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Journal of Molecular Catalysis A: Chemical 195 (2003) 113–124

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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Rhodium-sulfonated diphosphine catalysts in aqueous hydroformylation of vinyl arenes: high-pressure NMR and IR studies

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Received 17 July 2002; accepted 18 September 2002

Abstract

Hydroformylation of vinyl arenes (*p*-methoxystyrene and *p*-fluorostyrene) was performed in aqueous solutions using as catalyst precursor $[Rh(\mu\text{-}OMe)(cod)]_2$ (cod = 1,5-cyclooctadiene) associated with the sulfonated 1,3-diarylphosphines (tetrasulfonated 1,3-bis(diphenylphosphino)propane (dpppts)) and the chiral (*S*,*S*)-bdppts (2,4-bis(diphenylphosphino)pentane). The influence of pH on the reaction rate was studied. After 24 h conversion was practically total with the achiral system in basic medium for the substituted styrene substrates. Selectivities in aldehydes were >85%. At neutral pH, the asymmetric hydroformylation of *p*-substituted styrenes using the rhodium–bdppts systems provides low conversion but the enantioselectivities were as high as 66%, the highest reported so far for this kind of substrates in aqueous systems. Comparison experiments using rhodium precursors with the non-sulfonated bdpp in organic solvents indicated that the enantioselectivity was higher in aqueous solutions for the *p*-methoxystyrene derivative and slightly lower for *p*-fluorostyrene. However, in both the cases the conversions in aqueous systems were low. High-pressure NMR and IR experiments in water/methanol indicate that $[RhH(CO)_2$(sulfonated diphosphine)] species form under catalytic conditions in basic medium. At neutral pH, the main species observed in the case of the bdppts ligand is $[Rh(bdppts)_2]^+$ which may account for the low conversion in this medium.

Keywords: Rhodium; Hydroformylation; Sulfonated diphosphines; Aqueous systems; Asymmetric catalysis

1. Introduction

Since the water soluble rhodium–tppts system (tppts = $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$) [1,2] was first applied to the industrial hydroformylation of propene by Rhône-Poulenc/Ruhr-Chemie in 1984 [3,4], research in the area of biphasic catalysis has become very active [5]. Although other water-soluble ligands have

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1381-1169/02/$ – see front matter
PII: S1381-1169(02)00544-7

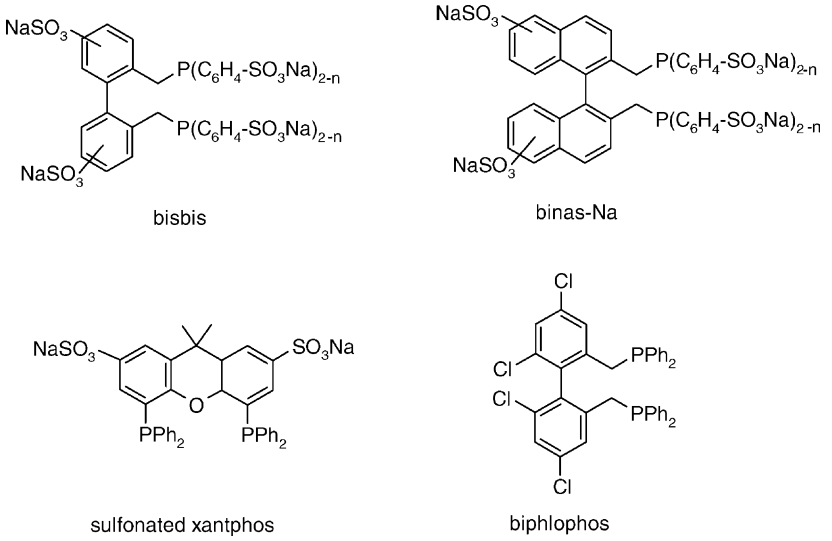


Fig. 1. Sulphonated diphosphines.

been used, most studies use the monodentate tppts ligand.

Although the activities and selectivities in the hydroformylation of propene are better with sulfonated diphosphines such as bisbis [6] or binas-Na [7] (Fig. 1) than with Rh–tppts very little can be found in the literature about sulfonated diphosphines. The Rh–dppets system (dppets: tetrasulfonated 1,2-bis(diphenylphosphino)ethane) [8] has been used in the hydroformylation of 1-octene (conversion = 5–25%) and the $[Rh(acac)(CO)_2]$/dppbts system (dppbts: tetrasulfonated 1,4-bis(diphenylphosphino)butane) in the hydroformylation of methyl acrylate [9]. The sulfonato group has also been incorporated into the xantene backbone in the sulfonated xantphos (Fig. 1) which has been used in the rhodium hydroformylation of 1-hexene [10]. Chelating diphosphines with sulfonated pendant groups p-C_6H_4–$(CH_2)_n$–$C_6H_4SO_3Na$ and a binaphtyl or biphenyl backbone [11,12] have also been used in the hydroformylation of 1-octene.

There are few reports about the asymmetric hydroformylation of vinyl arene derivatives in aqueous systems probably because the corresponding aldehydes are easy to racemize. Thus, the monophosphine $P(menthyl)[(CH_2)_8C_6H_4$–$p$-$SO_3Na]_2$ associated with rhodium complexes [13] gives higher conversion and regioselectivity in the branched aldehyde than the Rh–tppts system. However, no optical induction was observed. In the hydroformylation of styrene with water/toluene as the solvents, no enantiomeric excesses (e.e.) was observed when the chiral sulfonated derivative of biphlophos was used (Fig. 1) [14]. Nevertheless, the rhodium system with the chiral sulfonated diphosphine (*S*)-binas6-Na, provided an enantioselectivity as high as 18%, indicating that optical induction can be obtained in aqueous systems [15].

