

# Biphasic hydroformylation of olefins by the new binuclear water soluble rhodium complex $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$

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Received 24 January 2005; received in revised form 30 May 2005; accepted 2 June 2005

Available online 18 July 2005

## Abstract

The new water-soluble rhodium complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$  (**I**) with TPPTS tris-*meta*-sulfonatophenylphosphine and Pz = pyrazolate ligand, has been synthesized by the reaction of the rhodium precursor  $[\text{Rh}(\text{acac})(\text{CO})_2]$  with TPPTS and pyrazol in aqueous solution under inert atmosphere and characterized by FT-IR, UV-vis, <sup>1</sup>H NMR, <sup>31</sup>P{<sup>1</sup>H} NMR. This complex (**I**) shows high solubility and stability in water for long periods of time as demonstrated by UV-vis studies. The new rhodium complex was used as catalyst precursor during the two-phase catalytic hydroformylation of different olefins under the following reactions conditions: 373 K, 4981.3 kPa (CO/H<sub>2</sub> = 1:1), 600 rpm and S/C = 100/1, obtaining as reaction order: 1-hexene > styrene > allylbenzene > 2,3-dimethyl-1-butene > cyclohexene. The catalytic activity of the complex (**I**) in the equimolar and real mixture of olefins with or without the presence of thiophene was also studied and practically no change in the total conversion to aldehydes was observed. This experiments shows that the binuclear complex (**I**) is resistant to possible sulphur poisons present in refinery cuts.

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**Keywords:** Aqueous biphasic catalysis; Hydroformylation; Rhodium binuclear phosphine complexes

## 1. Introduction

Since the initials work by Kuntz [1] and the development work at Ruhrchemie/Rhone-Poulenc process for the hydroformylation of propylene to butyl aldehyde [2–5], the hydroformylation or oxo process continue to be one of the more important classes of homogeneously catalyzed reactions by

transition metal complexes [6–8]. Mononuclear rhodium phosphines (Rh/PAR<sub>3</sub>) catalysts dominate the hydroformylation industry predominantly for C<sub>3</sub> through C<sub>6</sub> 1-alkenes, where regioselectivity towards straight chain aldehyde products is still a problem [9].

Moreover, the use of binuclear rhodium complexes bearing bridge ligands as catalysts precursors for the hydroformylation of olefins has been less exploited considering that their catalytic activity is known for several years. As example of it, Stanley et al., reported an elegant work for the synthesis of the Rh complex  $[\text{Rh}_2(\text{NBD})_2\text{P-P}]$  with P-P: different diphosphines. They proposed the first mechanism for bimetallic hydroformylation with a cooperative effect of both metal [10,11].

Furthermore, Kalck and coworkers reported high catalytic activity in the hydroformylation of 1-hexene with the complex  $[\text{Rh}(\mu\text{-S-t-Bu})(\text{CO})(\text{P}(\text{OMe})_3)]_2$  (**A**) at low pressure in

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homogeneous system [12]. This reaction is selective to the formation of aldehydes without formation of alcohols or isomerization products. The same author reported the synthesis of *cis*-Rh<sub>2</sub>(μ-t-Bu)(μ-Pz)(CO)<sub>2</sub>L<sub>2</sub>, L = trimethylphosphite, triphenylphosphite or triphenylphosphine, where those complexes showed lower catalytic activity than complex (A) [13]. Usón et al. reported the catalytic activity for the binuclear rhodium complex with pyrazolate bridge ligands such as [Rh(μ-Pz)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> for the hydroformylation of 1-heptene. This catalyst precursor showed a moderate catalytic activity and selectivity to octanal from 40 to 60%, without hydrogenation products during the reaction [14].

Feringa et al. [15] reported the dinuclear complexes [Rh<sub>2</sub>L<sub>2</sub>(acac)<sub>2</sub>] and [Rh<sub>2</sub>L<sub>2</sub>C<sub>12</sub>(CO)<sub>2</sub>] with L a bidentate phosphine 1,4-bis{bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl-benzene and used for the hydroformylation of cyclohexene where cyclohexanecarbaldehyde was the only product formed with moderate rates.

