

Mechanistic study of the hydroformylation of styrene catalyzed by the rhodium/BDPP system

Inmaculada del Río ^a, Oscar Pàmies ^a, Piet W.N.M. van Leeuwen ^b, Carmen Claver ^{a,*}

^a *Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Pça. Imperial Tàrraco I, 43005 Tarragona, Spain*

^b *Institute of Molecular Chemistry, Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands*

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Abstract

The hydroformylation of styrene using the rhodium $[\text{Rh}(\mu\text{-OMe})(\text{COD})_2]/\text{BDPP}$ [(2*S*,4*S*)-bis(diphenylphosphine)pentane] system was studied. Since in situ infrared spectroscopic experiment studies showed a considerable number of absorptions at low pressure, an HPNMR exploration was carried out and a kinetic study was performed in the pressure range between 8 and 30 bar. These studies revealed the presence of different species as resting states depending on the CO/H_2 total pressure. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The hydroformylation of alkenes has been extensively studied in recent years [1], and several mechanistic and kinetic studies have been performed [2–10].

The hydroformylation of 1-heptene [2] has been studied with unmodified rhodium systems and it has been found that the hydrogenolysis of the acylrhodium intermediate is the rate-determining step [3]. Detailed kinetics studies, recently reported using unmodified rhodium-catalyzed systems in the hydroformylation of styrene, indicate that in this case the hydrogen activation is also the rate-limiting step [4].

Several kinetic studies of modified Rh/monophosphines have been performed [5,6]. In general, the reaction is first order in the concentration in alkene, first order in the rhodium concentration and zero order in hydrogen as is reported in the most detailed early study [5]. The oxidative addition of the hydrogen has been considered as the rate-determining step in other studies employing rhodium phosphine catalysts [6].

For bulky phosphites a detailed study has been carried out and it was found that in these relatively simple systems only one $\text{P}(\text{OR})_3$ is coordinated to Rh in the catalytic resting state [7]. Studies of the hydroformylation of 1-octene in the presence of the ligand tris(2-*tert*-butyl-4-methylphenyl)phosphite, and studies of the effects of the bulky phosphite and triphenylphosphine ligands in the hydroformylation of various substrates have also been reported [8]. While the coordination and/or migratory insertion into Rh–H of the terminal alkene are rate-limiting for the phosphine systems, hydroformylation is independent of the concentration of the terminal alkene for the bulky phosphite system.

Concerning chelate ligands, kinetic studies using bulky diphosphites in the hydroformylation of styrene and 1-octene are consistent with a kinetic scheme in which the alkene addition is the rate-determining step [9]. In the case of the phosphine–phosphite BINAPHOS, the effect of the reaction conditions on the reaction rate, as well as kinetic and mechanistic aspects have been studied in the hydroformylation of 1-hexene and styrene [10]. As far as we know, similar studies using diphosphines in rhodium systems have not been reported.

* Corresponding author. Tel.: +34-977-559574; fax: +34-977-559563.

E-mail address: claver@quimica.urv.es (C. Claver).

The solution structures of the rhodium intermediates containing phosphorus ligands have been analyzed in detail using in situ HPNMR [11,12] and HPIR [9,13] techniques in several hydroformylation systems.

Prior to this study, we investigated the species present during the hydroformylation with the Rh/BDPP system. The rhodium hydride $[\text{HRh}(\text{CO})_2\text{BDPP}]$ was proposed as the predominant species. Variable-temperature ^{31}P - and ^1H -NMR spectroscopic studies revealed that the diphosphine BDPP is equatorially–axially coordinated. The hydride species is in equilibrium with the dinuclear species $[\text{Rh}(\text{CO})_2\text{BDPP}]_2$ and their concentrations depend on the reaction parameters [11].

As a continuation of our investigations on the rhodium–phosphorus systems in hydroformylation reaction [11,14], we present here an HPIR and HPNMR study of the species present during the hydroformylation of styrene with the Rh/BDPP system at various pressures, together with a kinetic study at different pressures.