In this context, we recently reported the asymmetric hydroformylation of styrene using tetrasulfonated diphosphines (*S*,*S*)-bdppts ((tetrasulfonated 2,4-bis(diphenylphosphino)pentane) and (*R*,*R*)-cbdts (cbdts: tetrasulfonated 1,2-bis(diphenylphosphinomethyl)cyclobutane) (Fig. 2) [16]. The enantioselectivities for rhodium–bdppts systems were in the same range as those reported for binas-Na systems.

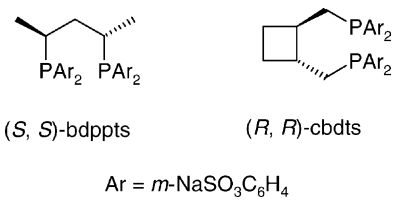


Fig. 2. Chiral sulphonated diphosphines.

To avoid racemization of the 2-phenylpropanal derivatives formed, the control of the pH is crucial in aqueous systems. Nevertheless, the pH of the solution affects the activity of the catalyst. It has been reported that hydroformylation reactions of alkenes are faster at basic pH [17–19]. Reactivity studies concerning sulfonated monophosphines showed that the chloro carbonyl complex [RhCl(CO)(tppms)$_2$] (tppms = $PPh_2(C_6H_4$–*m*-$SO_3Na)$) reacts with H_2 to form the species [RhH(CO)(tppms)$_3$] only when the pH is $\geq$5 [20] which explains the general observation that activity increases as pH increases.

In this paper, we present our study on the hydroformylation of *p*-methoxystyrene and *p*-fluorostyrene using rhodium catalysts with the 1,3-diphosphines 1,3-bis(diphenylphosphino)propane (dpppts) and the ligands (*S*,*S*)-bdppts. We also compare our results with the results provided by rhodium systems using the non-sulfonated diphosphine bdpp in organic solvents.

Due to the importance of the reaction medium's pH for activity and selectivity since it controls the species formed, we used high-pressure NMR and IR techniques to analyse the Rh-sulfonated diphosphine solutions under CO and H_2 as a function of pH in order to identify the species present under hydroformylation conditions. Although there are many spectroscopic studies under hydroformylation conditions with Rh–phosphine [21–23] and Rh–diphosphine [24,25] systems in organic solvents, the studies in aqueous solutions are very few [20].

2. Experimental

2.1. General methods

All syntheses of the rhodium catalyst precursors were carried out using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. All other reagents were used as supplied. The complex [Rh(μ-OMe)(cod)]$_2$ [26] and the diphosphines dpppts and (*S*,*S*)-bdppts were prepared as previously reported [27,28]. Gas chromatography analyses were performed in a 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 a FS-cyclodex β-I/P (50 m × 0.25 mm Ø) for the separation of the chiral carboxylic acids. The ^{1}H and ^{31}P NMR spectra were registered on a Varian 300 MHz instrument and referenced in the usual way. High-pressure NMR experiments (HP NMR) were carried out in a 10 mm diameter sapphire tube with a titanium cap [29]. High-pressure infrared experiments (HP IR) were performed in an IR cell equipped with a CaF_2 window, sample holders built from PTFE and mixing and heating facilities [30].

2.2. Catalysis

Hydroformylation experiments were carried out in an autoclave equipped with magnetic stirrer. The reaction mixtures were kept in a Teflon vessel and the inner part of the autoclave's cap 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. The standard procedure for the hydroformylation experiments in organic solvents has been reported previously [31].

2.2.1. Standard hydroformylation experiment

The catalyst precursor [Rh(μ-OMe)(cod)]$_2$ (0.015 mmol) and the sulfonated phosphorus compound were stirred in the corresponding ratio for 1 h in the corresponding solvent (6 ml) until they totally dissolved. The pH was adjusted to the desired value using NaOH (0.25 M) or H_2SO_4 (0.25 M). The substrate (15 mmol) was added and the whole mixture placed in the evacuated autoclave. The gas mixture was introduced and the heating started. When thermal equilibrium was reached, more gas mixture was introduced until the desired pressure. After the reaction time, the autoclave was cooled to room temperature and depressurized. The reaction mixture was extracted with dichloromethane (3 × 5 ml) and the organic phase was dried over magnesium sulfate and analyzed by GC. Enantiomeric excesses were measured by GC using a chiral column after the aldehydes had been transformed into carboxylic acids in accordance with described procedures [32].

2.3. HP NMR experiments

In a typical experiment, the rhodium complex [Rh(μ-OMe)(cod)]$_2$ (0.04 mmol) and dpppts (0.16 mmol) were dissolved in 2 ml of methanol-d_4/D_2O (3/1)

under nitrogen. The solution was placed into the sapphire NMR tube (Ø = 10 mm) which was closed. After the mixture had been pressurized with H_2/CO, the tube was shaken at 50 °C for 16 h, it was placed in the NMR spectrometer and the spectra were recorded.

2.4. HP IR experiments

In a typical experiment, the rhodium complex [Rh(μ-OMe)(cod)]$_2$ (0.02 mmol) and dpppts (0.08 mmol) were dissolved in a 4 ml of water/methanol mixture (1/1) under nitrogen. The solution was placed in the HP IR cell and pressurized with the H_2/CO mixture. The cell was placed in the IR spectrometer and the spectra were recorded.

3. Results and discussion

3.1. Catalytic studies

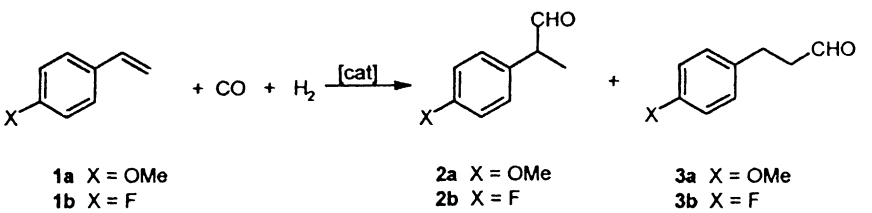
The hydroformylation of styrene derivatives **1a–c** and vinyl-naphthalene **1d** yields the corresponding branched aldehydes (**2a–d**) and linear aldehydes (**3a–d**) according to Eqs. (1) and (2). We previously reported the results obtained in the hydroformylation of **1c** in aqueous systems [16]. Table 1 shows the results in the hydroformylation of **1a** and **1b** using [Rh(μ-OMe)(cod)]$_2$ with the sulfonated diphosphines dpppts and (*S*,*S*)-bdppts as catalyst precursors in aqueous systems and with Rh–bdpp in organic solvents.

