

Synthesis, characterization and catalytic hydrogenation in aqueous-biphasic system of a new water soluble complex $\text{RuH}(\text{CO})(\text{NCMe})(\text{TPPMS})_3[\text{BF}_4]$

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Abstract

The new water soluble complex $\text{RuH}(\text{CO})(\text{NCMe})(\text{TPPMS})_3[\text{BF}_4]$ has been synthesized by the interaction of $\text{RuHCl}(\text{CO})(\text{TPPMS})_3$ with one equivalent of NaBF_4 in acetonitrile. The complex was characterized by spectroscopic techniques, and it shows high stability in water demonstrated by UV-Vis measurements. Because of this property, it can be used as a catalyst precursor for the liquid–liquid biphasic hydrogenation of various alkenes, such as 1-hexene, 1-decene, allylbenzene, styrene, cyclohexene, and 1-methyl cyclohexene. The catalytic activity of this complex is highly dependent of the reaction conditions as well as the type of substrate employed. Under normal conditions, the reaction order will be 1-hexene > cyclohexene > allylbenzene > 1-decene > styrene >>> 1-methyl-cyclohexane. This complex, can be recycled several times maintaining the same activity, the ruthenium remains in the aqueous phase without indication of partition of the complex between the water and the organic phase.

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1. Introduction

Since the discovery of the water soluble ligand tris-(sodium-*m*-trisulfonated- triphenylphosphine) $[\text{P}(\text{m}-\text{C}_6\text{H}_4\text{-SO}_3\text{Na})_3]$ by Kuntz, the use and applications of the water soluble catalysts in catalytic reactions under biphasic conditions has been a priority research area [1–3]. Hydrogenation constitutes one of the most important classes of homogeneously catalyzed reactions where several water-soluble ruthenium complexes have been used by the research workers in the recent years. In this sense, Joó and co-workers described the synthesis and characterization of some ruthenium complexes $\text{RuCl}_2(\text{TPPMS})_2$, $\text{RuHCl}(\text{TPPMS})_3$, and $\text{RuH}(\text{Oac})(\text{TPPMS})_3$. These complexes show catalytic activity in the hydrogenation of 1-hexene to hexane and styrene to ethyl benzene under mild

reaction conditions [4]. Andriollo et al. reported a novel route for the synthesis of the water-soluble ruthenium complex $[\text{HRu}(\text{CO})\text{Cl}(\text{TPPMS})_3] \cdot 2\text{H}_2\text{O}$, which shows catalytic activity in the hydrogenation of styrene to ethyl benzene and cyclohexene to cyclohexane [5].

The same research group reported the synthesis and characterization of two water-soluble ruthenium complexes— $[\text{HRuCl}(\text{CO})\text{P}_3^*]$, where P^* corresponds to *m*-monosulfonated and *m*-trisulfonated triphenylphosphine, respectively; both complexes were active in the hydrogenation of *trans*-cinnamaldehyde to cinnamyl alcohol [6]. Fache and Santini [7] have described the synthesis and characterization of seven water-soluble ruthenium complexes: $[\text{RuCl}_2(\text{TPPTS})_2]_2$, $\text{RuHCl}(\text{TPPTS})_3$, $\text{RuH}(\text{Oac})(\text{TPPTS})_3$, $\text{RuH}_2(\text{TPPTS})_4$, $\text{RuHI}(\text{TPPTS})_3$, $\text{RuCl}_2(\text{CO})_2(\text{TPPTS})_2$, and $[\text{Ru}(\text{OAc})(\text{CO})_3(\text{TPPTS})]_2$. They proved by the use of a spectroscopic techniques that all the complexes have the same structure of the organosoluble analog and they are active in the biphasic hydrogenation of propionaldehyde [8].

