

# Catalytic hydrogenation of olefins and their mixtures using $\text{HRh}(\text{CO})(\text{TPPMS})_3$ complex in an aqueous biphasic medium

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## Abstract

The synthesis and characterization of the catalyst precursor  $\text{HRh}(\text{CO})(\text{TPPMS})_3$  was carried out by ligand exchange techniques starting from  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  with an excess of TPPMS ligand  $[\text{TPPMS}] = (\text{C}_6\text{H}_5)_2\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})$ , or prepared in situ from  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and TPPMS under high purity syngas. When the hydrosoluble complex was used as a catalyst precursor in the two phase hydrogenation reaction of 1-hexene, cyclohexene, styrene and 2,3-dimethyl-1-butene, the main hydrogenated products were obtained with high conversion rates. Under the following reaction conditions  $T = 343 \text{ K}$ ,  $P = 13.6 \text{ atm}$ , 600 rpm and  $S/C = 600/1$ , the substrates showed the following reactivity order: styrene > 1-hexene > cyclohexene > 2,3-dimethyl-1-butene. A quaternary equimolar mixture and one quaternary mixture which simulates the olefin quantities present in real naphtha, showed the same hydrogenation order. The catalyst showed recycling properties without significant loss of activity and sulfur tolerance when benzothiophene is present in the olefin mixtures.

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## 1. Introduction

Since the discovery of the water-soluble ligand *tris* (sodium-*m*-trisulfonated-triphenylphosphine)  $[\text{P}(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3]$  by Kuntz, the use and applications of the water-soluble catalyst in catalytic reactions under biphasic conditions has been a continuous research area [1–4]. Hydrogenation constitutes a most important class of homogeneously catalyzed reactions where several water-soluble ruthenium complexes have been used for researchers in recent years. In this sense, Wilkinson and Borowski [5] reported the biphasic hydrogenation of olefins without the need of co-solvents using 1-hexene, cyclohexene and *cis*–*trans* 2-hexene as model molecules and  $\text{RhCl}(\text{TPPMS})_3$  and  $\text{RuHCl}(\text{TPPMS})_3$  as catalysts precursors showing good activity and selectivity particularly for terminal olefins. Furthermore, Dror and Manossen [6] reported the

hydrogenation of cyclohexene with  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in excess of TPPMS in the presence of co-solvents and proved that the catalytic activity of the resulted catalyst increase with its solubility in the reaction medium. Joo and co-workers [7] described the synthesis and characterization of some ruthenium complexes:  $\text{RuCl}_2(\text{TPPMS})_2$ ,  $\text{RuHCl}(\text{TPPMS})_3$  and  $\text{RuH}(\text{OAc})(\text{TPPMS})_3$  where they show catalytic activity in the hydrogenation of 1-hexene to hexane and styrene to ethyl benzene under mild reaction conditions. Furthermore, Andriollo et al. [8] reported a novel route for the synthesis of the water-soluble ruthenium complex  $[\text{HRu}(\text{CO})\text{Cl}(\text{TPPMS})_3] \cdot 2\text{H}_2\text{O}$ , and its uses on the hydrogenation of styrene to ethyl benzene and cyclohexene to cyclohexane.

Sánchez-Delgado and Amdriollo [9] reported the synthesis and characterization of the organo-soluble ruthenium complex  $[\text{RuH}(\text{CO})(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2]\text{BF}_4$  and its uses on the homogeneous hydroformylation reaction of 1-hexene. Moreover, Rosales et al. [10] employed that same complex in the homogeneous hydrogenation of different substrates such as cyclohexene, quinoline, acridine under mild reaction condition.

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Considering that the ruthenium and rhodium complexes have been claimed as good catalysts precursors for hydrogenation of different substrates, in this article, we report the catalytic activity of the complex  $\text{HRh}(\text{CO})(\text{TPPMS})_3$  and its uses on the liquid-biphasic hydrogenation of different olefin such as 1-hexene, styrene, cyclohexene and 2,3-dimethyl-1-butene and their mixture, which resemble the types of olefins present in naphtha cuts.