2. Results and discussion

2.1. High-pressure IR study

In situ infrared spectroscopic techniques can be used to study the mechanism of the hydroformylation reaction, because rhodium carbonyl complexes have strong absorptions for the CO stretching vibrations and actual catalysis conditions can be used with good signal-to-noise ratios and high resolutions [14,15].

We recorded the IR spectra for the $[\text{Rh}(\mu\text{-OMe})(\text{COD})_2]/\text{BDPP}$ system (BDPP/Rh = 2) in an HPIR autoclave under hydroformylation conditions (8 and 30 bar and 80°C). The only species present turned out to be the hydride complex $[\text{HRh}(\text{CO})_2\text{BDPP}]$ in accordance with previous work [11].

The substrate was then added and an infrared spectrum was recorded every 10 min to collect information about possible intermediates throughout the process. During the hydroformylation of 1-octene and styrene at 30 bar ($\text{H}_2/\text{CO} = 1/1$), the hydride complex was the only species observed.

During the hydroformylation of 1-octene at 8 bar the rhodium hydride complex was present again throughout. In the case of styrene, however, new signals appeared ($2026, 2001, 1987, 1971, 1945 \text{ cm}^{-1}$) when the total pressure dropped below 4 bar (Fig. 1) and the reaction rate decreased.

When the pressure was restored to 8 bar, the system reversed and the concentration of $[\text{HRh}(\text{CO})_2\text{BDPP}]$ increased to become the major compound, while the other signals disappeared and the reaction rate increased until the total conversion was reached.

According to these observations, we attributed the absorptions to species 1–6 in equilibrium (Fig. 2). Due to the low H_2 and CO pressure, the final hydrogenolysis or/and the acyl formation becomes relatively slow. When the pressure was restored the hydride complex was again the resting-state and no other species were observed. The stabilization due to the π -benzylic species in the case of the styrene (species 3a and 3b, Fig. 2) might be responsible for the difference between styrene and 1-octene.

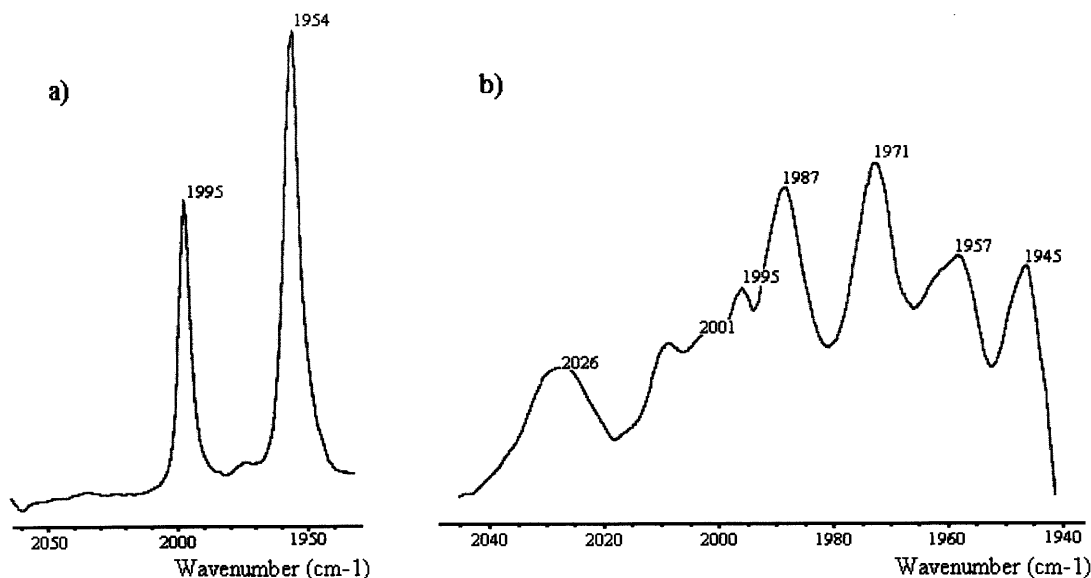


Fig. 1. HPIR spectra: (a) reaction of $[\text{Rh}(\mu\text{-OMe})(\text{COD})_2]$ with BDPP and styrene under hydroformylation conditions at 8 bar; (b) reaction of $[\text{Rh}(\mu\text{-OMe})(\text{COD})_2]$ with BDPP and styrene at 3 bar.

