresses: masdeu@quimica.urv.es (A.M. Masdeu-Bultó), sinou@univ-lyon1.fr (D. Sinou).
[1] Co-corresponding author. Tel.: +33-4-72446263; fax: +33-4-72448160.

1381-1169/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII: S1381-1169(01)00519-2



1 2 3

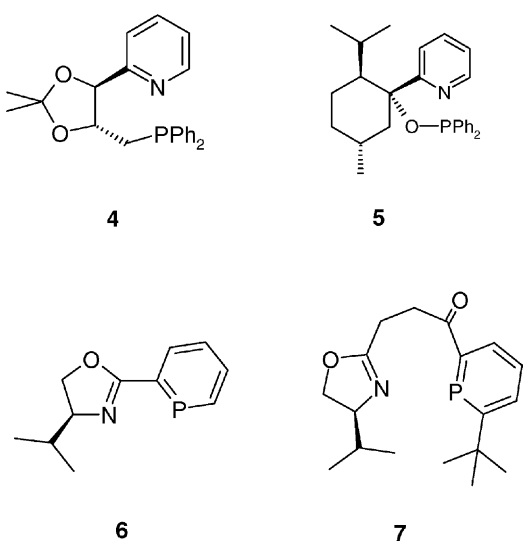
Fig. 1. Chiral diphosphines based on DIOP backbone.

The resting state in rhodium hydroformylation of 1-alkenes with diphosphine ligands is usually a pentacoordinate hydridorhodidum trigonal bipyramidal species [7]. Dissociation of CO takes place from this complex to form the active species that coordinates with the alkene [8]. It has been reported that the selectivity in the hydroformylation reaction is determined by the structure of this pentacoordinate alkene species [9–11]. Since the alkene species has not been detected, many efforts have been directed towards the characterisation of the resting state [$RhH(CO)_2$(diphosphine)] in order to obtain information about the coordination of the ligand and the geometry of the intermediates. The analogous bis(triphenylphosphine) pentacoordinate species exists in a mixture of the diequatorial (ee) and equatorial–apical (ea) isomers [12]. Bidentate ligands with the appropriate bite angle could, in theory, stabilise one of the isomers but they often exist also as a mixture of the ee and ea structures. Since equatorial–apical coordination sites are different, a heterobidentate ligand with the appropriate bite angle could differentiate and stabilise one of the species and decrease the number of diastereoisomeric intermediates, thus providing high enantioselectivities.

In general, *P*,*N*-chiral ligands have not been widely studied in hydroformylation reactions. The rhodium system with pyridine–phosphine ligand **4** (Fig. 2) produced negligible enantioselectivities in the hydroformylation of styrene [13]. By contrast, the menthyl-derivative **5** provided divergent enantioselectivities, depending on the substrate. With styrene or vinyl acetate, the ee's were very low (6–12%) but with 2-vinylnaphthalene ee's were as much as 78% [14]. Phosphabenzene-oxazolines such as **6** and **7** have recently been used in the hydroformylation of styrene. Although the regioselectivities were high, the ee's reported were never above 5% [15].

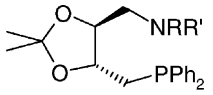
The low enantioselectivity reported may be caused by the formation of intermediates in the catalytic cycle with monodentate *P*,*N*-ligands, which should be ineffective in chiral induction. A strong coordinating species such as carbon monoxide can displace one of the coordination sites in the chelate. For this type of systems, therefore, the characterisation of the solution structures under hydroformylation conditions is of crucial interest.

Some of us recently reported the preparation of the chiral *P*,*N*-donor ligands (*S*,*S*)-**8a**–**d** (Fig. 3)



4 5 6 7

Fig. 2. *P*, *N*-chiral ligands applied in hydroformylation.



8a: R = H, R' = Tosyl; **8b:** R = R' = CH_2-naphthyl

8c: R = Ph, R' = α–naphthyl; **8d:** R = R' = Bn

Fig. 3. *P,N*-chiral ligands based on DIOP backbone.

based on the DIOP backbone and their use in palladium-catalysed allylic substitution [16,17]. In this paper, we report the use of these ligands in the hydroformylation of prochiral alkenes. The identification of the species formed under catalytic conditions is performed using NMR spectroscopy.

