

# Aqueous biphasic catalytic hydrogenation of olefins and olefin mixtures by the $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ complex, Pz = pyrazolate, TPPMS = $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})$

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Received 28 March 2007; received in revised form 9 July 2007; accepted 16 July 2007

Available online 19 July 2007

## Abstract

The hydrosoluble complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ , Pz = pyrazolate ligand, and TPPMS =  $(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})$  was used as catalytic precursor in the two phase hydrogenation reaction of the individual olefins (1-hexene, styrene, cyclohexene and 2,3-dimethyl-1-butene) to give the main expected saturated products. Under the best operational conditions (80 °C, 200 psi H<sub>2</sub>, S/C 535/1, and 600 rpm), the substrates showed the following hydrogenation reactivity order: 1-hexene > styrene > cyclohexene > 2,3-dimethyl-1-butene. The quaternary equimolar mixture of olefin and an olefin mixture that simulates a real composition of olefin present in a naphtha showed a different hydrogenation order; styrene > 1-hexene > cyclohexene > 2,3-dimethyl-1-butene. The catalyst can be recycled without significant loss of activity and showed sulfur tolerance, demonstrated by using benzothiophene in the olefin mixtures.

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**Keywords:** Hydrogenation; Rhodium binuclear phosphine complexes

## 1. Introduction

Olefins contained in gasoline represent a serious problem because under the operational conditions present inside engines, they polymerize and create a coating that interferes with the proper performance of the machines. To prevent these side reactions it is necessary to lower the olefin content of naturally occurring naphtha, which can be as high as 40% of the volume [1]. One possible route to decreasing the olefin content in naphtha, the starting material of gasoline, is to selectively hydrogenate olefins with an appropriate catalyst. Another possible solution is to use hydroformylation to create oxygenated products. There is an abundance of published work on hydrogenation and hydroformylation of

olefin with rhodium catalysts, predominantly in homogenous media.

One of the major drawbacks of homogeneous catalysis is the difficulty to separate and reuse the catalyst. For this reason the development of water-soluble metal complexes for the hydrogenation and hydroformylation of olefin has attracted a great deal of interest. The most common water-soluble catalysts are based on rhodium and different kinds of ligands, principally sulfonated phosphines and phosphites [2]. The most famous example of such a catalyst is the work of the Rûrhchemie/Rhône-Poulenc in the biphasic process for the hydroformylation of propene to butyraldehyde [3–5].

However, the study of binuclear rhodium water-soluble species has attracted much less attention, which is remarkable since their catalytic activity has been known for several years. Few reports deal with rhodium in binuclear systems; some of them were reported by Kalck [6] studying the complexes  $[\text{Rh}(\mu\text{-S-}t\text{-Bu})(\text{CO})(\text{P}(\text{O-Me})_3)_2]$  and  $\text{cis-Rh}_2(\mu\text{-}t\text{-Bu})(\mu\text{-Pz})(\text{CO})_2\text{L}_2$

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(L = trimethylphosphite, triphenylphosphite or triphenylphosphine) in the homogeneous hydroformylation of 1-hexene under low pressure. The first mechanism for bimetallic hydroformylation proving a cooperative effect between the metals was proposed by Stanley et al. [7] during the synthesis and study of the complexes  $\text{Rh}_2(\text{NBD})_2(\text{P}-\text{P})$  where P–P are different bidentate phosphines. Uson et al. [8] reported the catalytic activity of the binuclear rhodium complex with pyrazolate bridge ligands  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{PPh}_3)]_2$  in the hydroformylation reaction of 1-heptene, showing a moderate activity.

Furthermore, Schumann et al. [9] reported the synthesis of the water-soluble cationic binuclear rhodium complex  $[\text{Rh}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_3)(\mu\text{-S-}t\text{-Bu})_2[\text{BPh}_4]_2$  and the neutral binuclear complex  $[\text{Rh}(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NMe}_2)(\mu\text{-S-}t\text{-Bu})_2]$ ; both of them were highly active catalysts for olefin hydrogenation. Another example of bimetallic Rh hydrogenation was reported by Ajjou and Pinet [10], who generated a water-soluble rhodium complex *in situ* from  $[\text{Rh}(\text{COD})\text{Cl}]_2$  and TPPTS and found it to be a quite effective catalyst for transfer hydrogenation of aldehydes and ketones with isopropyl alcohol, under basic conditions. More recently, Ojeda et al. [11] reported the synthesis and reactivity of hetero-bimetallic complexes  $\text{RhO}-\text{M}$  (M = Si, Ti) in CO hydrogenation reactions.