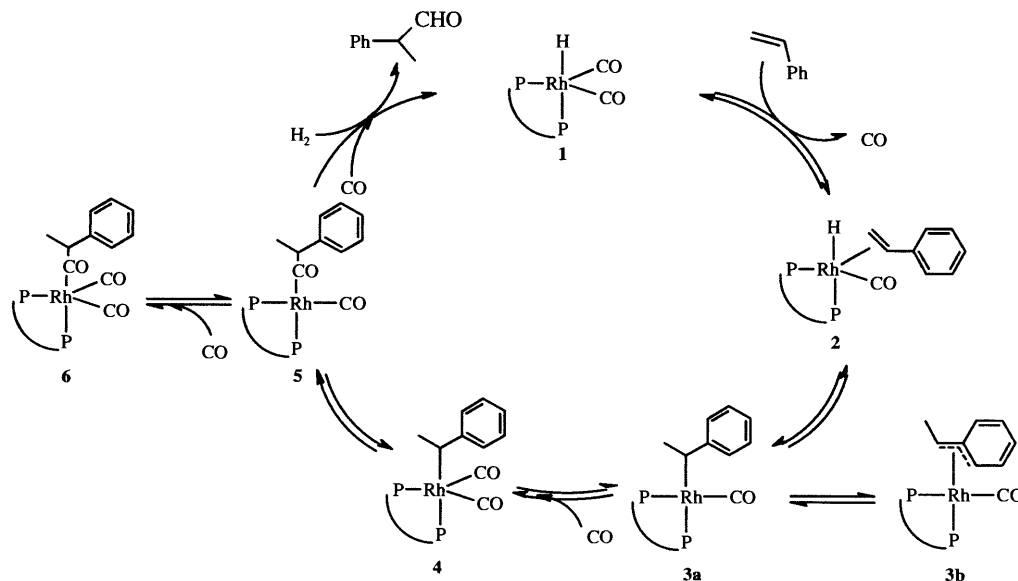


Fig. 2. Proposed catalytic cycle for the hydroformylation of styrene with diphosphines.

2.2. High-pressure NMR study

High-pressure NMR is often used as a technique to identify organometallic compounds at high pressure [16]. In order to obtain more information about the unknown species observed in the low-pressure HPIR experiments we studied the reactivity of the $[\text{Rh}(\mu\text{-OMe})(\text{COD})_2]/\text{BDPP}$ system in toluene- d_8 , under hydroformylation conditions at different pressures.

We focused on the intermediate species, other than the well known $[\text{HRh}(\text{CO})_2\text{BDPP}]$ and the dinuclear species $[\text{Rh}(\text{CO})_2\text{BDPP}]_2$, that had not been previously characterized [11].

We added the substrate in situ at low pressures in order to observe the species formed after substrate coordination. Styrene and *p*-OMe-styrene were used as substrates, because the $-\text{OMe}$ signal at 3.8 ppm might facilitate the observation of the coordination of the substrate.

At 8 bar CO/H_2 and a substrate/Rh ratio of 10.75, only the previously reported $[\text{HRh}(\text{CO})_2\text{BDPP}]$ and $[\text{Rh}(\text{CO})_2\text{BDPP}]_2$ were observed in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra during the hydroformylation of the styrene [11].

When the CO concentration was as low as 4 bar H_2 and 2 bar CO , the dinuclear species $[\text{Rh}(\text{CO})(\text{BDPP})_2]$ was predominant as evidenced by the absorption at 35.7 ppm ($^1J_{\text{Rh-P}} = 183$ Hz) [17].

In order to halt the cycle before the final hydrogenolysis step, the hydride species $[\text{HRh}(\text{CO})_2\text{BDPP}]$ was formed under standard conditions (8 bar CO/H_2 , 80°C) and the gas was removed before the styrene was added. Only a small amount of CO (1–2 bar) was added. Under these conditions new signals of low intensity were observed in the ^{31}P -NMR spectra (Fig. 3).