In all the experiments a 1/1 mixture of water/methanol was used since previous studies showed that these conditions provide the best chemioselectivity and activity [16]. In the experiments with the Rh–dpppts systems (entries 1–3, Table 1) the pH of the solution was adjusted to 11. The *p*-methoxy and *p*-fluoro substituted substrates **1a** and **b** were hydroformylated with the rhodium/sulfonated diphosphine dpppts system and the total conversions were higher than styrene **1c** although selectivity in aldehydes was slightly lower. The regioselectivity of the reaction for both the substrates **1a** and **1b** was similar to that of styrene **1c**.

When the asymmetric hydroformylation of the styrene derivatives was performed with the rhodium precursors and bdppts as the chiral ligand, the initial pH was adjusted to 7 to avoid racemization of the chiral aldehyde because of the keto-enol tautomerization. As reported in the literature on systems that use the monophosphine tppts as the ligand, a decrease in the pH means that the conversion into aldehydes is lower than when dpppts is used as the ligand (entries 4–6, Table 1) [17].

The enantioselectivities obtained with the Rh-bdppts catalysts for **1a** and **1b** were higher than those obtained in the hydroformylation of styrene **1c** (entry 6, Table 1). In the hydroformylation of the *p*-methoxy derivative **1a** with the Rh–bdppts system at 30 °C the enantiomeric excess for **2a** was 66% (entry 4, Table 1). At higher temperatures polymerization took place.

It is important to note that the neutralization should be done carefully in order to obtain repetitive results in enantioselectivity. Results were similar when a buffer solution (HPO_4^{2-}/PO_4^{3-}) was used.

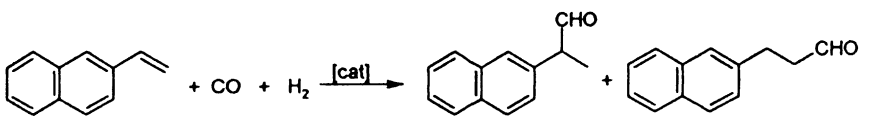


1a X = OMe
1b X = F
1c X = H

2a X = OMe
2b X = F
2c X = H

3a X = OMe
3b X = F
3c X = H

(1)



1d **2d** **3d**

(2)

Table 1
Hydroformylation of *p*-methoxystyrene (**1a**), *p*-fluorostyrene (**1b**), styrene (**1c**) and 2-vinylnaphthalene (**1d**) using $[Rh(\mu\text{-OMe})(cod)]_2$/L as catalyst precursors[a]

Entry	L	Substrate	T (°C)	t (h)	C_T (%)[b]	Selectivity in aldehyde (%)	**2/3**	e.e. (%)
1	dpppts	**1a**	80	24	99	85	91/9	–
2	dpppts	**1b**	80	24	99	89	94/6	–
3[c]	dpppts	**1c**	80	24	62	100	93/7	–
4	(*S*,*S*)-bdppts	**1a**	30	72	2	82	100/0	66 (+)
5	(*S*,*S*)-bdppts	**1b**	65	8	10	98	97/3	44 (*R*)
6[c]	(*S*,*S*)-bdppts	**1c**	65	24	4	100	90/10	14 (*R*)
7[d]	(*S*,*S*)-bdpp	**1a**	30	48	20	95	95/5	54 (+)
8[d]	(*R*,*R*)-bdpp	**1b**	65	8	99	100	95/5	54 (*S*)
9[d,e]	(*R*,*R*)-bdpp	**1c**	65	7	92	100	94/6	56 (*S*)
10[d]	(*R*,*R*)-bdpp	**1d**	50	14	54	100	96/4	65 (*S*)

L = dpppts, bdppts and bdpp.
[a] Reaction conditions: $[Rh(\mu\text{-OMe})(cod)]_2$ = 5.10–3 M, [substrate]/[Rh] = 500, P/Rh = 4, solvent 3 ml H_2O/3 ml MeOH, 14 atm pressure (CO/H_2 = 1/1), t = 24 h, initial pH = 11 for experiments 1–3; initial pH = 7 for experiments 4–6.
[b] Total conversion measured by GC integral ratio based on substrate.
[c] Ref. [16].
[d] Reaction conditions: solvent = THF; CO/H_2 = 1/1; substrate/precursor = 200; pressure = 10 atm.
[e] Ref. [31].

For substrate **1b**, when the same catalytic system was used the enantioselectivity at 65 °C was 44% e.e. (entry 5, Table 1).

When vinyl naphthalene was used as substrate in aqueous solution no aldehydes were detected because it is not very soluble in water.

Comparing the results obtained in aqueous systems with the ones obtained in THF (entries 4–6 compared to entries 7–10, Table 1) we observe that, as expected, conversions are lower in aqueous media but regioselectivities are similar. The enantioselectivity obtained with aqueous systems is higher for substrate **1a** under the same conditions. For substrate **1b**, the enantioselectivity in the aqueous system (44% e.e.) is lower than the one observed in THF (54% e.e.) but the value is still significative.

Vinyl-naphthalene was hydroformylated at 50 °C and the e.e. observed was 65% while in aqueous systems no conversion was detected.

In conclusion, the comparative study shows that it is possible to obtain moderate enantioselectivities if aqueous systems are used in the hydroformylation of vinyl arenes.