Our group recently reported the synthesis and catalytic activity of two rhodium binuclear water-soluble complexes  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$  and  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$  in the biphasic hydroformylation of a variety of olefins and their mixtures [12,13]. They showed high catalytic activity and were recycled several times without any significant drop in performance. In the present work we report the activity of  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPTS})]_2$  in the biphasic hydrogenation of 1-hexene, styrene, cyclohexene, 2,3-dimethyl-1-butene, and their mixtures as a simulation of naphtha.

## 2. Experimental

### 2.1. General procedure

All manipulations were carried out under nitrogen atmosphere using standard Schlenck techniques [14]. All the organic solvents were dried and purified by distillation and were stored under inert atmosphere. The olefins and their respective saturated products were reagent grade (Aldrich). Water was deionized and treated with nitrogen prior to use. TPPMS was prepared according to the modified reported procedures [15,16]. Rhodium trichloride hydrated and pyrazolic acid (Aldrich) were used without further purification. Gases were purchased from AGA-Gases Venezuela. The complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$  was prepared according to a previous report [12]. GC analyses were performed on a Hewlett Packard 5890 Series II chromatograph with a flame ionization detector coupled to a HP integrator 3392-A and HP-1 methylsilicone, 30 m  $\times$  0.53 mm column. Quantification was achieved by using the internal standard (naphthalene) method and the peaks were identified by comparison with pure samples analyzed by a GC/MS 5890/5971 coupled system using Quadrex PONA 5% phenylmethyl silicone. The UV–vis spectra were taken in a diode

array H/P 8452 spectrometer. Atomic absorption analyses were performed with a Perkin-Elmer 5000 instrument.

### 2.2. Catalytic biphasic hydrogenation

In a typical experiment, an aqueous solution of the rhodium catalyst precursor (0.005 g; 0.004 mmol) in 7 ml of water and a solution of 1-hexene (0.25 ml; 1.9 mmol) in 7 ml of iso-octane were introduced into a glass-lined stainless steel autoclave (Parr, 25 ml) fitted with internal mechanical stirring, a temperature control unit and a sample valve. The solution was purged three times with  $\text{H}_2$  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 by GC and GC–MS techniques.

## 3. Results and discussion

### 3.1. Olefin hydrogenation experiments

A complete synthesis and characterization of the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$  and its use as pre-catalyst for the hydroformylation of 1-hexene and styrene has been reported by our group [12]. It is well-known that long chain alkenes are slightly soluble in water and therefore their reaction occurs in the aqueous–organic interface. The surfactant properties of the TPPMS [17] provide our complex with the ability to be in high concentration in the interface allowing the long chain alkenes to be hydrogenated successfully. Preliminary experiments were conducted using 1-hexene as a model molecule in order to determine the optimal operational conditions by varying the temperature from 33 to 363 K (60–90 °C), the substrate/catalyst ratio (S/C) was varied from 270/1 to 810/1 and hydrogen pressure was varied from 6.84 to 54.79 atm (100–800 psi), with the stirring rate constant kept at 600 rpm. From this series of experiments it was determined that the best operational conditions are:  $P = 13.61$  atm (200 psi),  $T = 353$  K, S/C ratio 535/1 and stirring rate of 600 rpm. A typical reaction profile for the hydrogenation of 1-hexene under the best operational conditions is shown in Fig. 1.

Under the above parameters, the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$  was an efficient catalyst precursor for the two-phase hydrogenation of different olefins, namely 1-hexene, 2,3-dimethyl-1-butene, cyclohexene and styrene. The results are summarized in Table 1.

The data in Table 1 show that 1-hexene is completely converted to hexane in approximately 1 h with a TOF of  $535 \text{ h}^{-1}$ . The analysis of the product distribution as a function of time evidences a high selectivity for the production of *n*-hexane and some degree of isomerization, less than 10%, during the first hour of the reaction. However, at the end of the experiment, *n*-hexane represents 100% of the product composition. Styrene was selectively hydrogenated to ethylbenzene with 100% conversion after 1.8 h with a TOF of  $292 \text{ h}^{-1}$ . Cyclohexene was converted to cyclohexane with a 79% yield in approximately 8 h, which rep-