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Sánchez-Delgado et al. described the synthesis, characterization, and reformulation of the two water-soluble ruthenium complexes reported before as $[\text{RuCl}(\text{TPPMS})_2(\mu\text{-Cl})]_2$ and $[\text{RuHCl}(\text{TPPMS})_2]_2$ and also three new water-soluble complexes, $\text{OsH}_4(\text{TPPMS})_3$, $\text{OsHCl}(\text{CO})(\text{TPPMS})_2$, and $[\text{OsCl}(\text{TPPMS})_2(\mu\text{-Cl})]_2$. All these complexes catalyze the hydrogenation of cinnamaldehyde to cinnamyl alcohol under mild reaction conditions in aqueous-biphasic systems, and they proved that there is a clear advantage in the use of aqueous-biphasic mixtures over their analogous homogeneous solutions [9]. Also the same author reported the synthesis and characterization of the organo-soluble ruthenium complex $[\text{RuH}(\text{CO})(\text{CH}_3\text{CN})_2(\text{PPh}_3)_2]\text{BF}_4$ in the homogeneous hydroformylation reaction of 1-hexene [10]. Moreover, Rosales et al. employed this complex in the homogeneous hydrogenation of different substrates such as cyclohexene, quinoline and, acridine under mild reaction conditions [11].

Considering that the ruthenium complexes have been claimed as good catalyst precursors for different catalytic hydrogenation, in this paper, we are reporting the synthesis and characterization of the complex $[\text{RuHCO}(\text{CH}_3\text{CN})(\text{TPPMS})_3]\text{BF}_4$ and its uses in the liquid-biphasic hydrogenation of 1-hexene, 1-decene, styrene, allylbenzene, cyclohexene, and 1-methyl-cyclohexene to 1-hexane, 1-decane, ethyl benzene, cyclohexane, and 1-methyl cyclohexane, respectively.

2. Experimental

2.1. Experimental procedure

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were dried and deoxygenated. Acetonitrile was dried with P_2O_5 and distilled prior to use. The ligand TPPMS and the complex $\text{RuHCl}(\text{CO})(\text{TPPMS})_3$ were prepared according to literature procedures [12,13]. High-pressure, high-temperature reactions under a controlled H_2 pressure were performed in a stainless steel 300 ml Parr reactor instrument equipped with internal stirring, temperature control unit, and a sampling valve. Cs FAB-MS analyses were carried out using a VG-ZAB.2SEQ mass spectrometer (*m*-nitrobenzyl alcohol, matrix) at 35 kV and a mass resolution high enough to resolve peaks one mass unit apart. GC-MS analyses were performed with an HP 5890 system, HP-1 column, 50 m; split injection of 1:50. GC chromatograms were run on a Varian 3400 with a FI detector (Mega-bore type capillary column, 15 m; DB-5 phase; 1.5 μ FT, J&W Scientific). Quantification was achieved by using the internal standard method. ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker 400 MHz spectrometer, using deuterated solvents. All chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (^1H) or 85% H_3PO_4 (^{31}P). Atomic absorption

analyses were performed in a Perkin-Elmer 5000 instrument.

2.2. Synthesis of $\text{RuH}(\text{CO})(\text{NCMe})(\text{TPPMS})_3[\text{BF}_4]$ (**1**)

The complex $\text{RuHCl}(\text{CO})(\text{TPPMS})_3$ [13] (3 g, 2.38 mmol) and NaBF_4 (0.26 g, 2.38 mmol) were placed into a 100 ml round-bottomed flask. Acetonitrile (200 ml) was added and warmed gently under reflux for 1 h. After cooling to room temperature, the resulting solution was filtered and the solvent was evaporated until dryness. The white powder was washed with dichloromethane and was vacuum dried. Yield: 0.27 g, (72%). Complex **1** is air-stable and soluble in CH_3CN , MeOH, ethanol, THF, and water. $^{31}\text{P}\{^1\text{H}\}$ NMR (20 °C, D_2O): $\delta = 43.3$ ppm (d) $\delta = 23.9$ ppm (t), ($J_{\text{P-P}} = 29$ Hz); ^1H NMR (20 °C, D_2O): $\delta = 7.9$ – 6.9 ppm (m), 12 H (aromatic ring), $\delta = 1.98$ ppm (s) 3 H (CH_3CN), $\delta = -7.9$ ppm (dt), $J_1 = 90$ Hz, $J_2 = 31$ Hz; IR (KBr): 2359.9 cm^{-1} w (νCN), 1895.4 cm^{-1} s (νCO), 1201 cm^{-1} m, ($-\text{SO}_3$). FAB-MS (*m*-nitrobenzyl alcohol) (*z/e*): 1343 $[\text{Ru}(\text{CH}_3\text{CN})(\text{TPPMS})_3 + \text{H}]^+$; 902 $[\text{Ru}(\text{TPPMS})_2 + \text{H}]^+$; 502 $[\text{Ru}(\text{TPPMS}) + \text{H}]^+$.