2. Experimental

2.1. General methods

All rhodium catalyst precursor systems were synthesised using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. All other reagents were used as-supplied. Complex $[Rh(\mu\text{-OMe})(cod)]_2$ [18] and ligands **8a–d** [16,17] were prepared as previously reported. Gas chromatography analyses were performed in an Hewlett Packard 5890A in an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm Ø) for the separation of the aldehydes and in an FS-cyclodex β-I/P (50 m × 0.25 mm Ø) for the separation of the chiral carboxylic acids.

The ^1H and ^{31}P NMR spectra were registered on a Varian 300 MHz instrument and referenced in the usual way. High-pressure NMR experiments (HPNMR) were carried out in a 10 mm diameter sapphire tube with a titanium cap [19]. The spectra were simulated with gNMR 4.0 [20].

2.2. Catalysis

Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was kept in a Teflon vessel. The inside of the cap of the autoclave was also Teflon-covered to prevent the solution from coming into direct contact with the stainless steel. An electric heating mantle kept the temperature constant.

Standard hydroformylation experiment. A solution (7.5 ml) containing the complex $[Rh(\mu\text{-OMe})(cod)]_2$ (0.05 mmol), the ligand in the corresponding ratio and the substrate (10 mmol) was introduced into the evacuated autoclave. The system was pressurised and heated. When thermal equilibrium was reached, more gas mixture was introduced until the desired pressure was attained. After the reaction time, the autoclave was cooled to room temperature and depressurised. The final mixture was analysed by GC. Enantiomeric excesses were measured by GC using FS-cyclodex β-I/P (50 m × 0.25 mm Ø) chiral column after the aldehydes were transformed into the carboxylic acids following described procedures [21]. Using hydrogen as a gas carrier, the conditions and retention times for the separation of each enantiomer were as follows. **10a**: $T = 134\,^{\circ}C$ isothermic, 100 kPa carrier gas, split 1:150, (*S*)-**10a**: 44.3 min and (*R*)-**10a**: 47.1 min; **10b**: $T = 170\,^{\circ}C$ isothermic, 150 kPa carrier gas, split 1:150, (*S*)-**10b**: 19.1 min and (*R*)-**10b**: 20.3 min; **10c**: $T = 160\,^{\circ}C$ isothermic, 150 kPa carrier gas, split 1:150, (*S*)-**10c**: 15.9 min and (*R*)-**10c**: 17.3 min; **10d**: $T = 170\,^{\circ}C$ isothermic, 150 kPa carrier gas, split 1:150, (*S*)-**10d**: 70.3 min and (*R*)-**10d**: 74.6 min.

2.3. HPNMR experiments

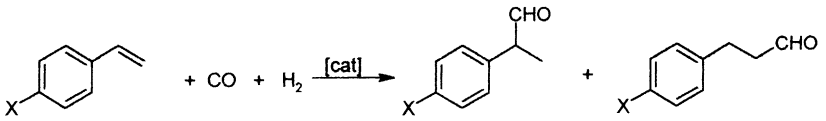
In a typical experiment, the NMR tube was filled under N_2 with a solution of $[Rh(\mu\text{-OMe})(cod)]_2$ (23.5 mg, 0.048 mmol), the ligand (108.6 mg, 0.213 mmol) and toluene-d_8 (2 ml). The tube was pressurised to the desired pressure and left for 2 h under agitation at room temperature, and the NMR spectra were recorded.

3. Results and discussion

3.1. Catalytic studies

Ligands (*S*,*S*)-**8a–d** containing R and R′ groups with different electronic and steric properties were used in the rhodium hydroformylation of styrene derivatives **9a–c** and vinylnaphthalene **9d** to yield the

branched aldehydes **10a–d** and the linear aldehydes **11a–d** (Eqs. (1) and (2)):

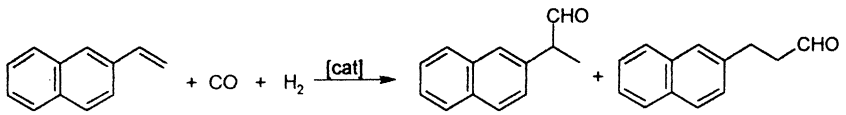


9a: X = H
9b: X = OMe
9c: X = F

10a: X = H
10b: X = OMe
10c: X = F

11a: X = H
11b: X = OMe
11c: X = F

(1)



9d **10d** **11d**

(2)

Catalytic precursors were prepared in situ by adding the ligands to solutions of $[Rh(\mu\text{-OMe})(cod)]_2$ in the ratio shown. Table 1 shows the results at different reaction conditions.