Table 1  
Aqueous biphasic hydrogenation of olefins using  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$

| Olefin                | Time (h) | Total conversion (%) | Olefin selectivity (%) | TOF ( $\text{h}^{-1}$ ) | $10^5 r_i$ ( $\text{Ms}^{-1}$ ) |
|-----------------------|----------|----------------------|------------------------|-------------------------|---------------------------------|
| 1-Hexene              | 1.0      | 100                  | 91                     | 535                     | 5.56                            |
| Styrene               | 1.8      | 100                  | 100                    | 292                     | 2.91                            |
| Cyclohexene           | 8.0      | 78                   | 100                    | 53                      | 0.23                            |
| 2,3-Dimethyl-1-butene | 24       | 87                   | 100                    | 20                      | 0.20                            |

$P_{\text{H}_2}$  : 200 psi,  $T=80^\circ\text{C}$ , S/C: 535/1 and stirring rate = 600 rpm.

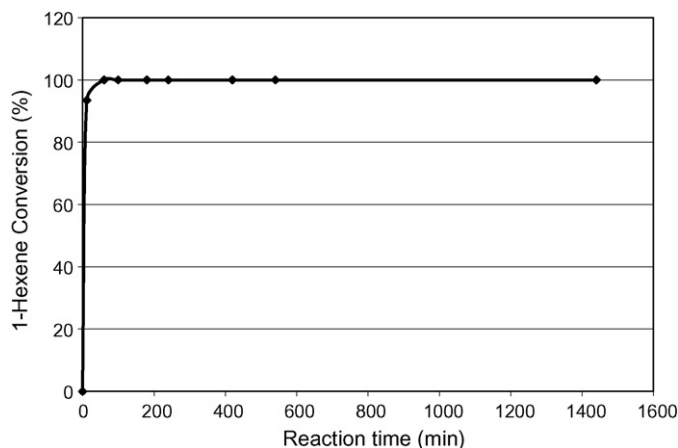


Fig. 1. Aqueous biphasic hydrogenation of 1-hexene with the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ . Conditions:  $P_{\text{H}_2}$  : 200 psi,  $T=80^\circ\text{C}$ , S/C: 535/1, stirring rate = 600 rpm and  $t=24$  h.

resents a TOF of  $53 \text{ h}^{-1}$  and was the only product detected during the reaction. 2,3-Dimethyl-1-butene was slowly converted to 2,3-dimethyl-1-butane in an 87% yield in 24 h, which is indicative of the difficulties to hydrogenate branch olefins because of the steric impediment. We were not able to observe the formation of isomeric products from this olefin under the reaction condition employed, thus the selectivity to the 2,3-dimethyl-1-butane was 100%. The initial rates of the hydrogenation for each olefin were calculated from the slope of the plot of molar concentration of the product as a function of the time (in seconds) at low percentage of conversion [18]; the data are also included in Table 1.

In order to discard the participation of metallic rhodium in the hydrogenation reactions, the mercury test was carried out performing the hydrogenation of 1-hexene under the best operational condition but adding one drop of mercury to the reaction mixture [19,20]. The reaction showed no interference of the Hg in the course of the hydrogenation of 1-hexene, confirming the absence of metallic particles or colloids during the catalysis. The metal content in the organic phase was determined by atomic absorption analysis in each run and the results show that less than 5 ppm was present in the organic phase, indicating that practically all of the rhodium remains in the aqueous phase.

### 3.2. Aqueous biphasic hydrogenation of olefin mixtures

Under the same reaction conditions used for the hydrogenation of the individual olefins, we carried out a series of experiments in order to simulate a  $\text{C}_6$  naphtha cut from a real

refinery and evaluated the performance of our catalyst precursor in the hydrogenation of the above-mentioned mixtures. The first mixture used for this purposes was equimolar amount of 1-hexene, styrene, cyclohexene and 2,3-dimethyl-1-butene which are representative of linear, aromatic, cyclic and sterically hindered olefins, respectively. The substrate/catalyst ratio of 535/1 refers to the total olefin content of the mixture.

As shown in Fig. 2, styrene was hydrogenated slightly faster than 1-hexene probably due to the competition for the active site of the catalyst that is occupied preferentially by styrene due its higher electronic density induced by the phenyl ring. Cyclohexene and 2,3-dimethyl-1-butene were hydrogenated slower than in the individual experiments due to the stability of the cyclic olefin and the steric impediments of the di-substituted olefin. The total conversion was 100% for styrene and 1-hexene, 88% for cyclohexene and 71% for 2,3-dimethyl-1-butene. The reactivity order was styrene > 1-hexene > cyclohexene > 2,3-dimethyl-1-butene.