2.3. Catalytic tests

In a 300 ml stainless steel vessel of a Parr autoclave containing 50 ml of water was dissolved 0.02 mmol of complex (**1**). 0.2 mmol of substrate, and 0.1 mmol of 2-methyl-naphthalene (as the internal standard) was placed in *n*-heptane (50 ml) and added to the aqueous solution. After pressurizing with 400 psi of H_2 , the reactor was heated to 100 °C, with stirring (600 rpm). After the desired time, the reactor was cooled to room temperature and the two phases were separated. The colorless organic phase was analyzed by GC and GC-MS and atomic absorption.

3. Results and discussion

Complex **1** was straightforwardly obtained as a white powder by reacting $\text{RuHCl}(\text{CO})(\text{TPPMS})_3$ [13] in acetonitrile with one equivalent of NaBF_4 under gentle heating condition. The new complex showed air stability and solubility in water, methanol ethanol, THF, and insoluble in toluene. The stability in water was determined by UV-Vis spectroscopy measurements, and the results obtained and placed in Fig. 1 indicate that the initial band located at 258 nm, assigned to LMCT characteristics of Ru(II) center coordinated with a phosphorus ligand [14], remains constant after 72 h at room temperature, which indicates that the nature of this complex is not influenced by the presence of water. Thus, complex **1** can be employed as a catalyst precursor in aqueous catalysis.

Furthermore, complex **1** was characterized by FTIR, and the analysis shows a band at 3451 cm^{-1} assigned to $-\text{OH}$ groups due to the presence of water in TPPMS. A band at

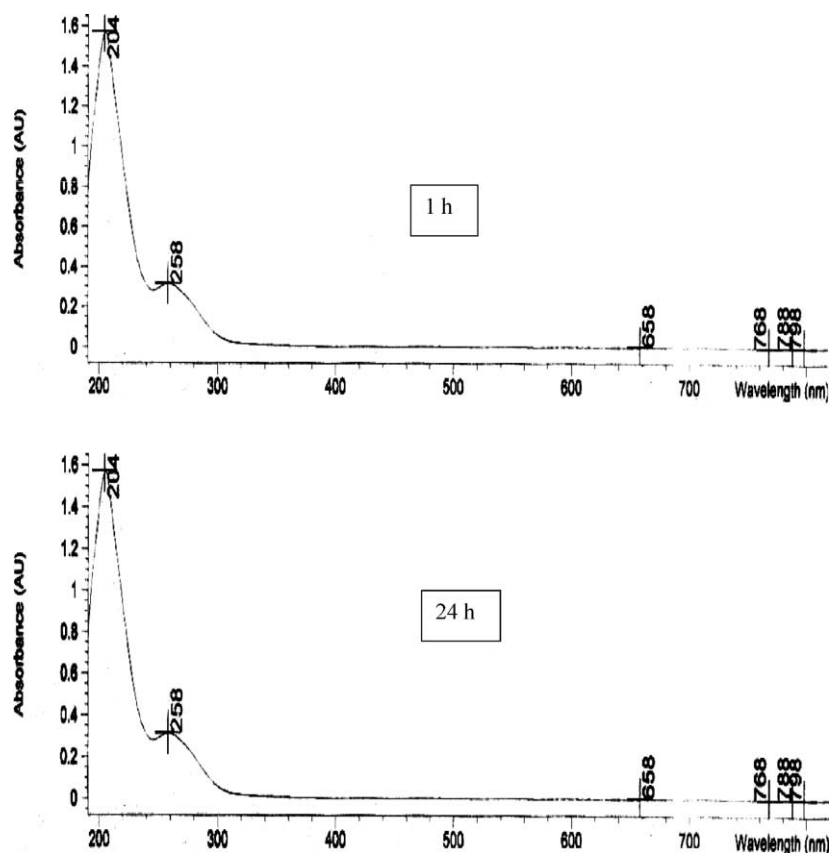


Fig. 1. Stability measurement by UV-Vis analysis for the complex (1).

