



## Influence of the addition of thiophenes on the catalytic activity of the rhodium binuclear complex $[\text{Rh}(\text{CO})(\mu\text{-Pz})(\text{TPPTS})]_2$ during the biphasic hydroformylation of 1-hexene<sup>☆</sup>

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### ABSTRACT

The preactivation of the binuclear complex  $[\text{Rh}(\text{CO})(\mu\text{-Pz})(\text{TPPTS})]_2$ , TPPTS = tris-*meta*-sulfonatophenylphosphine and Pz = pyrazolate ligand, during the two-phase catalytic hydroformylation of 1-hexene was studied under mild reaction conditions [1746.9 kPa of syngas (CO/H<sub>2</sub> = 1:1), S/C = 200, R.P.M. = 700, T = 343 K, t = 3 h], under which it was confirmed the formation of mononuclear active species responsible of the olefin hydroformylation. The presence of compounds such as thiophene and benzothiophene up to 2500 ppm did not interfere with the evolution of the reaction, confirming that the active specie is resistant to sulphur. It was found that under *anaerobic conditions*, the catalytic activity remains almost constant after four consecutive cycles, leading to the production of aldehydes and the corresponding isomerization products, *cis*- and *trans*-2-hexene.

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### 1. Introduction

Hydroformylation, or oxo process, is one of the most important classes of catalyzed reactions by transition metal complexes [1–4], both in homogenous media and in biphasic systems which include the traditional aqueous/organic combination [5] as well as novel ones involving ionic liquids [6] and perfluorinated hydrocarbons [7]. Mononuclear rhodium phosphines catalysts (Rh/PAr<sub>3</sub>) dominate the hydroformylation industry predominantly for C3 through C6 alkenes, where regioselectivity towards straight chain aldehyde products is still a problem [8]. One alternative has been explored using binuclear rhodium complexes bearing bridge ligands in homogeneous systems [9–18]. However, the use of binuclear catalyst precursors for liquid–liquid biphasic catalysis has not been well exploited so far. One example was initially reported by Kalck et al. [19] during the 1-octene hydroformylation using the binuclear water soluble complex  $[\text{Rh}_2(\text{-StBu})_2(\text{CO})_2(\text{TPPTS})_2]$ ; they found that the conversion falls from

87% to 81% when the aqueous phase was separated under argon, whereas the chemo- and regioselectivities were not affected. Baricelli et al. [20] reported the synthesis of a binuclear complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ , TPPMS = (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(*m*-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Na), which showed catalytic activity during the hydroformylation of 1-hexene and styrene in a two-phase reaction medium; heptanal was the main product obtained for 1-hexene, while 2-phenylpropanal and 3-phenylpropanal were obtained from styrene. Very recently, the same authors reported one analogue complex but using the highly soluble phosphine TPPTS to form the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$ , TPPTS = tris-*meta*-sulfonatophenylphosphine and Pz = pyrazolate ligand [21]. The resulted binuclear complex showed activity for the hydroformylation of 1-hexene, styrene, allylbenzene, 2,3-dimethyl-1-butene, cyclohexene and their mixtures in the absence or presence of thiophene, where practically no change in the total conversion to aldehydes was observed. In this work, we present the results obtained during the evaluation of the liquid–liquid biphasic hydroformylation of 1-hexene using as catalyst precursor the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$  in the presence of up to 2500 ppm of the sulphur-containing compound (thiophene or benzothiophene) with emphasis in studies of the recycling properties of this complex in order to determine their real stability under a sulphur-rich environment.

<sup>☆</sup> In memory of our dear partner and friend Ramón Eduardo Lujano.

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## 2. Experimental

### 2.1. General procedure

All manipulations were carried out under nitrogen atmosphere by using standard Schlenk technique [22]. Organic solvents were purified by distillation and deoxygenated prior to use. 1-Hexene, *n*-heptane, thiophene and benzothiophene were obtained from Aldrich Chemicals and used as received. The other chemicals were commercial products and used without further purification. All gases were purchased from Venezuela AGA Gases. Complex  $[\text{Rh}(\text{CO})(\mu\text{-Pz})(\text{TPPTS})]_2$  was prepared according to a previous report [20]. GC–MS analyses were performed in a HP 5890 SERIES II PLUS with FI detector and a Megabore type capillary column, 15 m (DB-5 phase; 1.5  $\mu$  FT, J and W Scientific) with the following temperature program: 35 °C/5 min//10 °C/min/150 °C/5 min.