It is important to emphasize that each naphtha produced in any refinery has a unique olefin distribution since each refinery processes crude with variable composition. The olefin distribution used in this work was a reference obtained from a naphtha cut provided by El Palito Refinery located in the north center of Venezuela [21]. It was analyzed in our laboratory with the following olefin distribution: terminal 18%, cyclic 15%, di- and trisubstituted: 67%. In order to simulate this particular cut, we

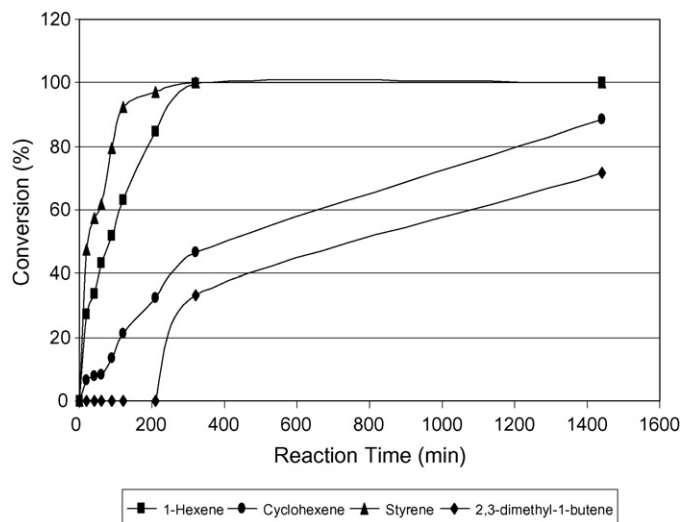


Fig. 2. Aqueous biphasic hydrogenation of an equimolar mixture of olefins using  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ . Conditions:  $P_{\text{H}_2}$  : 200 psi,  $T=80^\circ\text{C}$ , S/C: 535/1, stirring rate = 600 rpm and  $t=24$  h.

Table 2  
Aqueous biphasic hydrogenation of a quaternary mixture of alkenes simulating a real naphtha cut using  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$  in the presence of dibenzothiophene (DBT)

| Olefin                | Time (min) | Conversion without DBT (%) | $r_i \times 10^5$ ( $\text{Ms}^{-1}$ ) without DBT | Conversion with DBT <sup>a</sup> (%) | $r_i \times 10^5$ ( $\text{Ms}^{-1}$ ) with DBT |
|-----------------------|------------|----------------------------|--|--------------------------------------|---|
| 1-Hexene              | 240        | 100                        | 1.25   | 100                                  | 1.30  |
| Styrene               | 60         | 100                        | 1.69   | 100                                  | 1.95  |
| Cyclohexene           | 1440       | 86.41                      | 0.67   | 90                                   | 0.74  |
| 2,3-Dimethyl-1-butene | 1440       | 70.39                      | 0.23   | 68                                   | 0.36  |

Conditions:  $P_{\text{H}_2}$ : 200 psi,  $T = 80^\circ\text{C}$ , S/C: 535/1 and stirring rate = 600 rpm.

<sup>a</sup> 30 ppm DBT.

created the following quaternary mixture: 1-hexene 9%, styrene 9%, cyclohexene 15% and 2,3-dimethyl-1-butene 67%, intending to resemble the naphtha composition described earlier. As shown in Fig. 3, the hydrogenation of the mixture proceeded identically to that of the equimolar mixture presented above, indicating that our catalyst precursor is a potential candidate for the hydrogenation of a real naphtha cuts. Experiments using cuts from different refineries are in progress and will be published elsewhere.

### 3.3. Aqueous biphasic hydrogenation of olefin mixtures in the presence of dibenzothiophene

The presence of sulfur containing compounds in the naphtha cuts could inhibit the catalytic activity of our precursor due to the possibility of poisoning the catalyst by the coordination of sulfur to the metal center [22]. In order to investigate if our catalyst precursor is resistant to sulfur component present in real naphtha cuts, the activity of the complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$  was evaluated in the presence of 30 ppm of dibenzothiophene during the hydrogenation reaction of a quaternary mixture simulating a real naphtha. The results are summarized in Table 2. It was observed that under the best operational conditions the per-