The ultimate goal of this research is to demonstrate that an economic and reliable methodology to lower the olefin content present in naphtha cuts can be possible by using biphasic catalysis process to be implemented in a refinery.

## 2. Experimental

### 2.1. General procedure

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Organic solvents were dried and purified by distillation over standard agents under nitrogen prior to use.  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (Stream Chemicals) and *iso*-octane (Sigma–Aldrich) were used as received. The olefins (Sigma–Aldrich) were distilled from Na under argon. All gases were of U.A.P. grade and were purchased from AGA-Gases, Venezuela. TPPMS ligand [11],  $\text{Rh}(\text{CO})(\text{PPh}_3)_3$  [12],  $[\text{Rh}(\text{acac})(\text{CO})_2]$  [13] and  $\text{Rh}(\text{CO})(\text{TPPMS})_3$  [14] were synthesized according to published methods. The FTIR spectra were recorded in a Perkin–Elmer Spectrophotometer, 1000 FTIR using samples as KBr disks. NMR analyses were performed on a Bruker AM 300 spectrometer. GC analyses were carried out on a Hewlett Packard 5890 Series II chromatograph with a flame ionization detector and an ultra 2.5% phenyl methyl silicone, 25 m, 320  $\mu\text{m}$  column. Quantification was achieved by using the internal standard method (naphthalene) and the peaks were identified by comparison with pure samples analyzed by GC/MS HP 5890/5971 coupled system using a Quadrex PONA 5% phenyl methyl silicone, 25 m, 320  $\mu\text{m}$  column. 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.

### 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 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, 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 total pressure was adjusted via a high-pressure reservoir. Once the samples were extracted, they were cooled, the phases were separated and the organic phase analyzed by GC and GC–MS techniques. The optimized conditions obtained were: stirring rate of 600 rpm, temperature of 343 K; hydrogen pressure of 13.6 atm; and a substrate/catalyst ratio of 600/1.

## 3. Results and discussion

### 3.1. Olefin hydrogenation experiments

The complex  $\text{HRh}(\text{CO})(\text{TPPMS})_3$  has been reported by our group as a good catalyst precursor for the hydroformylation of C6 alkenes and their mixtures [15]. Long chain alkenes like 1-hexene, styrene, cyclohexene, and 2,3-dimethyl-1-butene, are only slightly soluble in water and therefore their reaction occur in the organic phase or in the aqueous–organic interface. Due to the inherent surfactant properties of the TPPMS ligand [16], the complex accumulates in high concentration in the interface allowing the long chain alkenes to be hydrogenated successfully.

The catalytic activity of the complex  $\text{HRh}(\text{CO})(\text{TPPMS})_3$  as a catalyst precursor for the liquid-biphasic hydrogenation of olefins was investigated. Preliminary tests were conducted using 1-hexene as a model molecule to determine the optimal operational conditions by varying the temperature from 343 to 393 K (70–120 °C); hydrogen pressure was varied from 13.6 to 544 atm (200–800 psi); the substrate/catalyst ratio was varied from 100/1 to 900/1, keeping the stirring rate constant at 600 rpm. From this series of experiments it was determined that the best operational conditions are:  $T = 343$  K,  $P = 13.6$  atm of  $\text{H}_2$ , S/C ratio 600/1 and stirring rate of 600 rpm. With this operational parameters, the biphasic hydrogenation of 1-hexene, cyclohexene, styrene and 2,3-dimethyl-1-butene were conducted. The results are summarized in Table 1.