Claver et al. [16] showed that complex [Rh(μ-S(CH<sub>2</sub>)<sub>3</sub>NMe)(COD)]<sub>2</sub>PR<sub>3</sub> (R = Ph, O-o-t-BuC<sub>6</sub>H<sub>4</sub>) can be used as a catalyst precursor for the hydroformylation of different benzyl-allylic ethers with steric hindrance and obtain α, β, and γ hydroxialdehydes with excellent conversions of 99%. Also, the same author used the complex [Rh(μ-Pz)(μ-SBu)(COD)]<sub>2</sub> as a catalytic precursor for the hydroformylation of styrene in the presence of triphenylphosphine and chiral diphosphines [17]. They found that excess of triphenylphosphine improve the *n/i* ratio and increase the absolute conversion to aldehydes. Moreover, the uses of chiral diphosphines produce the complete conversion to aldehydes with a good regioselectivity and enantiomeric excess.

Poyatos et al. [18] synthesized new dirhodium(I) bisimidazolium–carbene complex fully characterized by means of NMR spectroscopy and single-crystal X-ray diffraction. This complex was used as catalyst precursor in the hydroformylation reactions of different olefins such as styrene, 1-octene showing selectivity mainly towards branched aldehyde.

Kostas et al. [19] reported very recently two new dinuclear rhodium complexes such as bis[1-(2-methylphenolato)]bis[(η<sup>2</sup>:η<sup>2</sup>-cycloocta-1,5-diene)rhodium], di(1-docosanoato)bis[(η<sup>2</sup>:η<sup>2</sup>-norborna-2,5-diene)rhodium] and bis[1-(adamant-1-yl)carboxylato]bis[(η<sup>2</sup>:η<sup>2</sup>-norborna-2,5-diene)rhodium] were both complexes were used as catalysts precursor for the hydroformylation of styrene with under moderate reaction conditions. They found that both complexes displayed a regioselectivity towards the branched aldehyde of up to 97 and for 1-octene; the regioselectivity goes for the linear aldehyde of up to 55%.

Baricelli et al. also reported very recently, the synthesis, characterization and the catalytic activity of the binuclear complex [Rh(μ-Pz)(CO)(TPPMS)]<sub>2</sub> during the hydroformylation of 1-hexene and styrene in a two phase reaction medium [20]. This complex shows selectivity towards heptanal for 1-

hexene while 2-phenylpropanal and 3-phenylpropanal were obtained from styrene.

Continuing with the development of binuclear catalyst precursor for biphasic catalysis, this article reports the synthesis, characterization of the new water-soluble rhodium complex [Rh(μ-Pz)(CO)(TPPTS)]<sub>2</sub> and their catalytic behavior in the hydroformylation of 1-hexene, styrene, allylbenzene, 2,3-dimethyl-1-butene, cyclohexene and their mixtures.

## 2. Experimental

### 2.1. General procedure

All manipulations were carried out under nitrogen atmosphere by using standard Schlenk technique [21]. Organic solvents were purified by distillation and deoxygenated prior to use. RhCl<sub>3</sub>·3H<sub>2</sub>O, 1-hexene, cyclohexene, 2,3-dimethyl-1-butene, styrene, allylbenzene, thiophene, acetylacetone, dichloromethane, diethyl ether, methanol, *N,N*-dimethylformamide were obtained from Aldrich Chemical. The other chemicals were commercial products and were used without further purification. All gases were purchased from Venezuela AGA Gases. TPPTS was prepared according to the literature procedure [22]. Analyses by NMR were obtained on a Bruker AM 300 spectrometer. The UV–vis spectra were taken in a diode array Hewlett Packard 8452 spectrometer. Atomic absorption analyses were performed with a Perkin-Elmer 5000 instrument. GC analyses were performed on a Hewlett Packard 5890 Series II chromatograph with a flame ionization detector and ultra 2.5% phenyl methyl silicone, 25 m, 320 μm column. Quantification was achieved by using the internal standard (naphthalene) method and the peaks were identified by comparison with pure samples analyzed by GC/MS HP 5890/5971 coupled system using Quadrex PONA 5% phenyl methyl silicone, 25 m, 320 μm column. The Infrared spectra were recorded in a Perkin-Elmer Spectrum 1000 FT-IR using samples as KBr disks.