2360 cm^{-1} assigned to the Ru–CN stretching with an intense band at 1959 cm^{-1} assigned to the stretching of the carbonyl group C≡O bonded to the ruthenium center. Also is found a band at 1195 cm^{-1} due the presence of the SO_3 -group bands located at 743 , 693 , and 516 cm^{-1} assigned to the hydrogen vibrations of the phenyl groups of the TPPMS.

It is interesting to mention that the value of most of the stretching bands for this complex are close to those reported for the analogous organosoluble complex [9], meaning that no difference is detected between both complexes by changing the nature of the phosphine.

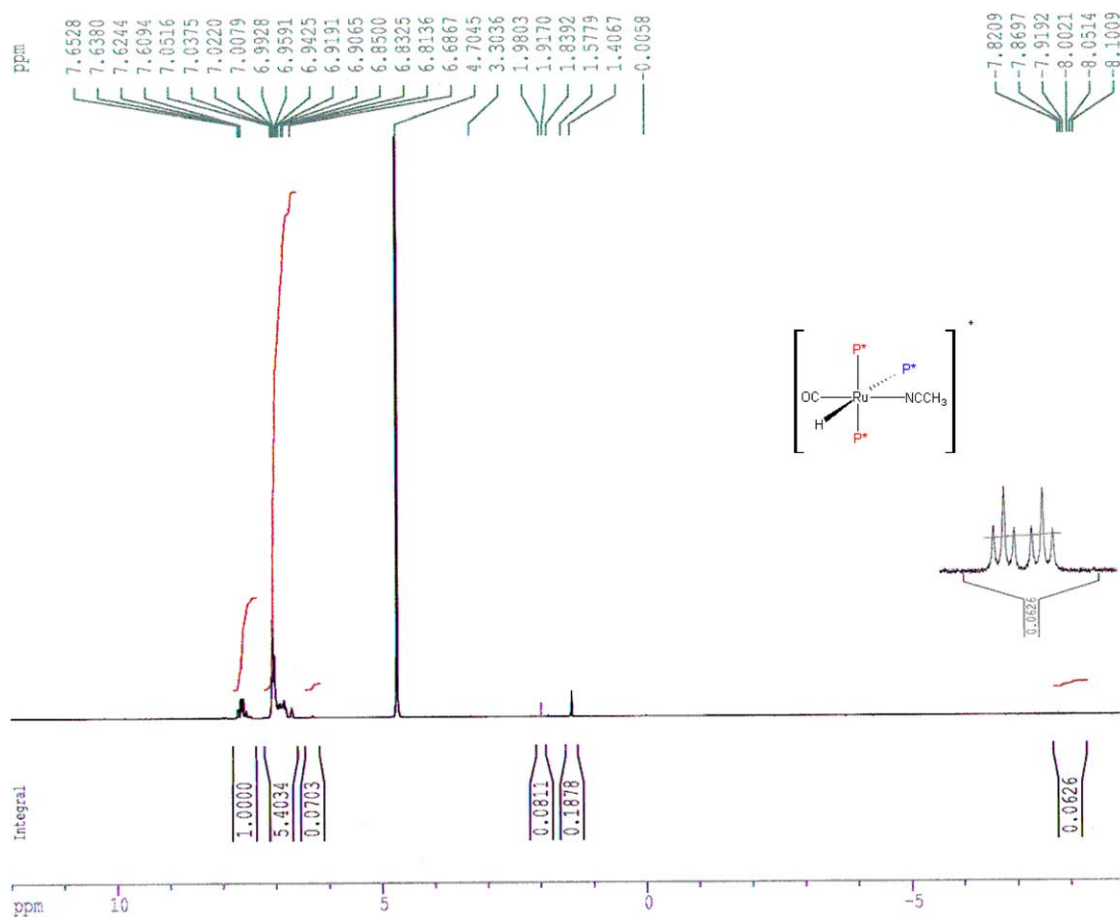
The ^1H NMR spectrum (CD_3OD) of $\text{RuH}(\text{CH}_3\text{CN})(\text{TPPMS})_3[\text{BF}_4]$ showed the signals characteristic of the proton of the TPPMS ligand in the region between $\delta = 7.9$ and 6.9 ppm ; a singlet in $\delta = 1.98\text{ ppm}$ corresponding to the methyl group of the CH_3CN coordinated to the ruthenium center. The hydride signal is observed in the high field region as a doublet of triplet centered at $\delta = -7.9\text{ ppm}$ with $J_1 = 90$, $J_2 = 31\text{ Hz}$, respectively, which is the result of the coupling of this hydride with one phosphorus atom in a *trans* position and with another two phosphorus atoms in a *cis* position. In Fig. 2, is displayed the ^1H NMR spectrum in the high field region is displayed, where the presence of the hydride ligand in the complex (1) is clearly observed.