### 2.2. Catalytic hydroformylation and recycling experiments

In a typical experiment, an aqueous solution of the rhodium catalyst precursor (24 mg; 0.015 mmol) in distilled water (40 mL), was introduced into a glass-lined stainless steel autoclave (Parr, 100 ml) connected to a continuous flow gases line which was fitted with internal mechanical stirring, temperature control unit and a sampler valve. The solution was purged three times with syngas ( $\text{H}_2/\text{CO} = 1/1$ ) and charged with 978.2 kPa of the gas mixture. Then, the catalyst was incubated at 343 K for 1 h, previous to the addition of the mixture of 1-hexene (254.90 mg; 2.92 mmol; S/C = 200/1) and the sulphur compound (500 ppm, 0.04 mmol of thiophene or benzothiophene) in 15 ml of heptane, which was introduced using a high-pressure burette, the reactor was 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 *anaerobic conditions* and the organic phase analyzed. The catalytic aqueous phase was mixed with a fresh organic phase that contained the mixture of 1-hexene (254.90 mg; 2.92 mmol; S/C = 200/1) and the sulphur compound (1000 ppm, 0.08 mmol of thiophene or benzothiophene) in 15 ml of heptane, introduced again into the autoclave, purged three times with syngas ( $\text{CO}/\text{H}_2$  1:1) and then charged with the required pressure and heated to the desired temperature. This operation was repeated three more times and in each recycle the concentration of the sulphur-containing compound was increased by 500 ppm to reach 2500 by the fifth run.

## 3. Results and discussion

Previously, our group reported the high activity of the  $[\text{Rh}(\text{CO})(\mu\text{-Pz})(\text{TPPTS})]_2$  complex during the two-phase hydroformylation of different olefins such as 1-hexene, styrene, allylbenzene, 2,3-dimethyl-1-butene and cyclohexene, in order to simulate a  $\text{C}_6$  naphta cut from a real refinery [21]. In those studies, it was also demonstrated using UV–vis techniques that the hydroformylation reaction involves a mononuclear catalytic species, which was also reported by Davis et al. [23a] and Ruiz et al. [23b]. Considering that the capability of reusing the catalyst precursor is an important aspect to address in biphasic catalysis [24], it is significant to know the stability of this complex in the presence of sulphur compounds.

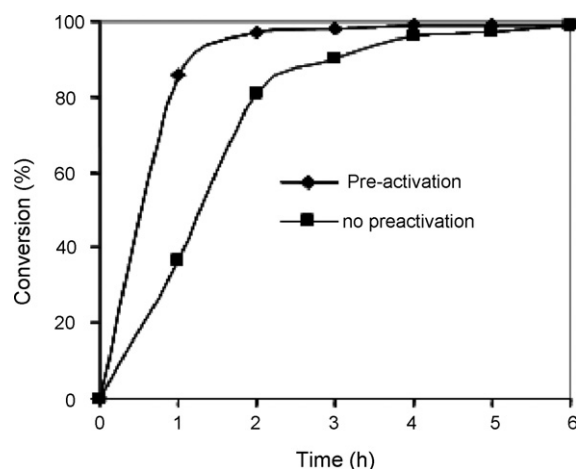


Fig. 1. Effect of the pre-activation of the catalyst precursor  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$ .

### 3.1. Effect of the pre-activation of the complex $[\text{Rh}(\text{CO})(\mu\text{-Pz})(\text{TPPTS})]_2$ with syngas

It has been reported for biphasic hydroformylation using a mononuclear rhodium-TPPTS catalysts that it is usually pre-formed from Rh(III)-precursors, e.g. Rh(III)-acetate, in the presence of TPPTS with syngas under hydroformylation conditions; during this process the precursor is transformed into a Rh(I)-containing catalyst [24]. In order to verify if our complex behaves as Rh-TPPTS catalyst system, the effect of the pre-activation of the catalyst precursor was carried out under 978.2 kPa of syngas at 343 K for 1 h, and the results for the reaction profiles are shown in Fig. 1.

The pre-activation of this complex under low pressure of syngas, leads to a species able to convert about 85% of the substrate in 1 h in comparison with the no pre-activated catalyst, which converts around 40% of 1-hexene in the same time. For this reason, all the subsequent recycling experiments were carried out with the preactivation of the binuclear complex  $[\text{Rh}(\text{CO})(\mu\text{-Pz})(\text{TPPTS})]_2$ . In order to confirm that the hydroformylation reaction proceeds via a molecular complex, the well known mercury test [25] was carried out in several independent experiments using one drop of mercury (~6 mmol, 1500 eq.) in the hydroformylation of 1-hexene; the results showed no interference with the evolution of the reaction.