### 2.2. Synthesis of [Rh(μ-Pz)(CO)(TPPTS)]<sub>2</sub> (I)

To a green solution of 100 mg (0.39 mmol) of the complex [Rh(acac)(CO)<sub>2</sub>] in methanol (30 ml) prepared and characterized according to the literature procedures [23] was added with stirring 26.4 mg (0.39 mmol) of pyrazole. After 15 min the color of the solution changed from green to yellow. Finally 206.4 mg (0.36 mmol) of TPPTS was added to the above solution and water (deoxygenated and saturated with nitrogen) was added by drop, until the TPPTS was completely dissolved. The solution was stirring during 15 min and its color changed from yellow to orange. The resulting solution was concentrated in vacuum and immediately 30 ml of diethyl ether was added and caused the precipitation of complex (I) as a yellow powder, which was collected and washed two times with 20 ml of diethyl ether and dried under vacuum; yield 0.24 g, 80%.

### 2.3. Catalytic hydroformylation

In a typical experiment, an aqueous solution of the rhodium catalyst precursor (0.015 g; 0.0098 mmol) in 15 ml of water and 1-hexene (0.24 ml; 1.6 mmol) in 15 ml of heptane, were introduced into a glass-lined stainless steel autoclave Parr (25 ml) fitted with internal mechanical stirring, temperature control unit and a sampler valve. The solution was purged three times with syn-gas (CO + H<sub>2</sub>, 1:1) and then charged with the required pressure and heated to the desired temperature. Samples of the reaction mixture were periodically extracted and the system total pressure was adjusted via a high pressure reservoir. Once the samples were extracted, they were cooled, the phases separated and the organic phase analyzed. The stirring rate was keeping constant at 600 rpm, the temperature of the reaction was varied from 333 to 363 K; syn-gas pressure varied from 698.8–6987.6 kPa; the substrate/catalyst ratio varied from 200/1 to 700/1. The liquid samples were removed from the reactor vessel and analyzed by GC and CG–MS techniques.

### 2.4. Catalyst recycling experiments

The recycling experiments were carried out under *aerobic* or *anaerobic* condition. A general procedure is described as follow: an aqueous solution of the rhodium catalyst precursor (0.015 g; 0.0098 mmol) in 15 ml of water and 1-hexene (0.24 ml; 1.6 mmol) in 15 ml of heptane, were introduced into a glass-lined stainless steel autoclave Parr (25 ml) fitted with internal mechanical stirring, temperature control unit and a sampler valve. The solution was purged three times with syn-gas (CO + H<sub>2</sub> 1:1) and charged with the required pressure and heated to the desired temperature. Samples of the reaction mixture were periodically extracted and the system total pressure was adjusted via a high pressure reservoir. Once the samples were extracted, they were cooled, the phases separated under *aerobic* condition and the organic phase analyzed. The catalytic aqueous phase was mixed with a fresh organic phase that contain 1-hexene, introduced again into the autoclave purged three times with syn-gas (CO + H<sub>2</sub> 1:1) and then charged with the required pressure and heated to the desired temperature. For *anaerobic* condition, the same procedure is used only the new fresh organic phase that contains 1-hexene is introduced into the high pressure reservoir, purged three times with syn-gas (CO + H<sub>2</sub> 1:1) and adjusted until the operation condition. The gas pressure from the reactor is released until 698.8 kPa and the substrate is introduced from the high pressure reservoir and adjusted again until the desired pressure.

Table 1  
Spectroscopy information of [Rh(μ-Pz)(CO)(TPPTS)]<sub>2</sub>

Spectroscopic analysis	Assignment	
FT-IR	3419 cm <sup>-1</sup>	ν(OH)
	2078, 1972 cm <sup>-1</sup>	ν(CO)
	1632, 1465, 1399 cm <sup>-1</sup>	ν(Ph)
	1195 cm <sup>-1</sup>	ν(SO <sub>3</sub> <sup>-</sup> )
	790, 690, 623 cm <sup>-1</sup>	ν(SO)
<sup>1</sup> H NMR	6.6, 5.8 ppm (s)	Pyrazolate protons
	7.4; 7.7; 8.0 ppm (m)	Aromatic protons
<sup>31</sup> P-{ <sup>1</sup> H} NMR	47.39 ppm (d)	TPPTS
UV-vis	230 nm	Charge transfer bands

s: singlet; d: doublet; t: triplet; m: multiplet.