The ^{31}P -NMR-spectrum shows two groups of signals in the phosphine region. From the signals in the region of 58 ppm we conclude that the phosphine phosphorus atoms are part of a five-membered ring as it was previously observed for phosphines coordinated to rhodium [18]. The double triplet in the -17 ppm region could be attributed to a free phosphorus atom coupled to two other phosphorus nuclei and a rhodium nucleus. In the ^1H -NMR no hydrido signal was observed. Data obtained by simulation are listed in Table 1.

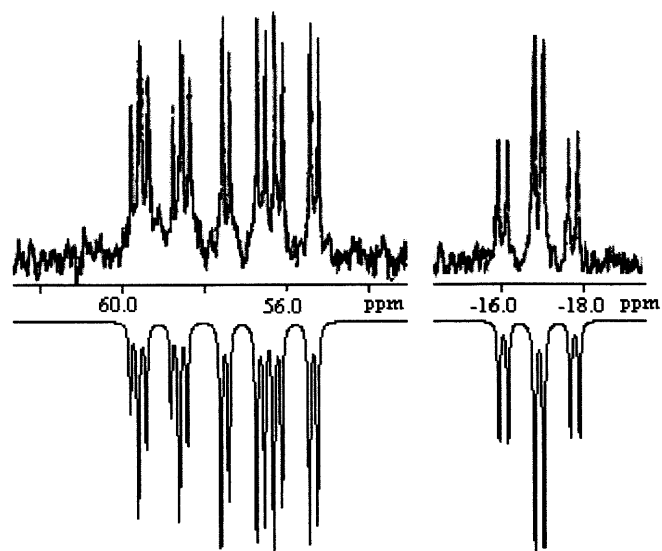


Fig. 3. ^{31}P -NMR spectrum of minority products obtained without H_2 . Top: experimental. Bottom: simulated with constants in Table 1.

Table 1
Simulation data for the ^{31}P spectra of metallated species

| <i>P</i> | δ (ppm) | $J_{\text{Rh-P}}$ (Hz) | $J_{\text{P-Pa}}$ (Hz) |
|----------|----------------|------------------------|------------------------|
| a | 56.3 | 157 | |
| b | 59.0 | 121 | 24 |
| c | -16.6 | 27 | 106 |

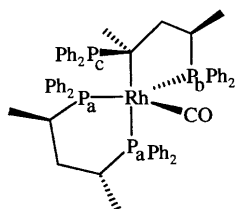


Fig. 4. Structure proposed for the metallated species.

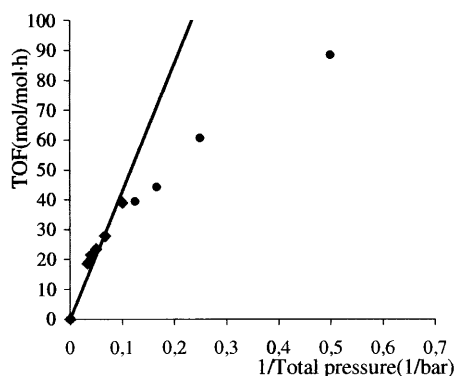


Fig. 5. Dependency of the aldehyde formation rate on the total pressure. Conditions: $T = 80^\circ\text{C}$, $\text{BDPP}/\text{Rh} = 2$, $0.0125 \text{ mmol } [\text{Rh}(\mu\text{-OMe})(\text{COD})]_2$, 10 mmol styrene, $P_{\text{H}_2} = P_{\text{CO}}$, in 15 ml of toluene.

Table 2
Influence of CO pressure on the rate of styrene hydroformylation at $P_{\text{H}_2} = 12 \text{ bar}^a$

| Run | P_{CO} (bar) | Conversion (%) (time (min)) | k_{ald} ($\text{mol mol}^{-1} \text{ h}^{-1}$) |
|-----|-----------------------|--------------------------------|--|
| 1 | 6 | 13.4(45) | 140.6 |
| 2 | 10 | 7.1(50) | 83.4 |
| 3 | 14 | 6.3(52) | 63.3 |
| 4 | 18 | 4.5(50) | 49.7 |

^a Conditions: $T = 80^\circ\text{C}$, $\text{BDPP}/\text{Rh} = 2$, $0.0125 \text{ mmol } [\text{Rh}(\mu\text{-OMe})(\text{COD})]_2$, 10 mmol styrene, in 15 ml of toluene. Regioselectivity $b/l = 94/6$; enantioselectivity $52\% \text{ ee}$.