### 3.2. Recycling experiment using pre-activating complex $[\text{Rh}(\text{CO})(\mu\text{-Pz})(\text{TPPTS})]_2$

When the recycling experiments were carried out under *aerobic conditions*, the complex activity decreases drastically, thus *anaerobic conditions* were necessary for the recycling experiments. The catalyst recycling was evaluated pre-activating the catalyst precursor before any reaction under the condition described above and under *anaerobic conditions*, accordingly to our previous results [21], using as reaction conditions:  $p_{\text{H}_2/\text{CO}} = 1746.9$  kPa, S/C = 200, R.P.M. = 700,  $T = 343$  K,  $t = 3$  h. It is remarkable to point out that the syngas pressure was reduced in order to diminish the conversion, thus all of the effect would be easier to be noticed. Four consecutive experiments were carried out and the results obtained are displayed in Fig. 2.

As it is shown in Fig. 2, the method of recycling affects significantly on the reusability of this complex. Using *aerobic conditions*, the complex loses practically all of its catalytic activity after the first cycle; this trend continues up to the third cycle. While under *anaerobic conditions*, the catalytic activity increases slightly during the four recycles. The above results indicate that the active specie

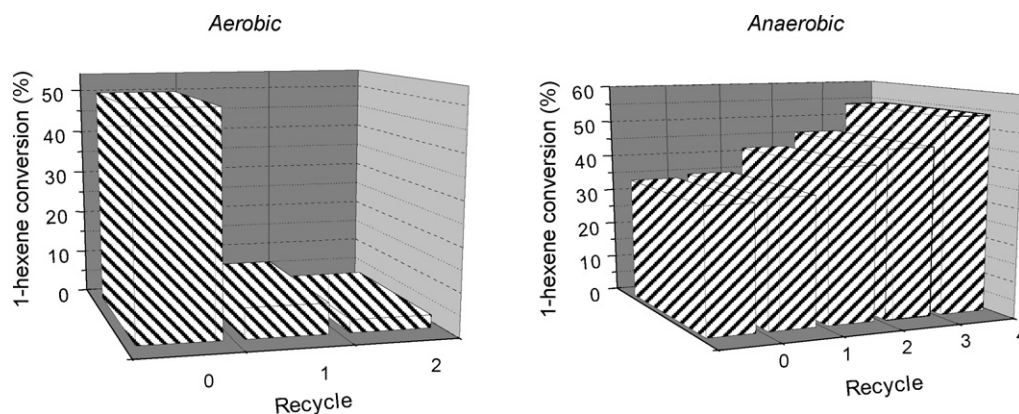


Fig. 2. Recycling experiments of catalyst precursor  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$ . Conditions as in Table 1.

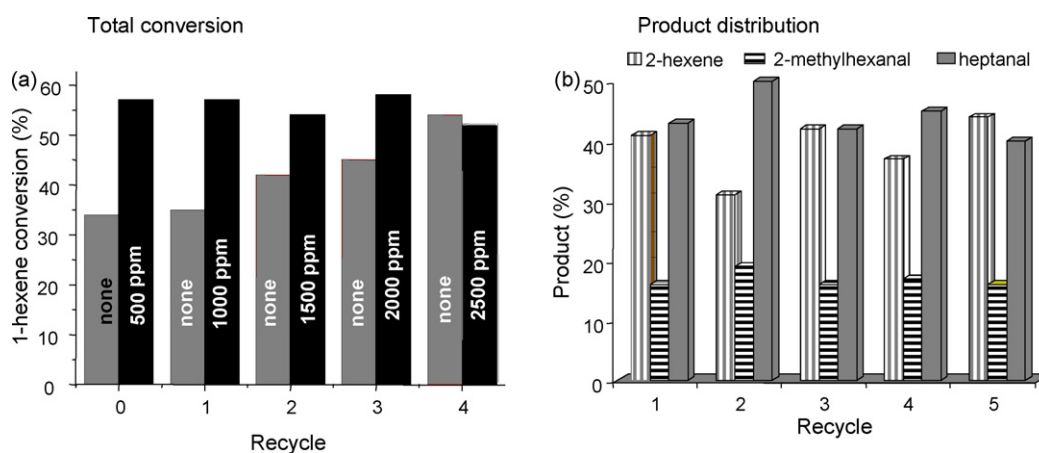


Fig. 3. Catalyst recycling experiment and product distribution using as catalyst precursor  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$  in the presence of thiophene.

is sensitive to the presence of air leading probably inactive oxides. The same behavior was reported by Kalck et al. [19] during the 1-octene hydroformylation with the binuclear water soluble complex  $[\text{Rh}_2(-\text{StBu})_2(\text{CO})_2(\text{TPPTS})_2]$ .