## 3. Results and discussion

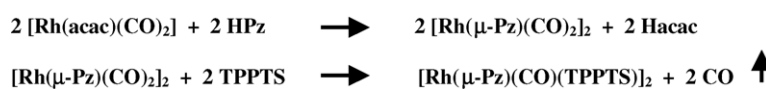
### 3.1. Synthesis and characterization of [Rh(μ-Pz)(CO)(TPPTS)]<sub>2</sub>

The new water-soluble complex [Rh(μ-Pz)(CO)(TPPTS)]<sub>2</sub> (**I**) was synthesized according to the modified method reported by our group [20], summarized in Scheme 1. The intermediary complex [Rh(μ-Pz)(CO)<sub>2</sub>]<sub>2</sub> was treated with two equivalents of TPPTS in methanol in the presence of some drops of distilled water in order to increase the solubility of TPPTS in this solvent leading the expected complex (**I**) as a orange microcrystalline powder.

The new complex shows stability in air, solubility in polar solvents including water which is stable for long periods of time, demonstrated by UV-vis analysis [24]. After 96 h at room temperature, the intense absorption band at 230 nm, characteristic of LMCT from the TPPTS ligand to the rhodium center remain constant, prove of the stability of (**I**) in water.

A complete characterization of the complex (**I**) was performed based on the spectroscopy data obtained using FT-IR, <sup>1</sup>H NMR, <sup>1</sup>H{<sup>31</sup>P} NMR, and UV-vis analysis. The main absorption bands are summarized in Table 1.

The FT-IR analyses of the complex (**I**) shows one wide band at 3419 cm<sup>-1</sup> characteristic of the stretching –OH group from the water bond to the sulfonate group. Two bands at 2078(m) and 1972(s) cm<sup>-1</sup> assigned to the vibrations of C≡O groups bonded to the rhodium centers which are in concordance with the observed bands reported by Kalck et al. [25], the strong and sharp band at 1972 cm<sup>-1</sup> suggest a trans arrangement in concordance with the observed bands in the similar complex reported by our group [20]. Three bands at 1632, 1465 and 1399 cm<sup>-1</sup> assigned to stretching C–H from the phenyl groups of the TPPTS and finally two bands at 1195 and 790 cm<sup>-1</sup> corresponding to the stretching of SO<sub>3</sub>



Scheme 1.

group from the TPPTS, also observed by our group in others hydrosoluble complexes [26,27].

The  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ ) of the complex (**I**) shows three multiplets at 7.3, 7.4 and 7.8 ppm assigned to the aromatic protons of the TPPTS coordinated to the rhodium centers. Three signals at 8.0(d), 6.6(d) and 5.8(t) ppm assigned to the pyrazolyl hydrogen were also observed. The  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{D}_2\text{O}$ ) shows a intense doublet at  $\delta = 47.39$  ppm with  $J(\text{P}-\text{Rh}) = 153.27$  Hz characteristic of the two equivalents TPPTS phosphine with the same chemical and magnetic environment coupled with the CO ligand *cis* in the axial plane. It's important to mention that those results are in accordance with the recent report for the analogue TPPMS complex and for the iridium complex  $[\text{Ir}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})_2]$  [20,28].

By examination of the  $^{31}\text{P}$  NMR, it was confirmed that complex (**I**) was obtained in a pure form, before start the catalytic hydroformylation experiments. From the above analyses of the spectroscopy evidences, we can infer a binuclear structure bridged by two pyrazolate ligands and each rhodium atom bonded to one TPPTS and one CO ligand, according with the proposed structure as shown in Fig. 3. Similar observations have been reported for analogue complex with  $\text{PPh}_3$  and  $\text{P}(\text{OPh})_3$  [25,29], which let us conclude that complex (**I**) is a binuclear structure in which each metal atom has a square planar geometry with  $\text{C}_{2v}$  symmetry, similarly to the structure reported by our group for the analog complex with TPPMS [20] (Fig. 1).

### 3.2. Aqueous biphasic hydroformylation of olefins

The complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$  is an efficient catalyst precursor for two-phase hydroformylation of different olefins namely 1-hexene, 2,3-dimethyl-1-butene, cyclohexene, styrene and allylbenzene at 343 K, 4891.3 kPa,  $[\text{subst}]/[\text{cat}] = 200/1$  and  $\text{CO}/\text{H}_2 = 1:1$ . Initially, some operation conditions were studies using 1-hexene as substrate. Initially the variation of syn-gas pressure was performed and the result is observed in Fig. 2. As can be seen, when the pressure was varied from 698.75 to 6987.5 kPa, it is observed an increasing of the formation of 2-hexene until 3493.8 kPa.