These results are consistent with the formation of a metallated complex $[\text{Rh}(\text{PPh}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{-PPh}_2)(\text{CO})\text{BDPP}]$ containing a highly favored, five-membered ring structure (Fig. 4). Similar compounds with a chelating phosphite ligand combined with allyldiphenylphosphine have been previously reported [19]. Recently an example of such a ligand metallation

accomplished by the alkene substrate has been reported for triphenylphosphite as the ligand [20].

From these experiments, the other intermediates observed in the HPIR during the hydroformylation at low pressures could not be characterized. It should be pointed out that in the HPNMR experiments the substrate/Rh ratio was lower than in the catalytic experiments so that the signal-to-noise ratio of the intermediate species is satisfactory. This contrasts with the HPIR experiments in which the conditions and concentrations of the reagents are identical to the catalytic experiments. Therefore no rhodium dinuclear compound is expected to be present as the catalytic resting state under hydroformylation conditions.

2.3. Kinetic study

In addition to the HPNMR experiments we explored the kinetics of the reaction in an attempt to determine how the total pressure affects the catalytic behavior.

First of all we determined the dependency of the hydroformylation rate on the total pressure by studying the gas consumption in an autoclave equipped with a reservoir and a pressure transducer. The drop in pressure and the turnover frequency was determined for several pressures (Fig. 5).

As can be concluded from the Fig. 5 the hydroformylation rate depends on the total pressure. Since the behavior of the system changed at about 10 bar and kinetic studies at pressures below $\sim 5 \text{ bar}$ are not reliable, we decided to study the dependence of the rate on the reaction parameters (CO and H_2 pressures, Rh and styrene concentration) at two different pressures: about 8 and 20 bar.

According to the previous results observed in the HPIR experiments, the coordination of the styrene and/or the migratory insertion into rhodium hydride is expected to be involved in the rate equation at high pressures, because only the hydride species **1** is observed during hydroformylation. At lower pressures the kinetics are expected to be different since an equilibrium exists between species **1–6** (Fig. 2).

At $P_{\text{H}_2} = 12 \text{ bar}$, the hydroformylation reaction rate shows an inverse dependency on the CO partial pressure, which corresponds to a negative order in CO (Table 2), while the formation of aldehydes is independent of the H_2 pressure (Table 3).

Thus, the negative order dependency on CO concentration and the zero order dependency on H_2 concentration indicate that the coordination of the styrene is part of the rate expression at pressures higher than 18 bar of CO/H_2 .

At low pressures, the rate expression obtained corresponds to a negative order in the CO concentration (Table 4), but the H_2 concentration has a slightly positive effect on the reaction rate (Table 5). This

Table 3

Influence of H₂ pressure on the rate of styrene hydroformylation at P_{CO} = 12 bar^a

| Run | P _{H₂} (bar) | Conversion (%) (time (min)) | k _{ald} (mol mol ⁻¹ h ⁻¹) |
|-----|----------------------------------|--------------------------------|--|
| 5 | 6 | 9.9(50) | 113.4 |
| 6 | 10 | 8.6(40) | 140.6 |
| 7 | 14 | 11.3(50) | 105.9 |
| 8 | 18 | 5.8(40) | 103.1 |

^a Conditions: T = 80°C, BDPP/Rh = 2, 0.0125 mmol [Rh(μ-Ome)(COD)]₂, 10 mmol styrene, in 15 ml of toluene. Regioselectivity b/l = 94/6; enantioselectivity 52% ee.

Table 4

Influence of CO pressure on the rate of styrene hydroformylation at P_{H₂} = 5 bar^a

| Run | P _{CO} (bar) | Conversion (%) (time (min)) | k _{ald} (mol mol ⁻¹ h ⁻¹) |
|-----|-----------------------|--------------------------------|--|
| 9 | 2 | 7.9(9) | 351.6 |
| 10 | 4 | 9.5(25) | 199.2 |
| 11 | 6 | 13.7(60) | 113.7 |
| 12 | 8 | 5.1(31) | 83.1 |

^a Conditions: T = 80°C, BDPP/Rh = 2, 0.0125 mmol [Rh(μ-Ome)(COD)]₂, 10 mmol styrene, in 15 ml of toluene. Regioselectivity b/l = 94/6; enantioselectivity 52% ee.