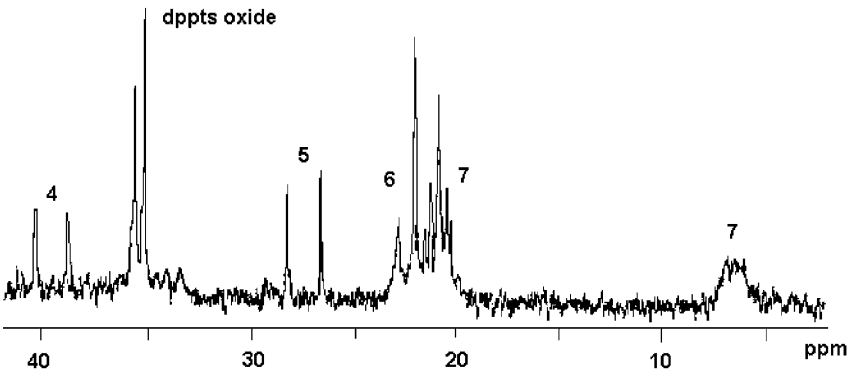
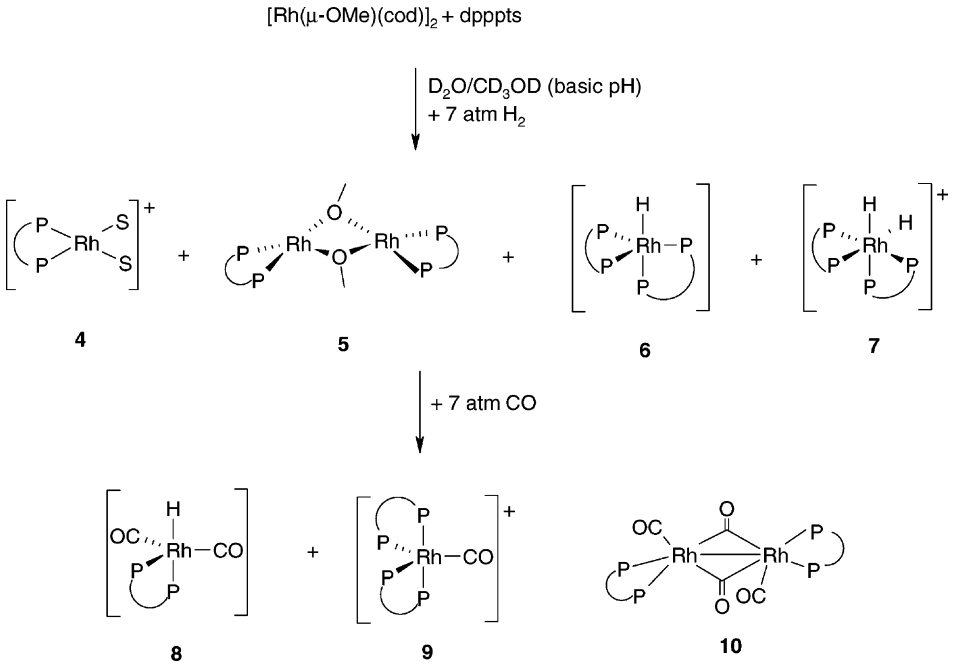


Fig. 3. ^{31}P NMR spectrum at 121.4 MHz in CD_3OD/D_2O of $[Rh(\mu\text{-OMe})(cod)]_2$/dpppts (P/Rh = 4) under 7 atm of H_2.



Scheme 1.

3.2. High-pressure NMR and IR studies

We analyzed the high-pressure NMR and IR spectra so that we could identify the species formed under catalytic conditions with sulfonated diphosphines.

We used methanol-d_4/D_2O (3/1) as solvent at basic pH to record the ^{31}P-$\{^1H\}$ and ^1H NMR spectra of solutions of the catalyst precursor [Rh(μ-OMe)(cod)]$_2$ associated with the corresponding sulfonated diphosphine. To facilitate the identification of the species, H_2 was first added (7 atm), subsequently, carbon monoxide was introduced up to 14 atm of total pressure (CO/H_2 = 1/1) and, finally the substrate was added and the spectra recorded after each step.

The ^{31}P-$\{^1H\}$ NMR spectrum of the solution of [Rh(μ-OMe)(cod)]$_2$/dpppts (P/Rh = 4) under 7 atm of H_2 at room temperature showed five groups of signals at δ = 39.6 (d), 27.6 (d), 21.6 (d), 21.0 (dt) and 6.5 (broad) ppm (Fig. 3). The signals corresponding to the oxidized phosphine at ca 35 ppm were also observed. The ^1H NMR spectrum in the hydride region showed three broad signals at δ = −10.4, −8.1 and −8.6 ppm.

The doublet at δ = 39.6 ppm ($^1J_{P,Rh}$ = 177 Hz) was attributed to the Rh(I) species with coordinated methanol [Rh(dpppts)(CD$_3$OD)$_2$]$^+$ (**4**; Scheme 1). The P–Rh coupling constants reported for analogous complexes [Rh(diphosphine)(CH$_3$OH)$_2$]$^+$ were 190 Hz for dppp and 175 Hz for the diphosphine (2*S*,3*S*)-bis(diphenylphosphino)butane [33].

The doublet at δ = 27.6 ppm with a high coupling constant ($^1J_{P,Rh}$ = 192 Hz) may correspond to a dimeric species [Rh(μ-OMe)(dpppts)]$_2$ (**5**) since it correlates well with the values reported for [Rh(μ-Cl)(dppp)]$_2$ ($^1J_{P,Rh}$ = 184 Hz) and [Rh(μ-Cl)(diop)]$_2$ ($^1J_{P,Rh}$ = 191 Hz) [33].