### 3.3. The effect of the presence of thiophene or benzothiophene on the catalytic activity and recycling properties of $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$ complex

It was previously reported, by Oswald et al. [26], that an olefinic cracked distillate feed containing organosulfur compounds (exceeding 0.1 wt%) treated with group VIII transition metal carbonyls produced alcohols and aldehydes with semilinear character containing in average less than one branch per molecule. The experiments carried out by them used homogeneous catalysts systems in a temperature range from 50 °C to 250 °C and high pressure of  $\text{H}_2/\text{CO}$  (50–6000 psi). Baricelli et al. [20,21] previously studied the stability of the water-soluble catalysts precursor in the presence of organosulphur compounds present in refinery cuts. It was found that the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$  was able to hydroformylate a mixture of olefins such as 1-hexene, styrene, allylbenzene, 2,3-dimethyl-1-butene and cyclohexene in the presence of 500 ppm of thiophene [21]. In that study, there were no indications of deactivation of the active specie after 24 h. However, recycling experiments were not performed in order to confirm the reusability of this complex. In the present work, recycling experiments were performed under *anaerobic conditions*. Thiophene (T) and benzothiophene (BT) were selected as models representative

of sulphur containing compounds present in refinery cuts. Thus, 1-hexene and 500 ppm of T or BT in *n*-heptane were introduced in the reactor after the pre-activation of the catalyst precursor and hydroformylation experiments were carried out using as reaction conditions:  $p_{\text{H}_2}/\text{CO} = 1746.9$  kPa,  $S/\text{C} = 200$ , R.P.M. = 700,  $T = 343$  K,  $t = 3$  h. In each cycle, the amount of sulfur-containing compound was increased.

From Fig. 3a it is clear that the addition of thiophene up to 2500 ppm (0.20 mmol) does not cause an inhibition of the activity of this precursor. In fact, at the initial cycles, the presence of sulphur enhances the activity (cycles 1–3) compared to the recycle in the absence of sulphur. In the fourth cycle, a slight drop of the activity is observed. Nevertheless, the catalyst still showed high activity. When the product distribution is analyzed, it seems that the presence of thiophene in the system promotes two parallel reactions, isomerization of 1-hexene to produce 2-hexenes and

Table 1  
Product selectivity during the recycling experiment using as catalyst precursor  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$  in the presence of thiophene

Recycle	n/i	Aldehyde/isomer
0	2.7	1.4
1	2.6	2.2
2	2.6	1.4
3	2.7	1.7
4	2.5	1.3

Pre-treatment conditions:  $p_{\text{H}_2}/\text{CO} = 978.2$  kPa,  $T = 343$  K,  $t = 1$  h. Reaction conditions:  $p_{\text{H}_2}/\text{CO} = 1746.9$  kPa,  $S/\text{C} = 200$ , R.P.M. = 700,  $T = 343$  K,  $t = 3$  h.

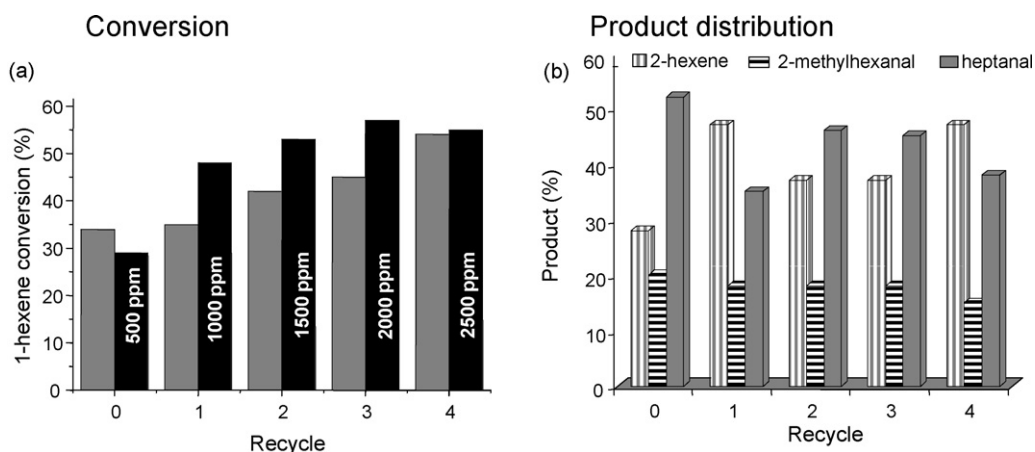


Fig. 4. Catalyst recycling experiment and product distribution using as catalyst precursor  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$  in the presence of benzothiophene.