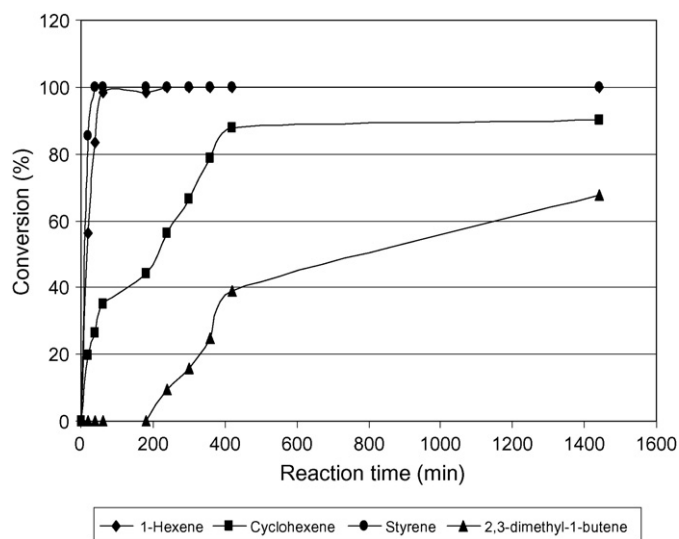


Fig. 3. Aqueous biphasic hydrogenation of a quaternary mixture of olefins simulating a real naphtha cut using  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$ . Conditions:  $P_{\text{H}_2}$ : 200 psi,  $T = 80^\circ\text{C}$ , S/C: 535/1, stirring rate = 600 rpm and  $t = 24$  h.

Table 3  
Reuse of the catalyst

| Run | Conversion (%) | Hexane (%) | 2-Hexene (%) |
|-----|----------------|------------|--------------|
| 1   | 100            | 99         | 1            |
| 2   | 100            | 99         | 1            |
| 3   | 100            | 99         | 1            |
| 4   | 100            | 98         | 2            |
| 5   | 100            | 98         | 2            |

$P_{\text{H}_2}$ : 200 psi,  $T = 80^\circ\text{C}$ , S/C: 535/1, stirring rate = 600 rpm and  $t = 24$  h.

formance of our catalyst precursor is enhanced by the presence of the sulfur containing compound as evidenced by the slight increase in the initial rates for the reactions. Similar results were obtained by Chuang and Pien who found that the hydroformylation of ethylene over  $\text{Rh}/\text{SiO}_2$  was favored by the presence of sulfides in the reaction media [23]. We suspect that in the biphasic system, rhodium-sulfide water-soluble specie is formed during the reaction pathway that is more active towards the hydrogenation of olefins, which results in an increment of the initial rates for the reactions. Experiments related to the isolation and characterization of the proposed specie is currently in progress and will be published elsewhere.

### 3.4. Reusing the aqueous biphasic hydrogenation catalyst

Perhaps the best advantage of the biphasic catalysis is the possibility of recovering and reusing the catalyst precursor during the reaction [24]. The capability of recycling our catalyst was confirmed after five consecutive hydrogenation experiments, with the same aqueous phase maintained and the organic phase containing 1-hexene changed, every 24 h in the presence of air. The long reaction times were necessary to test the thermal stability of our catalyst since the hydrogenation of 2,3-dimethyl-1-butene and other branched olefins present in naphtha takes at least that long to reach moderate conversions. The results, summarized in Table 3, demonstrate that under the best operational conditions, the activity of the complex remains stable without any indications of dropping the total conversion after 5 days of continuous performance even after air exposure.

## 4. Conclusions

The complex  $[\text{Rh}(\mu\text{-Pz})(\text{CO})(\text{TPPMS})]_2$  proves to be an efficient catalyst precursor for the biphasic hydrogenation

of 1-hexene, styrene, cyclohexene and 2,3-dimethyl-1-butene with the hydrogenation activity order 1-hexene > styrene > cyclohexene > 2,3-dimethyl-1-butene for the individual olefins, and styrene > 1-hexene > cyclohexene > 2,3-dimethyl-1-butene for the mixtures of olefins. This precursor proves to be active for all the substrates including the more sterically hindered ones such as 2,3-dimethyl-1-butene. The presence of 30 ppm of dibenzothiophene in the olefin mixture slightly improves the activity of the catalytic precursor, which is indicative of the sulfur tolerance of this catalyst. This tolerance allows it to be used as a catalyst precursor for the hydrogenation of real naphtha cuts. The mercury test also proved that the biphasic hydrogenation reaction proceeds through a molecular complex. Finally, the complex can be recycled five times without significantly dropping the activity of the catalytic precursor.

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