In the 20–23 ppm region of the ^{31}P NMR spectrum there was a group of broad signals among which a doublet was detected at δ = 21.6 ppm ($^1J_{P,Rh}$ = 142 Hz). The hydride region of the ^1H NMR spectrum had a wide signal at δ = −10.4 ppm. By comparison with published data for the analogous complex [RhH(dppp)$_2$] [34], these signals were attributed to [RhH(dpppts)$_2$] (**6**), the P–Rh coupling constant reported for [RhH(dppp)$_2$] was J = 142.5 Hz. The phosphorus and hydride sig-

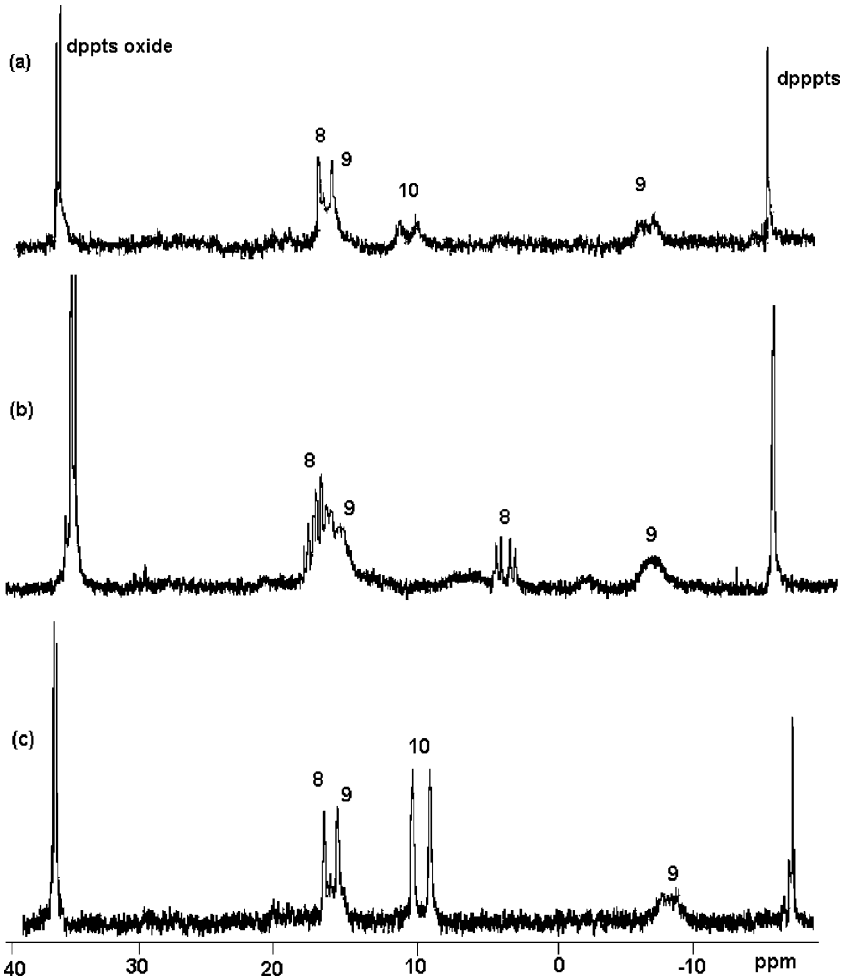


Fig. 4. ^{31}P NMR spectrum at 121.4 MHz in CD_3OD/D_2O of $[Rh(\mu\text{-}OMe)(cod)]_2$/dpppts (P/Rh = 4) under 14 atm of CO/H_2 (1/1) at: (a) 20 °C, (b) −60 °C, (c) 50 °C.

nal could not be resolved by decreasing the temperature.

In the same region, there was a doublet of triplets at $\delta = 21.0$ ppm ($^1J_{P,Rh} = 100$ Hz and $^2J_{P,P} = 30$ Hz) correlating with a broad signal at $\delta = 6.5$ ppm. The hydride region showed two broad signals at $\delta = -8.1$ and −8.4 ppm. These values agree with those reported for the analogous dihydrido species $[RhH_2(dppp)_2]^+$ (^{31}P: $\delta = 19.96$ ppm, $^1J_{P,Rh} = 99.6$ Hz and $^2J_{P,P} = 30$ Hz; $\delta = 9.12$ ppm, $^1J_{P,Rh} = 82.2.6$ Hz; ^{1}H (hydride region): $\delta = -8.2$ and −8.9 ppm, multiplets) [25,34]. Therefore, we assigned these signals to the dihydride species $[RhH_2(dpppts)_2]^+$ (**7**). No better resolution was found even at temperatures as low as −60 °C.

The solution was then pressurized up to 14 atm of CO/H_2 (1/1). The ^{31}P NMR spectrum at room temperature (Fig. 4a) showed signals at $\delta = 15.8$, 10.0 and −8.4 ppm and the ^{1}H NMR showed a broad hydrido signal at $\delta = -9$ ppm. The doublet at $\delta = 15.8$ ppm ($^1J_{P,Rh} = 112$ Hz) and the hydrido signal at $\delta = -9$ ppm in the ^{1}H NMR were assigned to the species $[RhH(CO)_2(dpppts)]$ (**8**) by comparison with reported data for similar complexes with dppp [25]. Cooling the solution to −60 °C (Fig. 4b) enabled the doublet at $\delta = 15.8$ ppm to be resolved into a doublet of

doublets ($\delta = 16.7$ ppm, $^1J_{P,Rh} = 103$ Hz and $^2J_{P,P} = 50$ Hz), which correlate with a new doublet of doublets now appearing at $\delta = 2.4$ ppm ($^1J_{P,Rh} = 132$ Hz and $^2J_{P,P} = 50$ Hz). These signals may be assigned to the axial and equatorial phosphorus of species **8**, respectively, in which the equilibrium was frozen at low temperature. The average of both coupling constants ($J = 117$ Hz) was in the range observed at room temperature. Although these signals are not usually observed, the polar solvent and the ionic nature of the ligand may allow these signals to be resolved. When the solution was heated to 50 °C (Fig. 3c), the doublet at $\delta = 15.8$ ppm was formed again.