The data in Table 1 show that 1-hexene is completely converted to hexane with 91% conversion and the isomer 2-hexene was obtained in 9% yield. Styrene was selectively hydrogenated to ethylbenzene in 100% conversion in 4 h. The inductive effect of the benzene ring and the impossibility to form structural isomers are operating in this substrate. Cyclohexene is transformed to cyclohexane with a 91% yield after 8 h and the highly substituted olefin; 2,3-dimethyl-1-butene is slowly converted to

Table 1  
Aqueous biphasic hydrogenation of olefins using  $\text{HRh}(\text{CO})(\text{TPPMS})_3$

Olefin	Time (h)	Total conversion (%)	Alkane selectivity	TOF ( $\text{h}^{-1}$ )
1-Hexene	5	100	91	119
Styrene	4	100	100	150
Cyclohexene	8	91	100	68
2,3-Dimethyl-1-butene	24	58	100	14

Conditions:  $P_{\text{H}_2} = 13.6$  atm (200 psi),  $T = 343$  K, S/C = 600/1, stirring rate = 600.

Table 2  
Velocity constants of hydrogenation reactions

Olefin	Correlation factor	$k$ (h <sup>-1</sup> )
1-Hexene	0.9902	0.0722
Styrene	0.9979	0.0743
Cyclohexene	0.9886	0.0496
2,3-Dimethyl-1-butene	0.9973	0.0078

Conditions:  $P_{H_2} = 13.6$  atm (200 psi),  $T = 343$  K, S/C = 600/1, stirring rate = 600

2,3-dimethylbutane in a moderate yield of 58%. Even though isomerization to 2,3-dimethyl-2-butene was theoretically possible, we did not observe the formation of this product under the reaction conditions employed, thus the selectivity for the alkane was 100%. All reactions present kinetics of first order with respect to olefin concentration and the constants rates are summarized in Table 2.

In order to confirm that the hydrogenation reaction proceeds via a molecular complex, the well known mercury test [17,18] was carried out in several independent experiments using one drop of mercury (~6 mmol, 1500 equivalents) in the hydrogenation of 1-hexene as well as the olefin mixtures; the results showed no interference with the evolution of the reaction as it is shown in Fig. 1, confirming the absence of metallic particles or colloids in the catalysis. The metal content in the organic phase was determined by atomic absorption analysis in each run and the results show that <5 ppm was present in the organic phase, indicating that practically all of the metal remains in the aqueous phase.

The complex  $\text{HRh}(\text{CO})(\text{TPPMS})_3$  shows a high activity in the hydrogenation of olefins compared to similar catalytic systems reported in the literature. Patin and co-workers reported the hydrogenation of styrene with  $\text{RhCl}_3/\text{TPPTS}$  in a water:methanol mixture, achieving 100% conversion after 40 h [19]. In the present system we reach 100% conversion of styrene after 4 h. This high activity motivated us to perform hydrogenation reactions of olefin mixtures that simulate the conditions present in naphtha cuts.

### 3.2. Aqueous hydrogenation of olefin mixtures

In order to simulate a C6 naphtha cut from a real refinery, our group pioneered the use of alkene mixtures and evaluated the performance of our catalyst precursors in the hydrogenation of the above-mentioned substrates.

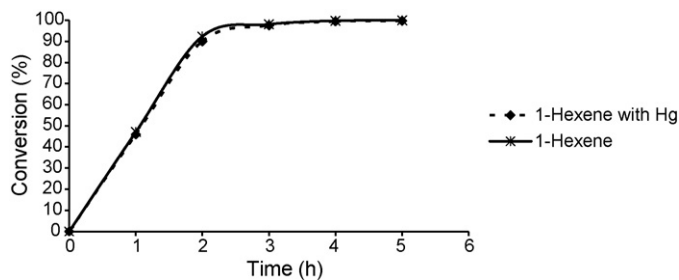


Fig. 1. Mercury test. Hydrogenation of 1-hexene with the complex  $\text{RhH}(\text{CO})(\text{TPPMS})_3$ . Conditions:  $P_{H_2} = 13.6$  atm (200 psi),  $T = 343$  K, S/C = 600/1, stirring rate = 600, Hg = 1 drop (~6 mmol, 1500 equivalents).