The conversions into aldehydes obtained with the *N*-tosylate derivative **8a** in the hydroformylation of styrene **9a** were nearly total after 24 h reaction time (Table 1, entries 1–3). Activity was maintained even at very mild conditions such as 5 bar H_2/CO pressure and 298 K (Table 1, entry 3). The regioselectivities in the branched aldehyde **10a** were high (92–94%), but the enantioselectivities of the product obtained were low (11–13% ee). In these experiments, the ratio ligand/Rh was 2, and so species with two monodentate ligands per rhodium, which would provide low enantioselectivity, could be formed. To favour chelation avoiding bis-monodentate species, the ligand/Rh ratio was decreased to 1.1, but this did not improve the enantioselectivity (Table 1, entry 4).

Table 1
Hydroformylation of **9a–d** using $[Rh(\mu\text{-OMe})(cod)]_2$/**8a–d** systems as catalyst precursors[a]

Entry	Ligand	Substrate	*P* (bar)	*T* (K)	**8**/Rh	Conversion (%)[b]	Percent of **10**	Percent of ee[c]
1	**8a**	**9a**	20	323	2	99.6	91.9	11 (*R*)
2	**8a**	**9a**	30	298	2	97.7	93.6	13 (*R*)
3	**8a**	**9a**	5	298	2	97.2	93.1	12 (*R*)
4	**8a**	**9a**	5	298	1.1	72.0	93.3	5 (*R*)
5[d]	**8b**	**9a**	30	338	2	99.5	90.0	15 (*S*)
6	**8c**	**9a**	30	338	2	99.9	91.3	8 (*R*)
7	**8c**	**9a**	30	323	2	99.8	91.0	18 (*R*)
8[e]	**8d**	**9a**	5	298	2	48.0	93.8	18 (*S*)
9[d,f]	**8d**	**9a**	5	298	2	77.0	93.0	17 (*S*)
10[e,g]	**8d**	**9a**	5	298	2	66.5	80.5	–
11[e]	**8d**	**9a**	5	298	4	42.0	93.0	18 (*S*)
12[e]	**8d**	**9b**	5	298	2	22.0	93.0	19 (*S*)
13[e]	**8d**	**9c**	5	298	2	52.0	95.0	20 (*S*)
14[e]	**8d**	**9d**	5	298	2	58.0	95.0	23 (*S*)

[a] Reaction conditions: substrate (10 mmol), complex (0.05 mmol), tetrahydrofurane (7.5 ml), $CO/H_2 = 1$, time = 24 h.
[b] Aldehyde conversion measured by chromatography integral ratio.
[c] Measured by chromatography integral ratio on the corresponding acid 2-phenylpropanoic.
[d] Time = 8 h.
[e] Time = 4 h.
[f] Toluene was used as the solvent.
[g] $CO/H_2 = 1/4$, conversion = 99%, hydrogenation = 44%.

The activities and regioselectivities provided by the rhodium systems with the bis(methylnaphthyl) derivative **8b** and the naphthyl-phenyl derivative **8c** were similar (Table 1, entries 5–7). When the amino-phenyl-naphthyl derivative **8c** was used, the enantioselectivity obtained at 323 K was 18%.

The rhodium system with the bis-benzyl derivative **8d** provided a 48% conversion in 4 h using tetrahydrofurane as a solvent at 5 bar and 298 K (Table 1, entry 8). Enantioselectivity in (*S*)-**10a** was of 18% under this conditions. When toluene was used, the activity of the system decreased (Table 1, entry 9) but the regio- and enantioselectivity were similar.

For PPh_3 and diphosphines, at low hydrogen pressure conditions, a dimeric inactive complex $[RhL_2(CO)(\mu\text{-}CO)]_2$ is reported to be in equilibrium with the pentacoordinate species $[RhH(CO)_2L_2]$ [22–25]. To prevent the formation of this dimeric species, we performed an experiment at a H_2/CO ratio of 4:1. Under these conditions, chemoselectivity in the aldehydes dropped dramatically to 56%, because of the formation of hydrogenation products, and no enantioselectivity was observed (Table 1, entry 10).

On the other hand, in some diphosphine systems the enantioselectivity can be improved by increasing the ligand to rhodium ratio [26,27]. However, in the Rh/**8d** system, the enantioselectivity was the same as with ligand/Rh = 2 or 4 (Table 1, entry 11).