Table 5

Influence of H₂ pressure on the rate of styrene hydroformylation at P_{CO} = 5 bar^a

| Run | P _{H₂} (bar) | Conversion (%) (time (min)) | k _{ald} (mol mol ⁻¹ h ⁻¹) |
|-----|----------------------------------|--------------------------------|--|
| 13 | 2 | 10(35) | 159.4 |
| 14 | 4 | 10.9(35) | 170.6 |
| 15 | 6 | 12.3(30) | 201.6 |
| 16 | 8 | 20.8(45) | 228.5 |

^a Conditions: T = 80°C, BDPP/Rh = 2, 0.0125 mmol [Rh(μ-Ome)(COD)]₂, 10 mmol styrene, in 15 ml of toluene. Regioselectivity b/l = 94/6; enantioselectivity 52% ee.

Table 6

Dependency of the reaction rate on the concentration of the catalyst precursor^a

| Run | P (bar) | mmol Rh | Conversion (%) (time (min)) | Rate (mmol h ⁻¹) |
|-----|---------|---------|--------------------------------|---------------------------------|
| 17 | 8 | 0.00625 | 7.2(42) | 1.2 |
| 18 | 8 | 0.0125 | 10.5(35) | 1.9 |
| 19 | 8 | 0.025 | 21.5(36) | 4.0 |
| 20 | 20 | 0.00625 | 7.8(86) | 0.6 |
| 21 | 20 | 0.0125 | 7.4(43) | 1.2 |
| 22 | 20 | 0.025 | 22.8(40) | 3.6 |

^a Conditions: T = 80°C, BDPP/Rh = 2, precursor: [Rh(μ-Ome)(COD)]₂, 10 mmol styrene, in 15 ml of toluene. Regioselectivity b/l = 94/6; enantioselectivity 52% ee.

means that the hydrogenolysis reaction could be involved in the rate equation.

In order to confirm these results and to exclude the possibility that formation of a dinuclear rhodium species occurs, the order in rhodium concentration was also determined, both for high (20 bar) and low pressures (8 bar) (Table 6).

The rate of aldehyde formation is linearly proportional to the rhodium precursor concentration. Thus, it can be concluded that the reaction has an approximate first-order dependency on the rhodium concentration and the dinuclear species [Rh(CO)₂BDPP]₂ is not involved.

To establish whether the hydrogenolysis could be the rate-determining step at low pressure, the effect of the styrene concentration was studied (Table 7).

At 20 bar the reaction rate is first-order in the styrene concentration, as expected. This confirms that the set of rate-limiting reactions will be dissociation of CO, complexation and migratory insertion into Rh–H of styrene. At 8 bar, however, the order in styrene concentration is slightly less than 1 in accordance with the previous observation that hydrogenolysis is involved in the rate equation at low pressures.

It is important to note that in all the experiments the regioselectivity (94/6) and the enantioselectivity (52R% ee) of the system were constant and that these values did not depend on the conditions. This indicates that one predominant active species is responsible for the hydroformylation reaction.

Because the various species can only be observed as resting state at low pressures, an order in H₂ of about one and an order in styrene of about zero might be expected at a pressure below 4 bar. No reliable kinetic studies, however, could be obtained at such a low pressure.

The ratio of the different intermediates present during the catalysis depends on the total pressure. Therefore, an analytical derivation of the expression for the rate becomes rather complicated and the present data do not allow such a treatment.

3. Conclusions

HPIR spectroscopic and kinetic studies revealed the presence of different species as resting states depending on the CO and H₂ pressure in the hydroformylation of styrene.

At high pressures the rhodium hydride is the resting state of the catalyst during the hydroformylation of styrene. The first order in styrene, the negative order in CO and zero order in hydrogen confirm that the set of rate-limiting reactions are dissociation of CO, coordination and migratory insertion into Rh–H of styrene.