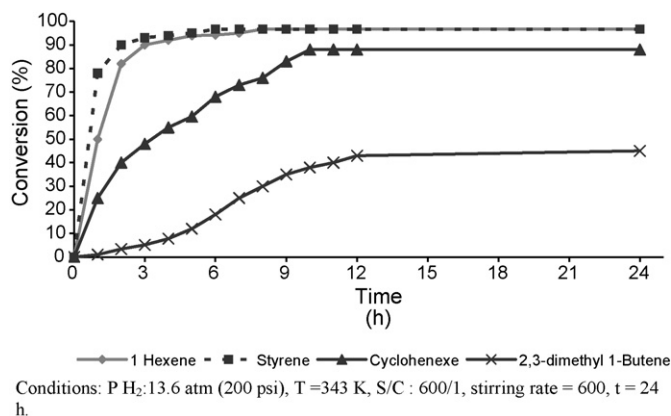
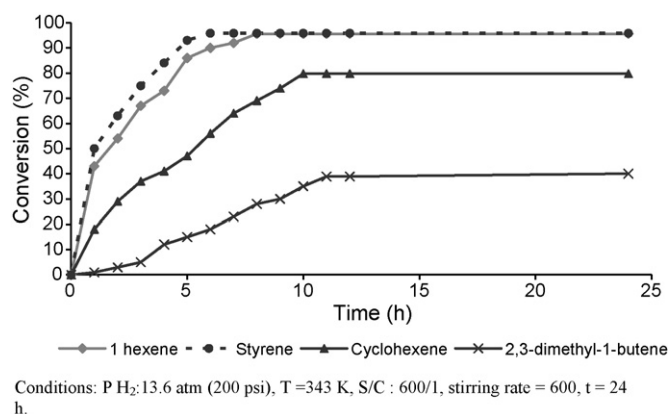


Fig. 2. Aqueous biphasic hydrogenation of an equimolar mixture of alkenes using  $\text{RhH}(\text{CO})(\text{TPPMS})_3$ . Conditions:  $P_{H_2} = 13.6$  atm (200 psi),  $T = 343$  K, S/C = 600/1, stirring rate = 600,  $t = 24$  h.

The first mixture employed was using equimolar components: 1-hexene (a linear olefin), styrene (an aromatic olefin), cyclohexene (a cyclic olefin) and 2,3-dimethyl-1-butene (a sterically hindered olefin). As shown in Fig. 2, styrene was hydrogenated slightly faster than 1-hexene as expected from the individual experiments. Cyclohexene and 2,3-dimethyl-1-butene were hydrogenated slower due to steric impediments and the competition for the active site of the catalyst. The observed order for the mixture was styrene > 1-hexene > cyclohexene > 2,3-dimethyl-1-butene. The total conversion was 97% for styrene and 1-hexene, 88% for cyclohexene, and 45% for 2,3-dimethyl-1-butene under the same reaction conditions ( $P_{H_2} = 13.6$  atm,  $T = 343$  K, S/C = 600:1).

Each naphtha from a different refinery has a unique distribution of alkenes. The olefin distribution used in this work was a reference obtained from a naphtha cut provided by El Palito Refinery located in Venezuela [20], analyzed in our laboratory with the following alkene distribution: terminal 18%, cyclic 15%, di- and trisubstituted: 67%. In order to simulate this particular cut, we created the following quaternary mixture: 1-hexene, 9%; styrene, 9%; cyclohexene, 15% and 2,3-dimethyl-1-butene, 67%. As shown in Fig. 3, the hydrogenation of the mixture pro-



Conditions:  $P_{H_2} = 13.6$  atm (200 psi),  $T = 343$  K, S/C : 600/1, stirring rate = 600,  $t = 24$  h.