Two broad signals at $\delta = 15$ and -8.4 ppm in the ^{31}P-{^{1}H} NMR spectra were assigned to the monocarbonyl species $[Rh(CO)(dpppts)_2]^+$ (**9**) by comparison to published data [35,36]. These signals could not be resolved in the range from -60 to $+50$ °C.

Finally, the broad doublet observed at $\delta = 10.0$ ppm in the ^{31}P NMR spectrum at room temperature increased in intensity and resolved at 50 °C ($^1J = 150$ Hz; Fig. 4c). It was attributed to the dimeric species $[Rh(\mu\text{-}CO)(CO)(dpppts)]_2$ (**10**) [37].

We confirmed the presence of species **8** by carrying out HP IR experiments in a solution of the complex $[Rh(\mu\text{-}OMe)(cod)]_2$ with ligand dpppts (P/Rh = 4) in a mixture of 1/1 of water/methanol at 14 atm CO/H_2 (1/1). The IR spectrum of this solution after 1.5 h of stirring at 50 °C showed three strong absorptions at 1955, 1990 and 2034 cm^{-1} in the ν(CO) stretching region (Fig. 5). A reference experiment under the same conditions with $[Rh(\mu\text{-}OMe)(cod)]_2$ associated with the non-sulfonated ligand dppp in THF showed strong absorptions at 1943 and 1985 cm^{-1}. These absorptions were attributed to the species $[RhH(CO)_2(dppp)]$ in which the phosphorus atoms are coordinated in the equatorial and axial position [25]. For diphosphines with larger bite angles, the complex $[RhH(CO)_2(diphosphine)]$ may exist as mixtures of equatorial–axial and –equatorial isomers. The infrared spectra observed in these cases showed four absorptions in the carbonyl region [24,25]. The band at 2034 cm^{-1} for the Rh–dpppts system may correspond to the equatorial–equatorial species or to a Rh–H stretching frequency. The ν(CO) reported for the equatorial–equatorial complex $[RhH(CO)_2(binas\text{-}Na)]$ were 2041 and 1981 cm^{-1} [15]. For species **8**, we were unable to detect the expected second absorption maybe because the resolution of the spectrum was low. No carbonyl frequencies were detected in the region of the bridged carbonyl stretching frequencies.

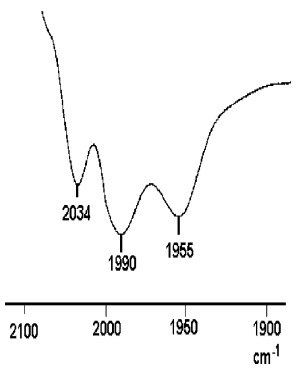


Fig. 5. ν(CO) stretching region of the IR spectra in $MeOH/H_2O$ of $[Rh(\mu\text{-}OMe)(cod)]_2$/dpppts (P/Rh = 4) under 14 atm of CO/H_2 (1/1).

Finally, a solution containing the rhodium complex $[Rh(\mu\text{-}OMe)(cod)]_2$ with ligand dpppts (P/Rh = 4) and styrene as a model substrate (substrate/catalyst = 5) was pressurized at 14 atm CO/H_2 (1/1) and the evolution of the hydroformylation reaction was monitored by NMR. The ^{31}P NMR of this solution showed wide signals in the 15–16, 10 and -7 ppm regions corresponding to species **8**, **9** and **10** and the ^{1}H NMR a broad signal at $\delta = -9$ ppm. These signals could not be resolved in the temperature range from +60 to -40 °C.

The rhodium catalyst precursor system with bdppts was also studied by HPNMR at different pH values. The ^{31}P NMR spectrum of $[Rh(\mu\text{-}OMe)(cod)]_2$ with the ligand bdppts (P/Rh = 4), 14 atm CO/H_2 (1/1) (Fig. 6a) and basic pH showed only a clean doublet at $\delta = 29.8$ ppm ($^1J_{P,Rh} = 111.7$ Hz) and a broad signal at $\delta = 23.8$ ppm. In the hydride region of the ^{1}H NMR spectrum a doublet of triplets at $\delta = -9.4$ ppm ($^2J_{H,P} = 56.4$ Hz, $^1J_{H,Rh} = 11.7$ Hz) was observed. The signal at $\delta = 29.8$ ppm and the hydride was attributed to the complex $[RhH(CO)_2(bdppts)]$ (**11**) (Scheme 2) by comparison with the reported data for the analogous non-sulfonated bdpp complex [25]. The intermediate values of the phosphorus–hydride coupling constants indicate that there is an equilibrium between the two equatorial–axial diastereomers of **11** in fast exchange in the NMR time scale [25]. When