Moreover, the stereochemistry is confirmed with the analysis of the ^{31}P NMR spectra, which consist of a clear

AX_2 pattern—doublet at $\delta = 43.5\text{ ppm}$ and triplet at $\delta = 23.5\text{ ppm}$ with a $J_{P-P} = 24\text{ Hz}$, where the value of the coupling constant are in concordance with the results obtained for the analogous organosoluble complex [10].

One additional aspect to be mentioned at this time, is regarding the purity of this new complex; the analysis of the ^{31}P NMR shows that this complex is obtained with 75% purity. Other signals of a minor intensity corresponding to the TPPMS oxide $\delta = 33.3\text{ ppm}$ (5%) and $\delta = -3.3\text{ ppm}$ corresponding the free TPPMS (20%) were also observed. The FABMS analysis shown as main signal the signal corresponding to the molecular species (*z/e*) 1343 assigned to $[\text{Ru}(\text{CH}_3\text{CN})(\text{TPPMS})_3 + \text{H}]$; (*z/e*) 902 $[\text{Ru}(\text{TPPMS})_2 + \text{H}^+]$, and (*z/e*) = 502 $[\text{Ru}(\text{TPPMS}) + \text{H}^+]$. No other fragmentations due to the presence of any other molecular complex were detected. All information obtained from the spectroscopic techniques such as FTIR and NMR, together with the complementary results obtained from FAB-MS analysis, is consistent with the stereochemistry founded for the earlier organosoluble complex ruthenium hexacoordinated whose arrangement is analogous to that displayed in Fig. 3.

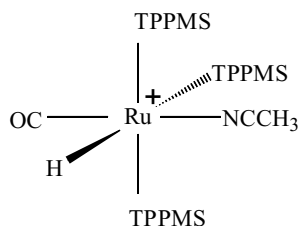
By the examination of the synthesis of the analogous organosoluble complex $\text{RuH}(\text{CO})(\text{CH}_3\text{CN})(\text{PPh}_3)_3[\text{BF}_4]$ [10], which is obtained through a two-step process starting from $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, it is interesting to point

Fig. 2. ^1H NMR spectra of the hydride region.

out that the new complex is obtained directly from $\text{RuHCl}(\text{CO})(\text{TPPMS})_3$, and we believe that it was possible due the slight excess of TPPMS from the precursor that is commonly observed in the synthesis of this type of water-soluble complex [14]. The fact that these were only metallic species present in this solid corresponding to complex **1**, allows us to use this as catalyst precursor in the olefin hydrogenation in biphasic system.