We studied the hydroformylation of the *para*-substituted styrenes (*p*-OMe **9b** and *p*-F **9c**) with the rhodium system using ligand **8d** and compared the results with those for styrene. Activity and regioselectivity in the branched product decreased when the substrate contained an electron-donating substituent such as a methoxy group (**9b**). However, the enantioselectivity was similar to that for styrene (Table 1, entry 12). On the other hand, activity and selectivity increased with **9c**, which contained an electron-withdrawing substituent (Table 1, entry 13). This variation in regioselectivity agreed with reported data for hydroformylation of *p*-substituted styrenes with Rh/PPh_3 systems, where increasing the electron-withdrawing properties of the substituents raised the selectivity in 2-arylpropanal products [28].

We also performed the hydroformylation of vinylnaphthalene (**9d**) with the Rh/**8d** system. The results (Table 1, entry 14) were similar to those for *p*-fluorostyrene, although the enantioselectivity was slightly higher (23% in (*S*)-**10d**).

From the hydroformylation study, some conclusions can be derived. The fact that the enantioselectivity depended on the substituent of the nitrogen is indirect evidence of the *P*,*N*-coordination of the ligand. The ligands with the disubstituted bulkier substituents (naphthyl and benzyl) provided the highest chiral inductions. However, the low ee's may be due to the formation of species with monodentate ligands or to the system's low intrinsic chiral induction. In order to get further information on this point, we performed NMR spectroscopy experiments under hydroformylation conditions.

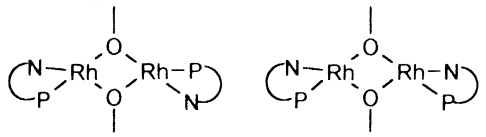
3.2. In situ identification of the species by HPNMR

The *P*,*N*-ligands can coordinate either as a chelate or as a monodentate (probably through the P atom), which would clearly affect their chiral induction. To elucidate the coordination mode of the *P*,*N*-ligands, we performed NMR experiments under catalytic conditions (HPNMR). Although the NMR technique requires a higher concentration of the complexes than catalytic experiments, it can provide valuable information about the species present during the catalytic reaction.

We recorded the $^{31}P\{^1H\}$ and ^1H NMR spectra of a solution of the catalyst precursor $[Rh(\mu\text{-}OMe)(cod)]_2$/**8d** in toluene-$d_8$ at the same molar ratio as in the catalytic experiments and under carbon monoxide and hydrogen pressure. The concentration on this complex in the solution was ca. 2.4×10^{-2} M. In some cases, we also performed experiments at lower concentration (ca. 8×10^{-3} M) which is more similar to the concentration in the catalytic experiments.

In the $^{31}P\{^1H\}$ NMR spectrum, an initial reference experiment at 2.4×10^{-2} M without synthesis gas showed a major doublet at $\delta = 47.6$ ppm ($^1J_{P-Rh} = 190.5$ Hz) and another small doublet (ratio ca. 91/9) at $\delta = 48.6$ ppm ($^1J_{P-Rh} = 195.0$ Hz). Signals corresponding to the free ligand ($\delta = -25.0$ ppm) and oxide ($\delta = 27.8$ ppm) were also observed. Signals of very low intensity also appeared in the $\delta = 32$–44 ppm region, but these were not detected when the concentration was 8×10^{-3} M.

The low chemical field ($\delta \approx 48$ ppm) and large coupling constant for these signals ($J = 190.5$ and 195.0 Hz) suggest the formation of the binuclear species [(*P*,*N*-**8d**)Rh(μ-OMe)(*P*,*N*-**8d**)] (**12**). The $^{31}P\{^1H\}$ NMR spectra for [Rh(μ-Cl)(dppp)]$_2$ (dppp = 1, 3-bis(diphenylphosphino)propane) and [Rh(μ-Cl)(DIOP)]$_2$ showed doublets with coupling constants of $\delta = 184$ and 191 Hz, respectively [29]. The two signals may correspond to the possible *trans*-**12a** and *cis*-**12b** isomers.



This solution was pressurised to 2.5 atm of H_2. As well as the signals of species **12**, there was a wide signal in the $\delta = 30$–35 ppm region in the $^{31}P\{^1H\}$ NMR spectrum at room temperature and two wide signals ($\delta = -9.2$ and -9.7 ppm) in the hydride region of the ^1H spectra. The spectra could not be resolved in the 213–323 K range.