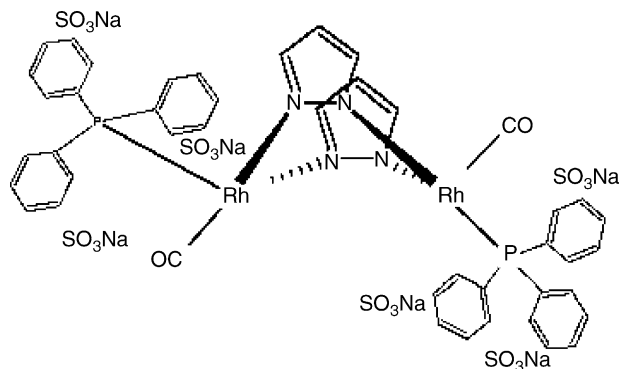


Fig. 1. Structure proposed for the complex (**I**).

However, above to 3493.8 kPa, the production of aldehydes is increased as expense from the isomerization reaction, maintaining this behavior almost constant until 6987.6 kPa. It is clear from Fig. 2, that the best operational pressure to lead better conversions and good selectivity to aldehydes is around 4981.3 kPa.

One point which deserves some attention regards in the behavior observed for this catalyst precursor when the syn-gas pressure varies which is totally different to the observed for the analog complex with TPPMS using the same substrate [20].

For the TPPMS complex, the conversion of 1-hexene to hydroformylation products was independent of the gas pressure indicating that under the range of pressure evaluated, the same active specie is forming while for TPPTS complex, because different conversion and selectivity are obtained probably is related with the type of phosphine employed. In earlier works it was reported that the type of phosphine plays a relevant role on the activity and selectivity during the hydrogenation of different substrates [30].

We suspect that using TPPTS as ligand, at lower syn-gas pressure help the formation of specie responsible for olefin isomerization whereas at higher syn-gas pressure, the active specie which conduces to hydroformylated products is formed. Still further experiments need it to address this point.

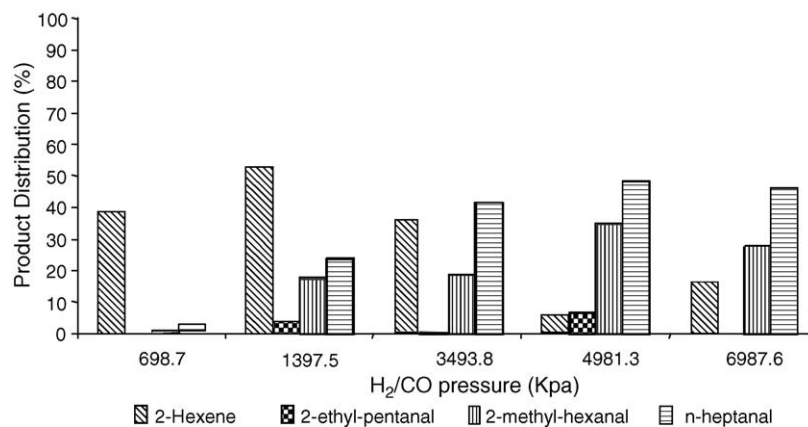


Fig. 2. 1-Hexene hydroformylation by complex (**I**). Effect of the  $\text{H}_2/\text{CO}$  pressure.

Table 2  
Products of the hydroformylation of olefins by the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$

Olefin	Products distribution (%)	Total conversion <sup>a</sup> (%)	Aldehydes (%)	<i>n/i</i>
1-Hexene	<i>n</i> -Heptanal (48), 2-methyl-hexanal (33), 2-hexene (7), 2-ethyl-1-pentanal (10)	98	91	1.45
2,3-Dimethyl-1-butene	3,4-Dimethyl-1-pentanal (94), 2,3-dimethyl-2-butene (6)	100	94	
Cyclohexene	Cyclohexanecarboxyaldehyde (83)	83	83	
Styrene	2-Phenyl-2-propanal (20), 3-phenyl-1-propanal (80)	100	100	4
Allyl benzene	2-Methyl-3-phenyl-1-propanal (49), 4-phenyl-1-butanal (50)	99	99	1.02

Operational conditions:  $P_{(\text{H}_2+\text{CO})} = 4891.3$  kPa, 343 K,  $[\text{subs}]/[\text{cat}] = 200/1$ ,  $t = 24$  h.

<sup>a</sup> Total conversion (aldehydes + isomerization products).

The effect of the reaction temperature was also studied. It found that below to 343 K, the catalytic activity drop considerably, however from 343 to 363 K, the activity reaches almost 100% after 24 h. We select 343 K as operation temperature. After found the best operation values, it was studied the effect of the olefin, first in a pure form, second in a binary and total mixture. The results are presented in Table 2.