3.1. Olefin hydrogenation experiments

The catalytic activity of the complex was examined in the olefin hydrogenation in a biphasic medium using 1-hexene

Fig. 3. Structure proposed for the complex $\text{RuH}(\text{CH}_3\text{CN})(\text{TPPMS})_3[\text{BF}_4]$ (**1**).

with the following initial reaction conditions: temperature of 80°C , 400 psi of H_2 with 0.02 mol of complex **1** in a mixture of water/*n*-heptane with a substrate/catalyst ratio of 100:1 at 600 rpm. As is shown in Fig. 4, complex **1** has a good activity during the hydrogenation reaction of 1-hexene. The reaction profile shows that total conversion is reached in 11 h. The GC–MS analysis of the organic phase confirms that the only product obtained is the corresponding saturated product, with no indication of isomerization products

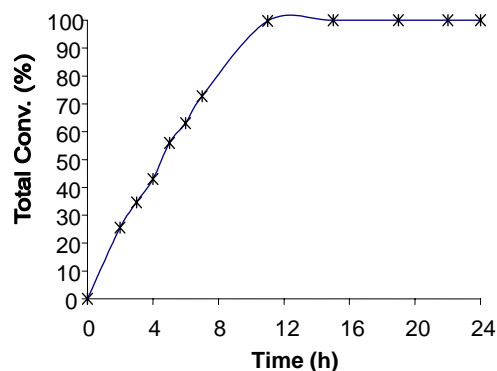
Fig. 4. 1-Hexene hydrogenation profile using $\text{RuH}(\text{CH}_3\text{CN})(\text{TPPMS})_3[\text{BF}_4]$ (**1**).

Table 1
Hydrogenation of 1-hexene as a function of the H₂ pressure

[H ₂] (psi)	Percent of conversion of 1-hexene
200	40
400	84
600	81
800	83
1000	38

Condition: catalyst precursor, 0.02 mmol; 1-hexene, 0.2 mmol; naphthalene, 0.1 mmol; *n*-heptane, 50 ml; H₂O, 50 ml.

as observed with other water-soluble Ru(II) complexes [15].

At the end of the reaction, the aqueous phase solution remained colorless, and the organic phase result was analysed by atomic absorption and confirmed that less than 5 ppm of ruthenium was detected, indicating that practically all of the metal remains in the aqueous phase.

After the reaction profile was obtained, a series of 1-hexene hydrogenation experiments were carried out with the modification of the reaction conditions, including the effect of the hydrogen pressure. As can be seen in Table 1, the complex shows good activity between 400 and 800 psi and a sudden decrease in activity for higher pressures.

The high activity behavior observed for this complex in the region from 400 to 800 psi of H₂ prompted us to analyze the aqueous phase by using UV-Vis spectroscopic measurements. The resulting spectra show the presence of two bands located at 232 and 268 nm, which can be assumed with the possible species responsible for the hydrogenation reaction. However, additional experiments in order to fully characterize this species are in progress in order to understand better the species involved in this reaction. Finally, when the pressure reaches 1000 psi, the original species at 258 nm is found which indicates that at high hydrogen concentration, the initial complex is not transformed to the real active species (presumably λ 232 and 268 nm), and therefore, a low activity is achieved.

The effect of the reaction temperature was revised for this catalyst precursor, using 400 psi of H₂ pressure and 6 h of reaction time. The results obtained are presented in Fig. 5.

As can be observed in Fig. 5, the activity of this catalyst precursor increased almost three times, from 20 to 63% of conversion, when the temperature varies from 60 to 80 °C. At higher temperature, the activity remains almost constant around 60% of conversion, where the results indicate that presumably the same active species acts in that temperature range.

After determining that up to 80 °C we reach the maximum activity for this complex, the capability of reusing it as a catalyst precursor was confirmed with the hydrogenation of 1-hexene. In this order, three consecutive hydrogenation experiments were carried out *maintaining the same aqueous phase* during the experiments and changing every 6 h the

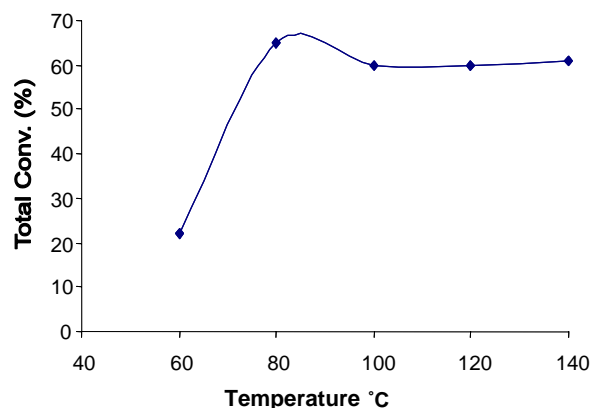


Fig. 5. Hydrogenation of 1-hexene as a function of the temperature.