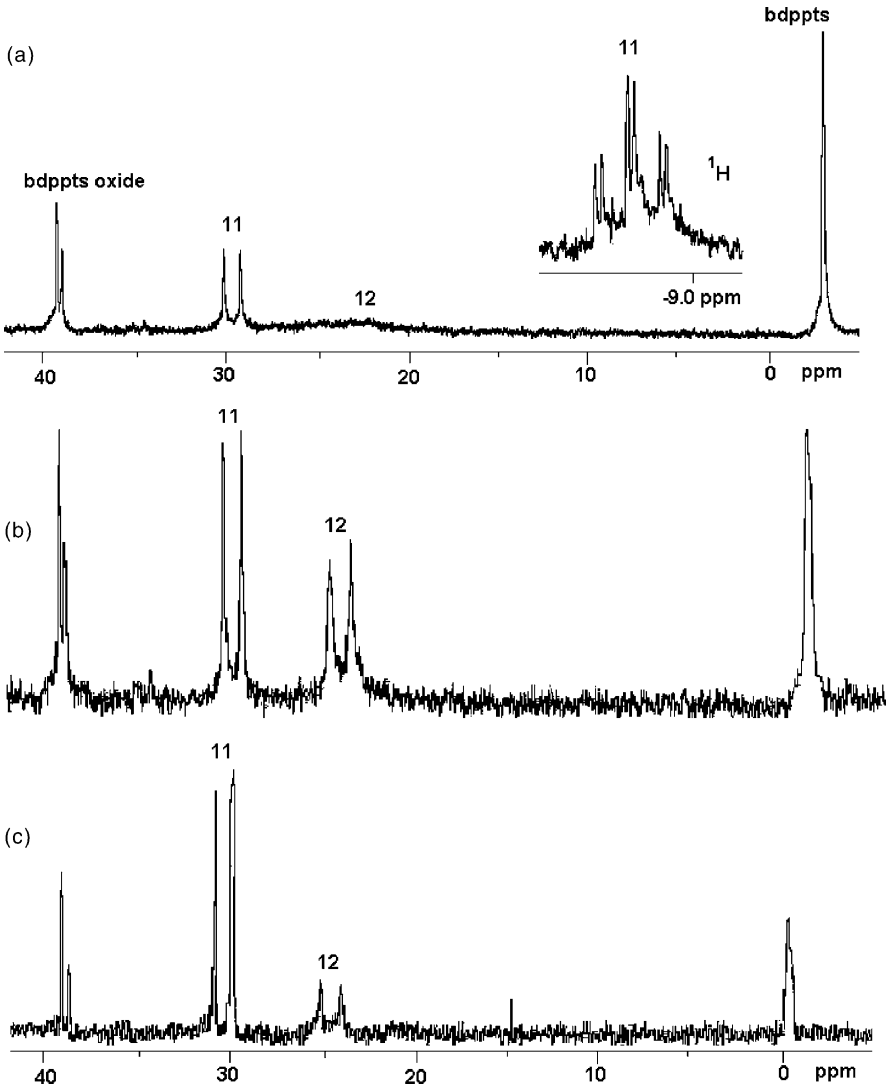
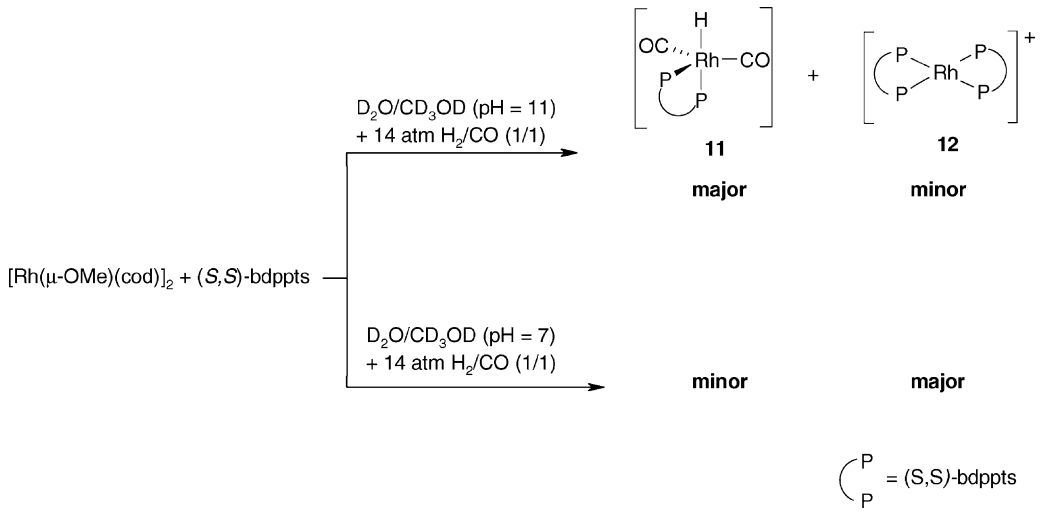


Fig. 6. ^{31}P NMR spectra at 121.4 MHz in CD_3OD/D_2O of $[Rh(\mu\text{-}OMe)(cod)]_2$/bdppts (P/Rh = 4) under 14 atm of CO/H_2 (1:1) at pH = 11 at: (a) 20 °C (300.0 MHz ^{1}H NMR hydride region inserted), (b) 80 °C, (c) 80 °C with styrene (Rh/styrene = 1/5).

the sample was cooled to −40 °C, the signals became less resolved.

When the solution was heated, the broad signal at δ = 23.8 ppm was resolved into a doublet (Fig. 6b). At 80 °C, the coupling constant observed for this doublet was J = 131.8 Hz. A doublet at δ = 23.7 ppm with a coupling constant of 130 Hz has been reported for the bisphosphine species $[Rh(bdpp)_2]^+$ in THF-d_8. This species was reported to form in a solution of $[Rh(\mu\text{-}OMe)(cod)]_2$ with excess of bdpp under nitrogen[24b] but it disappeared under H_2 or H_2/CO pressure. In our case, we attribute the signal at δ 23.8 ppm to the analogous complex $[Rh(bdpp)_2]^+$ (**12**), which may be present even under CO/H_2 pressure because the gases are not very soluble in the aqueous solution and the polar solvents favored its formation. The ^{31}P and ^{1}H signals corresponding to species **11** were also observed at 80 °C. Cooling again the solution to room temperature, the ^{31}P spectra was similar to the one presented in Fig. 6a.



Scheme 2.