As is shown in Table 2, for 1-hexene is observed that *n*-heptanal (lineal isomer) represent 48% of the product composition whereas the branched aldehydes 2-methyl-hexanal reach 33% with *n/i* ratio of 1.45. The isomerization product was present in 7% which is hydroformylated as well; leading 2-ethyl-1-pentanal in 10%. Those observations confirm the difficulties of these internal olefins to be converted using the above reaction conditions. Also Table 2 shown that 2,3-dimethyl-1-butene is converted to the lineal aldehyde; 3,4-dimethyl-1-pentanal in (94%) with low tendency for isomerization product; 2,3-dimethyl-2-butene (6%) without formation of the branched isomer, presumably due to steric repulsions that obstruct the formation of the corresponding alkyl intermediate.

The cyclohexene, under only is converted to cyclohexanecarboxaldehyde (83%). Styrene generates a lineal aldehyde 3-phenyl-1-propanal (80%) and a branched isomer 2-phenyl-1-propanal (20%) with *n/i* ratio = 4. Allylbenzene produce almost equal quantities of lineal isomer 4-phenyl-1-butanal (49%) and branched isomer 2-methyl-3-phenyl-1-propanal (50%) with lowest *n/i* ratio (1.02) obtained in this work.

After interesting catalytic results, we were encourage to find some indication of the possible species involve during the hydroformylation. In this sense, we analyzed aqueous phase by UV–vis spectroscopy, during the hydroformylation of 1-hexene. The results are shown in Fig. 3.

As it is observed therein, during the first 4 h, the spectrum showed one band at 230 nm which is shifted to 208 nm.

At 8 h it is observed the band at 230 nm with the formation of two new bands at 270 and 322 nm, which all three bands remain constant until 24 h. From these observations we can infer that new catalytic specie is formed during the second part of the reaction probably due to the formation of a very active mononuclear rhodium species. Additional studies using high-pressure NMR spectroscopy are in progress in order to identify such species.

### 3.3. Catalyst recycling experiment

One aspect that is important to address in biphasic catalysis is the capability of reusing the catalyst precursor [31]. Taking account this, a set of recycling experiments using the complex (I) during the hydroformylation of 1-hexene were performed. In this sense, two different strategies were used (as described in the experimental section). The first one consist in the separation of both phases at the end of the reaction by simple decantation under *aerobic* condition, changing each 3 h the organic phase for another fresh organic phase which contain 1-hexene and running the experiment maintaining the same reaction conditions (namely strategy I).

The second one consist in the continuing recharging of the fresh organic phase which contain 1-hexene from the high pressure reservoir under *anaerobic* condition, meaning that in all experiments, the catalyst solution was keep it under  $\text{H}_2/\text{CO}$  atmosphere (namely strategy II). By using both strategies, four consecutive experiments were carried out and the results obtained are presented in Table 3.

As is shown in Table 3, the type of strategy used has a remarkable effect of the recycling properties for this complex. Using strategy I, the complex (I) loose practically the activity after the first cycle and this trend continue to the second cycle.

The above results indicate that the active specie is sensitive to the presence of air, leading probably their transformation in catalytically inactive specie. Kalck et al. reported for the

Table 3  
Recycling experiments using  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$  as catalyst precursor

	Strategy I			Strategy II				
	0	1	2	0	1	2	3	4
Recycle	0	1	2	0	1	2	3	4
Conversion (%) of 1-hexene	100	10	3	100	99	99	99	98
<i>n/i</i> ratio	2.1	2.6	2.8	3.2	2.6	2.5	2.5	2.4

Operational conditions:  $P_{(\text{H}_2+\text{CO})} = 4891.3$  kPa, 343 K,  $[\text{subs}]/[\text{cat}] = 200/1$ ,  $t = 24$  h. Total conversion (aldehydes + isomerization products).