the corresponding hydroformylation products of 1-hexene, as it is shown in Fig. 3b. The presence of thiophene promotes the formation of the aldehydes from 1-hexene but no oxygenated products from 2-hexene. It seems that thiophene induces the production of a species capable of hydroformylate and isomerize 1-hexene. However, this specie is not able to hydroformylate the internal olefin. Experiments aimed at the identification and characterization of the proposed specie by FTIR, NMR and UV-vis are currently underway and will be reported elsewhere. The selectivity found in this set of experiments is presented in Table 1.

As it is observed, the  $n/i$  ratio slightly varies from 2.7 to 2.5 with the subsequent recycles. In all cases, the linear aldehyde is preferred over the branch product. It was also observed that the aldehydes/isomer ratio was maintained between 1.3 and 2.2 with the evolution of the cycles; however, the production of the aldehydes still remains preferential over the olefin. As it was pointed out in a previous article, [21] the enhancing of the activity during olefin hydroformylation with the presence of sulphur has been revised by some authors. Chuang et al. [27–30] reported during the ethylene hydroformylation experiments using supported rhodium, nickel and ruthenium catalysts over  $\text{SiO}_2$ , that the Rh system is more active than those containing Ni and Ru, and that with the Rh/ $\text{SiO}_2$  was detected a rhodium sulfide, which enhanced the hydroformylation to a greater extend. Our results could be in the same direction; however, more experiments regarding to the characterization of the aqueous phase are needed. Considering that thiophene is a sulphur molecule present in light fractions of naphtha, the study of benzothiophene (BT) is also important because this compound and its derivatives are present in heavier naphtha or diesel fractions. Thus, the same recycling experiments described for thiophene were carried out maintaining the same reactions conditions, and the results corresponding for 1-hexene conversion and product distribution after each experiment are presented in Fig. 4.

From Fig. 4a, it is apparent that the addition of benzothiophene up to 2500 ppm does not cause an inhibition of the activity of this precursor compared to the recycling in the absence of benzothiophene; the results are rather similar to those found for thiophene. The analysis of the product distribution (Fig. 4b) reveals that, similar to the thiophene case, the presence of benzothiophene promote two parallel reactions, isomerization and hydroformylation of the 1-hexene; the selectivity found in this set of experiments is shown in Table 2; the  $n/i$  ratio varies from 2.6 to 1.1 after four consecutive cycles.

The results described above reflect that the activity of the system is also enhanced by the presence of benzothiophene. It gives the impression that the sulfur containing molecules participate in the

Table 2  
Selectivity during the recycling experiment using  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$  as catalyst precursor in the presence of benzothiophene

Recycle	$n/i$	Aldehyde/isomer
0	2.6	2.6
1	2.0	1.1
2	2.6	1.7
3	2.5	1.7
4	2.5	1.1

Conditions as in Table 1.

formation of a “rhodium sulfide specie” that enhances the biphasic hydroformylation to a great extend. Recently, Rosales et al. [31] reported that the addition of thiophene, benzo[*b*]thiophene and dibenzo[*b,d*]thiophene increased the activity of the hydroformylation of 1-hexene catalyzed by diphos-modified rhodium complexes.

#### 4. Conclusions

The pre-activation of the water-soluble binuclear rhodium complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})_2]$  with a low pressure of syngas, leads to a highly mononuclear catalytic species for 1-hexene hydroformylation. The resultant active specie showed high capacity for recycling, when it is handling under *anaerobic conditions*. The stability of this complex in the presences of sulfur containing compounds such as thiophene and benzothiophene up to 2500 ppm was also demonstrated after four consecutive recycling experiments, meaning that sulfur does not act as a poison of this catalyst. The active specie formed in the presence of such compounds showed selectivity for the hydroformylation of the  $\alpha$ -olefin.

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