The solution was then pressurised at 5 atm of a mixture 1/1 of carbon monoxide and hydrogen. The $^{31}P\{^1H\}$ spectrum at room temperature (Fig. 4) showed several signals corresponding to the four species **13**–**16** (Table 2) in calculated ratio 1:2.5:2.2:1.1, respectively. In the ^1H NMR (Fig. 4) spectra, only one signal (dt) appeared in the hydride region ($\delta = -9.54$ ppm, $^2J_{H-P} = 15.2$ Hz, $^1J_{H-Rh} = 6.7$ Hz.

The doublet at $\delta = 28.4$ ppm in the $^{31}P\{^1H\}$ and the double triplet in the hydride region ($\delta = -9.54$ ppm) of the ^1H NMR proved the formation of a rhodium species with two time-averaged phosphorous atoms. Since the chemical shifts and the coupling constants correlated well with those reported for monophosphines in the complex [RhH(PEtPh)$_2$(CO)$_2$] ($\delta_P = 31.2$ ppm (d), $^1J_{P-Rh} = 131$ Hz; $\delta_H = -9.3$ ppm (td), $^2J_{H-P} = 15$ Hz, $^1J_{H-Rh} = 7$ Hz) [30], we propose that the structure for the species **13** is [RhH(*P*-**8d**)$_2$(CO)$_2$] in which two ligands **8d** are monodentate. As reported for PPh_3 and $PEtPh_2$, the coupling constants indicate that complex **13** exists as a mixture of ee and ea isomers. Only small changes in chemical shift were observed when the temperature was dropped to 213 K.

The doublet at $\delta = 28.7$ ppm showed a P–Rh coupling constant $J = 113.0$ Hz, which is in the range reported for monohydrido trigonal bipyramidal species with chelated diphosphines [RhH(CO)$_2$(diphosphine)] [25]. This value for the P–Rh coupling constant is considered an average between P in the apical and equatorial position of the trigonal bipyramidal species. The corresponding hydrido signal could not be observed at 5 atm at different temperatures (213–333 K). At 213 K, the ^{31}P signal at $\delta = 28.7$ ppm broadened

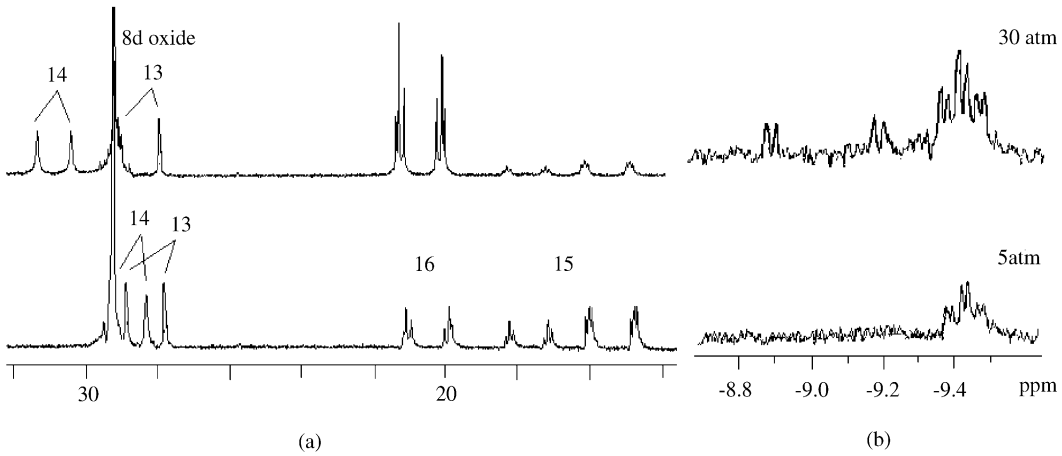


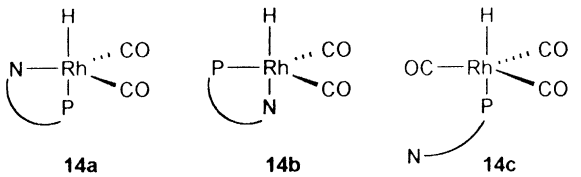
Fig. 4. NMR spectra of a toluene-d$_8$ solution of [Rh(μ-OMe)(cod)]/**8d** (Rh/P = 1/2): (a) $^{31}P\{^1H\}$: 5 atm CO/H_2 (1/1) (bottom); 30 atm CO/H_2 (top). (b) Hydride region of the ^1H NMR: 5 atm CO/H_2 (1/1) (bottom); 30 atm CO/H_2 (top).