Table 7
Dependency of the hydroformylation reaction rate on the substrate^a

| Run | <i>P</i> (bar) | mmol Styrene | Conversion (%) (time (min)) | <i>k</i> _{ald} (mol mol ⁻¹ h ⁻¹) |
|-----|----------------|--------------|-----------------------------|--|
| 23 | 8 | 5 | 6.4(30) | 59.8 |
| 24 | 8 | 10 | 8.3(30) | 136.4 |
| 25 | 8 | 20 | 5.6(30) | 181.8 |
| 26 | 20 | 5 | 4.8(50) | 21.0 |
| 27 | 20 | 10 | 5.1(50) | 54.4 |
| 28 | 20 | 20 | 4.9(50) | 91.7 |

^a Conditions: *T* = 80°C, BDPP/Rh = 2, 0.0125 mmol [Rh(μ-OMe)(COD)]₂, in 15 ml of toluene. Regioselectivity b/l = 94/6; enantioselectivity 52% ee.

At low pressures the hydrogenolysis is involved in the rate equation. The kinetic order observed for styrene is lower and for hydrogen is higher, than the ones observed at high pressures. New absorptions in the in situ infrared spectra are due to an equilibrium between the various intermediates in the catalytic cycle. Although the infrared absorptions could not be assigned and the HPNMR spectra were inconclusive, a new metallated species was observed and identified by NMR spectroscopy.

4. Experimental

4.1. General methods

Rhodium complexes were synthesized using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. Styrene was filtered over alumina and distilled over sodium to remove the inhibitors. All other reagents were commercial samples and were used as purchased. Gas chromatography analyses were performed on a Hewlett-Packard 5840A, a gas chromatograph with a flame ionization detector and an Ultra-2 (5% diphenylsilicone–95% dimethylsilicone) (25 m × 0.2 mm ϕ) capillary column. Enantiomeric excesses were measured by GC on the same equipment using an FS-cyclodex β -I/P (50 m × 0.25 mm ϕ) capillary column.

4.2. Standard hydroformylation experiments

Hydroformylation experiments were carried out in a specially designed autoclave with magnetic stirring. The catalytic solution was contained in a glass vessel. The inside part of the cover is made from Teflon to protect the solution from direct contact with the stainless steel. Constant temperature was maintained by the circulation of water through a double jacket. The gas mixture was introduced at constant pressure from a gas reservoir using a pressure regulator.

A solution of the catalyst precursor (0.0125 mmol) and the phosphorus compound (0.05 mmol) was placed

in the evacuated autoclave. The gas mixture (CO/H₂) was introduced, the system was heated and the stirring initiated when the thermal equilibrium was reached. After 1 h the active species was formed and the substrate was added. Two types of hydroformylation experiments were performed at constant pressure: in one the pressure drop was monitored in the ballast using a pressure transducer connected to an electronic measuring device and printing unit, and in the other type a number of samples were taken during the reaction. Conversion and regioselectivities were determined by GC analysis of the crude samples. The reaction rates were calculated with the averaged differential rates for the time intervals.

4.3. The 'in situ' HPIR experiments

The HPIR spectra were performed using equipment previously described [14]. The rhodium complex [Rh(μ-OMe)(COD)]₂ (0.0125 mmol) and the corresponding phosphorus ligand (0.05 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 was pressurized and the mixture heated, the autoclave was placed in the infrared spectrometer. While the sample was 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 was done, the reaction started, as was shown by a pressure drop, and the spectra were recorded. The final solution was analyzed by GC.

4.4. The 'in situ' HPNMR experiments

In a typical experiment, the in situ HPNMR experiments were carried out in a sapphire tube (ϕ = 10 mm). The rhodium complex [Rh(μ-OMe)(COD)]₂ (0.04 mmol) and BDPP (0.1 mmol) and styrene (0.43 mmol) were dissolved in toluene-*d*₈ (1.5 ml) under nitrogen, and the sapphire tube was closed. After pressurizing the

mixture with H₂/CO, the tube was placed in the NMR spectrometer and the spectra were recorded.

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