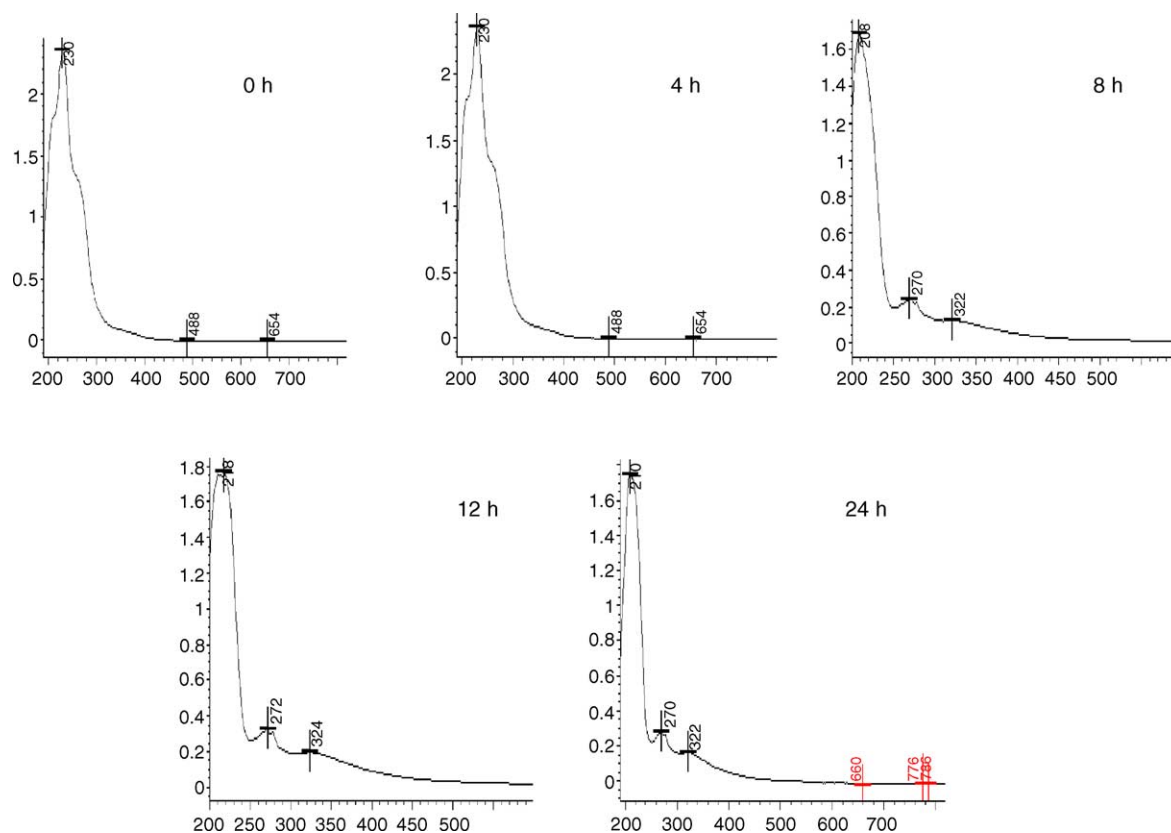


Fig. 3. UV-vis studies of the aqueous phase during the hydroformylation of 1-hexene.

1-octene hydroformylation using the dinuclear water soluble complex  $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$  that the conversion decreases from 87 to 81%, when the aqueous phase was separated under argon whereas the chemo- and regio-selectivities are not affected [32]. These results indicate that the recycling experiment would be better performing under *anaerobic* condition, reason why it was set up the strategy II.

As can be shown, the catalytic activity remains constant during the first run and the first recycle and it continues constant until four cycles. Regarding to the *n/i* ratio, the results show that it reaches a value around 2.5 and keeps it constant after each catalyst cycle. The above results suggest that definitely, the nature of the active species is maintained under  $\text{H}_2/\text{CO}$  atmosphere, allowing recycling this catalyst precursor, conditioning achieved using strategy II.

#### 3.4. Aqueous biphasic hydroformylation of olefin mixtures

In order to test the performance of the new catalyst  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$  in hydroformylation reaction of mixtures of olefins, two different systems were prepared. System (1) consists in binary mixture of 1-hexene with other olefin such as styrene, allylbenzene, 2,3-dimethyl-1-butene, cyclohexene respectively. The system (2) consists in the equimolar

mixture of the five olefins both systems tested under the best operational parameters found for the pure olefins. The results obtained are reported in Table 4.

As it is present in Table 4, in all cases, the hydroformylation was efficiently achieved, although a decrease in the total conversion of each olefin was observed compared with the pure olefin, indicating a possible competition between the more active olefins to the active species.