Table 2
NMR signals (δ, ppm; J, Hz) of the species formed in a solution of [Rh(μ-OMe)(cod)]$_2$/**8d** (**8d**/Rh = 2) in toluene-d$_8$ at 5 atm CO/H$_2$ (1/1)[a]

Species	^{31}P (J)	^{1}H (J)
[RhH(*P*-**8d**)$_2$(CO)$_2$] (**13**)	28.2 d ($^1J_{P-Rh}$ = 131.3 Hz)	−9.54 dt ($^2J_{H-P}$ = 15.2, $^1J_{H-Rh}$ = 6.7)
14	30.8 d[c] ($^1J_{P-Rh}$ = 113.0 Hz)	−9.04 dd[c] ($^2J_{H-P}$ = 88.8, $^1J_{H-Rh}$ = 7.2)
[(*P*-**8d**)$_2$(CO)Rh(μ-CO)$_2$Rh(CO)$_2$(*P*-**8d**)] (**15**)	17.6 pt ($^1J_{P-Rh}$ = 130.7 Hz, $^2J_{P-P}$ = 12.2 Hz) 15.3 ddd ($^1J_{P-Rh}$ = 152.1 Hz, $^3J_{P-Rh}$ = 8.5 Hz)	–
[(Rh(μ-CO)(CO)$_2$(*P*-**8d**)]$_2$ (**16a**)	20.6[b] ($^1J_{P-Rh}$ = 140.2 Hz, $^3J_{P-P}$ = 26.6 Hz, $^3J_{P-Rh}$ = 5.6 Hz)	–

[a] d: doublet; pt: pseudotriplet; dt: double triplet; ddd: double of double doublet.
[b] Data obtained from simulation for a system AA′XX′.
[c] Data obtained at 30 bar.

and shifted to δ = 33 ppm and the signal corresponding to the free ligand also broadened indicating a fluxional process. When we increased the total pressure to 30 bar, a new double doublet appeared in the ^{1}H NMR at δ −9.04 ppm ($^2J_{H-P}$ = 88.8 Hz, $^1J_{H-Rh}$ = 7.2 Hz), while in the ^{31}P{^{1}H} (Fig. 4) the broad signal resolved at δ = 30.8 ppm as a doublet with the same coupling constant as under 5 atm (J = 113 Hz). The large H–P coupling constant of the hydrido signal indicates a *trans*-disposition of both nuclei. From the multiplicity of the hydrido signal, we can conclude that only one phosphorus atom is coordinated to the metal. Since the coupling constant is similar to the ones reported for some diphosphine systems, a pentacoordinate [RhH(*P*,*N*-**8d**)(CO)$_2$] structure in which ligand **8d** acts as a chelate may be proposed for **14**. The P–Rh coupling constant of J = 113 Hz may correspond to an average of the P that occupy the equatorial and axial positions (**14a** and **14b**). Nevertheless, the fact that increasing the total pressure the signal of **14** increased slightly may indicate the formation of a species with more content of CO per rhodium such us [RhH(*P*-**8d**)(CO)$_3$] (**14c**) in which the ligand act as a monodentate.



The signals at δ = 17.6 and 15.3 ppm (1:2 ratio) were assigned to the dimeric Rh(0) species [(*P*-**8d**)$_2$(CO)Rh(μ-CO)$_2$Rh(CO)$_2$(*P*-**8d**)] **15**. The coupling constants and multiplicity of species **15**, in which **8d** acts as a monodentate ligand, are in good agreement with those reported for the analogous [(PEtPh$_2$)$_2$(CO)Rh(μ-CO)$_2$Rh(CO)$_2$(PEtPh$_2$)] (δ = 20.3 ppm (dt), $^1J_{P-Rh}$ = 135 Hz, $^2J_{P-P}$ = 12 Hz; 16.4 ddd, $^1J_{P-Rh}$ = 152 Hz, $^2J_{P-Rh}$ = 8 Hz) [30]. However, the corresponding dimeric species [(*P*-**8d**)$_2$(CO)Rh(μ-CO)$_2$Rh(CO)(*P*,*N*-**8d**)] in which **8d** is coordinated as a chelate to one of the rhodium centres cannot be discarded.