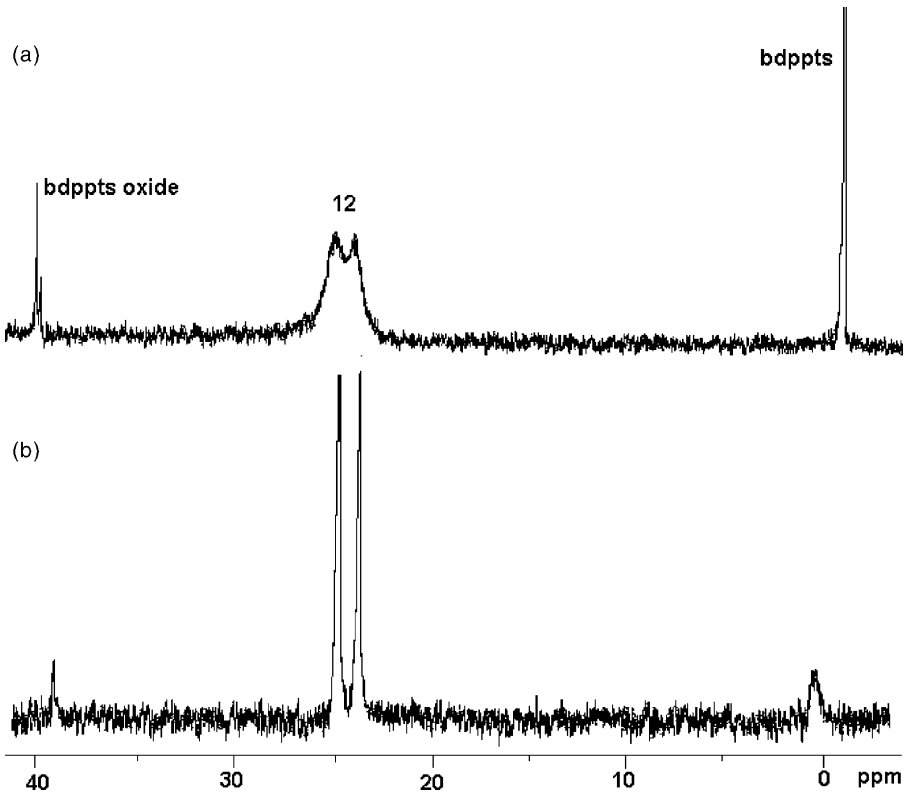


Fig. 7. ^{31}P NMR spectra at 121.4 MHz in CD_3OD/D_2O of $[Rh(\mu\text{-}OMe)(cod)]_2$/bdppts (P/Rh = 4) under 14 atm of CO/H_2 (1/1) at neutral pH after 1 h reaction at: (a) 20 °C, (b) 80 °C.

Finally, this solution was depressurized, styrene was added in a 5:1 molar ratio respect to Rh and the solution was re-pressurized to 14 atm ($CO/H_2 = 1/1$). At 80 °C, the main signal observed in the ^{31}P-$\{^1H\}$ spectrum (Fig. 6c) was the doublet at $\delta = 30.6$ ppm ($^1J_{P,Rh} = 111.6$ Hz). The double triplet hydride signal at −9.4 ppm in the ^1H spectrum confirmed the formation of species **11**. The spectrum also showed a broad doublet at $\delta = 24.7$ ppm ($J = 122.6$ Hz), which probably corresponds to species **12**. The variation of the coupling constant and the broadening of the signal are indicative of fluxionality, probably because of the reaction with the substrate.

To sum up, the spectroscopy studies showed that, like in organic solvents, $[RhH(CO)_2$(bdppts)] is formed in basic aqueous solutions. The inactive dimeric species $[Rh(\mu\text{-}CO)(CO)(bdpp)]_2$ was reported to form also in organic solvents under CO/H_2 pressure. In aqueous systems, however, we observed cationic bisphosphine species **12**. The formation of this species together with the low solubility of the substrates in aqueous solutions may account for the lower activity observed in water/methanol solutions.

At neutral pH, the ^{31}P NMR spectrum of $[Rh(\mu\text{-}OMe)(cod)]_2$ with the bdppts ligand (P/Rh = 4) at 14 atm CO/H_2 (1/1), 20 °C (Fig. 7a) and after 1 h reaction time shows a broad doublet at $\delta = 24.5$ ppm, which resolves at 80 °C ($\delta = 24.9$ ppm, $J = 132.7$ Hz; Fig. 7b) and which is attributed to cationic species **12**. After a reaction time of 16 h a small doublet at $\delta = 30.1$ ppm ($J = 106.1$ Hz) corresponding to species **11** was also detected. The formation of cationic species **12** as a major product explains the drastic decrease in activity at neutral pH. When styrene was added to this solution (styrene/Rh ratio = 5/1) the ^{31}P NMR spectra under 14 atm CO/H_2 (1/1) were similar.

After aqueous sodium hydroxide had been added to the solution containing species **12** and **11** and it had been repressurized to 14 atm ($CO/H_2 = 1/1$), the ^{31}P NMR spectra showed an increase in species **11**. This process could be reversed by changing the pH.

4. Conclusions

We used the catalyst precursor $[Rh(\mu\text{-}OMe)(cod)]_2$ with sulfonated diphosphines in aqueous solutions to perform the hydroformylation of vinyl arenes. Conversions into aldehydes were low at neutral pH but some of the enantioselectivities obtained with the chiral systems were higher than the ones obtained in organic solvents.

High-pressure NMR and IR experiments in water/methanol showed that $[RhH(CO)_2$(sulfonated diphosphine)] species, which are analogous to those observed in organic systems, form under catalytic conditions at basic pH. When the pH of the solution was neutral the main species formed was the cationic inactive bischelated $[Rh(bdppts)_2]^+$ which reacts with H_2 and CO only at basic pH so enabling this process to be reversed.

Acknowledgements

We thank the Ministerio de Educación y Ciencia, the Generalitat de Catalunya and the Commision for the European Communities for financial support (PB97-0407-C05-01, “Acció integrada” ACI-96, COST D10 Action 01). G. Laurenczy thanks the Swiss National Science Foundation for financial support (Grant 2100-061653.01). We also thank Dr. L. Nádasdi for useful help in the realization of the HP IR experiments.

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