Table 4  
Products of the hydroformylation of olefin mixtures with the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$

System	Total conversion (%)	Aldehydes (%)
Equimolar mixture		
1-Hexene	99	
2,3-Dimethyl-1-butene	84	92.2
Cyclohexene	50	
Styrene	97	
Allylbenzene	95	
Real quantities (present in refinery cuts)		
1-Hexene	100	
2,3-Dimethyl-1-butene	100	87.2
Cyclohexene	64	
Styrene	93	
Allylbenzene	96	

Operational conditions:  $P_{(\text{H}_2+\text{CO})} = 4891.3 \text{ kPa}$ , 343 K,  $[\text{subs}]/[\text{cat}] = 200/1$ ,  $t = 24 \text{ h}$ .

Table 5  
Effect of the thiophene

Olefin	% Conversion (none thiophene)	% Conversion (500 ppm of thiophene)
1-Hexene	100	100
2,3-Dimethyl-1-butene	100	100
Cyclohexene	64	48
Styrene	93	100
Allylbenzene	96	100

Operational conditions:  $P_{(H_2+CO)} = 4891.3$  kPa, 343 K, [subs]/[cat] = 200/1,  $t = 24$  h, thiophene: 500 ppm.

### 3.5. Aqueous biphasic hydroformylation of olefin mixtures in the presence of thiophene

The deactivation of the catalyst by organosulfur compounds present in the refinery cuts is one of the main aspects to be considered in our research work. For this purpose, the mixture of the five olefins, 1-hexene, styrene, allylbenzene, 2,3-dimethyl-1-butene and cyclohexene were treated with 500 ppm of thiophene, in order to determine the sulfur tolerance of the rhodium complex  $[Rh(\mu-Pz)(CO)(TPPTS)]_2$  under the best operational conditions already described. The results are summarized in Table 5.

The results shown in Table 5 indicate that the activity of the complex was not significantly affected by the presence of the thiophene. A decreasing on the conversion of cyclohexene was observed however this olefin remains active until the end of the reaction. Finally an increasing in the conversion for allylbenzene and 2,3-dimethyl-1-butene was observed reaching 100% of conversion.

The fact that presence of sulfur in the media enhances the activity during hydroformylation reactions has been revised by Chuang et.al. [33] employing supported rhodium catalyst and using FT-IR techniques to follow the reaction. They found for ethylene hydroformylation over Rh/SiO<sub>2</sub> that formation of the rhodium sulfide favored the homogeneous hydroformylation to a greater extend than the reaction with Rh metal. Also, these studies have been extended to others metals sulfide of the group VIII for hydrogenation and hydroformylation reactions. The same author in other reports clearly explains that the heterogeneous hydroformylation reaction of ethylene over Rh/SiO<sub>2</sub> is more active than those performed with Ni/SiO<sub>2</sub> and Ru/SiO<sub>2</sub> [34–36]. We suspect that in this biphasic system, rhodium–sulfide water soluble specie is formed during the reaction pathway which could be responsible for the increase of the activity towards oxygenated products.

Experiments related with the hydroformylation of olefin in the presence of sulfur and nitrogen compounds are in progress and the results will be delivery in a next communication.

## 4. Conclusion

The new water-soluble binuclear rhodium complex  $[Rh(\mu-Pz)(CO)(TPPTS)]_2$  was prepared and fully character-

ized using spectroscopy techniques. It shows to be efficient catalyst precursor for the aqueous biphasic hydroformylation of different olefins such as 1-hexene, 2,3-dimethyl-1-butene, cyclohexene, styrene and allylbenzene. Under the best operational parameters, the substrates showed the following hydroformylation order:

1-hexene > styrene > allylbenzene

> 2, 3-dimethyl-1-butene > cyclohexene

This order of activity is maintained in the hydroformylation of equimolar mixture, real quantities (present in the refinery cuts) and real quantities (present in refinery cuts + thiophene) of the olefins. However, some competition effects are observed causing a slight decrease of the rates for all the olefins. The presence of thiophene, cause an increase in the conversion of styrene and allylbenzene, possibly due to the formation of rhodium–sulfide water soluble complex. From the last experiment, we can infer that  $[Rh(\mu-Pz)(CO)(TPPTS)]_2$  is resistant to some possible sulfur poisons present in refinery cuts.

## Acknowledgments

We thank FONACIT (Caracas) for financial support through Project F-97003766, CONIPET Project 97-003777 and CODECIH-UC Project 94017. We thank also the CYTED Project V.9 (Programa Iberoamericano de Ciencia y Tecnología para el Desarrollo) for the logistical support to our group. We are grateful to Universidad de Carabobo for permitting the publication of this work.

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