The signal at δ = 20.6 ppm had a second-order multiplicity. The calculated coupling constants and chemical shift (Fig. 5, Table 2) may correspond to a Rh(0) dimeric species which has one phosphorus atom per rhodium centre. Formulae that fit this description are [Rh(μ-CO)(CO)$_2$(*P*-**8d**)]$_2$ (**16a**) and [Rh(μ-CO)(CO)(*P*,*N*-**8d**)]$_2$ (**16b**). The fact that the signal for **16** is at a lower field than **15** may be due to a higher content of CO per rhodium. The variation of the chemical shift in the analogous PPh$_3$ complexes are [Rh(μ-CO)(CO)$_2$(PPh$_3$)]$_2$ > [(PPh$_3$)(CO)$_2$Rh(μ-CO)$_2$Rh(PPh$_3$)$_2$(CO)] > [(Rh(μ-CO)(CO)(PPh$_3$)$_2$]$_2$ [31]. Another factor that points to the hexacarbonylated species **16a** is that its concentration increased when total pressure increased (Fig. 4). We therefore attributed the structure **16a** to the signal at δ = 20.6 ppm.

It has been reported that the dimeric Rh(0) species are formed at high rhodium concentration and low hydrogen pressure [7]. When we performed the same experiment at lower concentration (8×10^{-3} M) we also observed the formation of these dimers. Therefore,

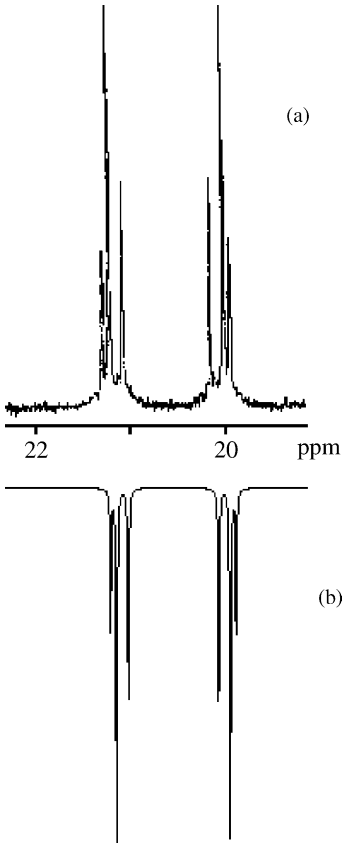


Fig. 5. $^{31}P\{^{1}H\}$ NMR spectra of species **16**: (a) experimental; (b) simulated with constants in Table 2.

they are also likely to be present under catalytic conditions.

Finally, we removed the pressure, added the substrate **9b** in a ratio of 5:1 respect to Rh and re-pressurised the HPNMR tube to 5 atm CO/H_2. In the $^{31}P\{^{1}H\}$ NMR spectra, at 323 K a major doublet was observed at $\delta = 28.2$ ppm ($J = 125$ Hz), which we attributed to species **13**. The variation of the coupling constant may be due to a fluxional process. The signal of the free ligand also broadened. There was no hydride signal for the ^{1}H spectra. Because of the overlap with the phosphine oxide signal, the ^{31}P spectra provided no clear evidence of the signal corresponding to species **14**. A new broad signal appeared at $\delta = 25$ ppm, which gave a broad doublet ($\delta = 23.6$ ppm, $^{1}J_{P-Rh} = 142$ Hz) when the solution was cooled at 253 K. The dimeric species **15** and **16** were also present giving broad signals. The spectra did not change substantially when the hydroformylation finished. The signals were the same when the concentration of the complex was lower.

HPNMR experiments confirmed the initial evidence that species with monodentate *P*-ligands formed under catalytic conditions and there are no enough evidences to assert that chelated *P,N*-species are also present. The *P*-coordinated species may be responsible for the low enantioselectivities. However, the ee's achieved are in the same range as those for the related Rh/DIOP systems in the hydroformylation of styrene [2]. Therefore, from this study we cannot rule out the possibility that species bearing chelated *P,N*-ligands participate in the hydroformylation.

Further work is in progress in order to confirm the nature of the species detected by HPNMR.

4. Conclusions

We used *P,N*-donor chiral ligands with DIOP skeleton in the hydroformylation of vinylarenes and obtained enantioselectivities of up to 23%. In situ $^{31}P\{^{1}H\}$ and ^{1}H NMR experiments under catalytic conditions showed the formation of species with monodentate phosphorus ligands. This could be the reason for the low enantioselectivities obtained.

Acknowledgements

We thank the Ministerio de Educación, Cultura y Deporte and the Generalitat de Catalunya (Direcció General de Recerca) for financial support (PB97-04070CO5-01). We also thank Dr. I del Río for interesting discussion.