Fig. 3. Aqueous biphasic hydrogenation of a quaternary mixture of alkenes simulating a real naphtha cut using  $\text{RhH}(\text{CO})(\text{TPPMS})_3$ . Conditions:  $P_{H_2} = 13.6$  atm (200 psi),  $T = 343$  K, S/C = 600/1, stirring rate = 600,  $t = 24$  h.

Table 3

Aqueous biphasic hydrogenation of a quaternary mixture of alkenes simulating a real naphtha cut using  $\text{HRh}(\text{CO})(\text{TPPMS})_3$  in the presence of dibenzothiophene (DBT)

Olefin	Time (h)	Conversion without DBT (%)	$k$ ( $\text{h}^{-1}$ ) without DBT	Conversion in the presence of DBT <sup>a</sup> (%)	$k$ ( $\text{h}^{-1}$ ) with DBT
1-Hexene	8	96	0.0624	96	0.0635
Styrene	6	96	0.0702	96	0.0716
Cyclohexene	10	80	0.0412	80	0.0430
2,3-Dimethyl-1-butene	24	40	0.0061	40	0.0059

Conditions:  $P_{\text{H}_2} = 13.6$  atm (200 psi),  $T = 343$  K, S/C = 600/1, stirring rate = 600 rpm.

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

ceeded identically as in the equimolar mixture described 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 hydrogenation of olefin mixtures in the presence of dibenzothiophene

In real naphtha cuts, there are a variety of sulfur-containing compounds that could be poisonous to the catalyst. In order to investigate if our catalyst precursor is resistant to the sulfur present in naphtha, we studied the behaviour of  $\text{HRh}(\text{CO})(\text{TPPMS})_3$  in the biphasic hydrogenation reaction of the quaternary mixture simulating naphtha with 30 ppm of benzothiophene. The results are presented in Table 3, remarkably the conversion rates and the velocity constants for all the olefins remained practically unchanged in the presence and in the absence of sulfur. Thus, it was demonstrated that under the best operational conditions, our catalyst is sulfur tolerant.

### 3.4. Reusing of the aqueous biphasic hydrogenation catalyst

One of the principal benefits of biphasic catalysis is the possibility of recovering and reusing the catalytic precursor during the reaction [21]. The capability of reusing our catalytic precursor was confirmed with four consecutive hydrogenation experiments using the best operational conditions reported above and 1-hexene as a model molecule. The aqueous phase containing the catalyst was maintained during the experiment and the organic phase containing 1-hexene was replaced every 24 h for 4 consecutive days without any indications of dropping the total conversion. However, we infer that the presence of 2-hexene in the products starting from the second recycle could be related

Table 4

Reuse of the catalyst

Run	Conversion (%)	Hexane (%)	2-Hexene (%)
1	100	100	0
2	100	100	0
3	100	94	6
4	100	88	12

Conditions:  $P_{\text{H}_2} = 13.6$  atm,  $T = 343$  K, S/C = 600/1, stirring rate = 600,  $t = 24$  h.

with a small loss of the catalytic activity of our complex due to air exposure in each recycle. The results are summarized in Table 4.

## 4. Conclusions

The complex  $\text{HRh}(\text{CO})(\text{TPPMS})_3$  showed to be an efficient catalyst precursor for the biphasic hydrogenation of 1-hexene, styrene, cyclohexene and 2,3-dimethyl-1-butene with the following hydrogenation activity: styrene > 1-hexene > cyclohexene > 2,3-dimethyl-1-butene. This precursor is active for all of substrate including the more sterically hindered such as 2,3-dimethyl-1-butene. The presence of 30 ppm of dibenzothiophene in the olefin mixtures does not affect 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 a real naphtha cut. Also, the mercury test proved that the biphasic hydrogenation reaction proceed through a molecular complex. Finally, the complex can be recycled during four times without significant dropping of the activity of the catalytic precursor.

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