References

[1] H.B. Kagan, T.-P. Dang, J. Am. Chem. Soc. 94 (1972) 6429.
[2] C. Salomon, G. Consiglio, C. Botteghi, P. Pino, Chimia 27 (1973) 215.
[3] C.U. Pittman, Y. Kawabata, L.I. Flowers, J. Chem. Soc., Chem. Commun. (1982) 473.
[4] G. Parrinello, R. Descheneaux, J.K. Stille, J. Org. Chem. 51 (1986) 4189.
[5] I. Toth, I. Guo, B.E. Hanson, Organometallics 12 (1993) 848.

[6] A. Pfaltz, M. Lautens, in: E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Vol. 2, Springer, Berlin, 1999, p. 833 (Chapter 24).
[7] P.W.N.M. van Leeuwen, C.P. Casey, G.T. Whiteker, in: P.W.N.M. van Leeuwen, C. Claver (Eds.), Rhodium Catalyzed Hydroformylation, Kluwer Academic Publishers, Dordrecht, 2000, p. 63.
[8] L.A. van der Veen, P.H. Keeven, G.C. Schoemaker, J.N.H. Reek, P.C.J. Kamer, P.W.N.M. van Leeuwen, M. Lutz, A.L. Spek, Organometallics 19 (2000) 872.
[9] C.P. Casey, G.T. Whiteker, M.G. Melville, L.M. Petrovich, J.A. Garney Jr., D.R. Powell, J. Am. Chem. Soc. 114 (1992) 5535.
[10] C.P. Casey, L.M. Petrovich, J. Am. Chem. Soc. 117 (1995) 6007.
[11] L.A. van der Veen, M.D.K. Boele, F.R. Bregman, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, H. Schenk, C. Bo, J. Am. Chem. Soc. 120 (1998) 11616.
[12] J.M. Brown, A.G. Kent, J. Chem. Soc., Perkin Trans. 2 (1987) 1597.
[13] C. Basoli, C. Botteghi, M.A. Cabras, G. Chelucci, M. Marchetti, J. Organomet. Chem. 488 (1995) C20.
[14] C.G. Arena, F. Nicolò, D. Drommi, G. Bruno, F. Faraone, J. Chem. Soc., Chem. Commun. (1994) 2251.
[15] B. Breit, J. Mol. Catal. A 143 (1999) 143.
[16] F. Robert, N. Gaillard, D. Sinou, J. Mol. Catal. A 144 (1999) 473.
[17] F. Robert, F. Delbecq, C. Nguefack, D. Sinou, Eur. J. Inorg. Chem. (2000) 351.
[18] R. Usón, L.A. Oro, J. Cabeza, Inorg. Synth. 23 (1985) 126.
[19] A. Cusanelli, U. Frey, D.T. Richens, A. Merbach, J. Am. Chem. Soc. 118 (1996) 5265.
[20] P.H.M. Budzelaar, gNMR, Ivory Soft, Cherwell Scientific Publishers, Oxford, 1998.
[21] A. Abiko, J.C. Roberts, T. Takemasa, S. Masamune, Tetrahedron Lett. 27 (1986) 4537.
[22] D. Evans, G. Yagupsky, G. Wilkinson, J. Chem. Soc. A (1968) 2660.
[23] C.K. Brown, G. Wilkinson, Tetrahedron Lett. 22 (1969) 1725.
[24] C.K. Brown, G. Wilkinson, J. Chem. Soc. A (1970) 2753.
[25] A. Castellanos-Páez, S. Castillón, C. Claver, P.W.N.M. van Leeuwen, W.G.J. de Lange, Organometallics 17 (1998) 2523.
[26] A.M. Masdeu-Bultó, A. Orejón, A. Castellanos, S. Castillón, C. Claver, Tetrahedron Asymmetry 7 (1996) 1829.
[27] M. Diéguez, M.M. Pereira, A.M. Masdeu-Bultó, C. Claver, J.C. Bayón, J. Mol. Catal. A 143 (1999) 111.
[28] T. Hayashi, M. Tanaka, I. Ogata, J. Mol. Catal. 13 (1981) 323.
[29] D.A. Slack, I. Greveling, M. Baird, Inorg. Chem. 18 (1979) 3125.
[30] Z. Freixa, M.M. Pereira, A.A.C.C. Pais, J.C. Bayón, J. Chem. Soc., Dalton Trans. (1999) 3245.
[31] C. Bianchini, H.M. Lee, A. Meli, F. Vizza, Organometallics 19 (2000) 849 and references therein.