Table 2
Hydrogenation of 1-hexene catalyzed by the complex [RuH(CO)(CH₃CN)(TPPMS)₃]BF₄

Run	Percent of <i>n</i> -hexane
1	100
2	98
3	98

Condition: catalyst precursor, 0.02 mmol; 1-hexene, 0.2 mmol; 2-methyl naphthalene, 0.1 mmol; *n*-heptane, 50 ml; water, 50 ml; S/C, 100; rpm, 600; time, 24 h.

organic phase for another *fresh* solution containing 1-hexene. The results obtained are displayed in Table 2.

As is shown in Table 2, this complex efficiently catalyzed the 1-hexene hydrogenation in three consecutive experiments without any major indication of decreased activity. This test clearly shows, the recycling capabilities of this type of compound as a catalyst precursor in biphasic system. It is worth mentioning that the organic phase result of each catalytic experiment was analyzed by atomic absorption. The analyses detected less than 5 ppm of ruthenium in the organic phase, indicating that practically all the metal remains in the aqueous phase.

After the evaluation of the effect of the reaction conditions in the performance of this catalyst precursor and its recycling capability, other substrates were tested at the same reaction conditions. The results are present in Table 3.

Table 3
Alkene hydrogenation reactions catalyzed by the complex [RuH(CO)(CH₃CN)(TPPMS)₃]BF₄

Substrate (percent of conversion)	Product (percent of selectivity)
1-Hexene (63)	<i>n</i> -Hexane (100)
1-Decene (20)	<i>n</i> -Decane (100)
Styrene (18)	Ethylbenzene (100)
Allylbenzene (24)	Propylbenzene (100)
Cyclohexene (33)	Cyclohexane (100)
1-Me-cyclohexene (0)	1-Me-cyclohexane (0)

Condition: catalyst precursor, 0.02 mmol; 1-hexene, 0.2 mmol; naphthalene, 0.1 mmol; *n*-heptane, 50 ml; water, 50 ml; T, 80 °C; S/C, 100; rpm, 600; time, 6 h.

As is present in Table 3, this catalyst precursor is able to hydrogenate different type of olefin; styrene, allylbenzene cyclohexene, 1-hexene, and 1-decene selectively converted to ethylbenzene, propylbenzene, cyclohexane *n*-hexane, and *n*-decane, respectively. The 1-methyl-1-cyclohexane, a substrate with high steric hindrance close to the C=C bond, did not hydrogenate.

Also, it is found that for linear olefins, the hydrophobic character of 1-decene may be responsible for the different hydrogenation rates observed. This had been observed by us using other water-soluble complexes [15,16]. In the case of the aryl olefins such as allylbenzene and styrene, the aryl substitute close to the double bond may produce enough steric hindrance to the metal center. This may cause impediments to the coordination of the olefin with the ruthenium center, which is claimed as a fundamental step for the hydrogenation process carried out for this type of complex [17].

The order of reactivity obtained for this complex during the olefin hydrogenation was found as follows:

1-hexene > cyclohexene > allylbenzene > 1-decene
> styrene >>> 1-methyl - cyclohexane

Finally, the aqueous phase, which was analyzed after each catalytic experiment by atomic absorption, confirmed that less than 5 ppm of ruthenium was present in the organic phase, indicating that the metal remains in the aqueous phase.

4. Conclusions

The new complex RuH(CH₃CN)(TPPMS)₃[BF₄] is an effective catalyst precursor for the aqueous-biphasic hydrogenation of different types of olefins. The complex is soluble and stable in water for long periods. The activity of this complex depends of the reaction conditions employed and the nature of the substrate, where steric effects may influence its behavior. Also, it was demonstrated that this complex can be recycled without significant decrease of its activity, as long as the ruthenium remains in the aqueous phase.

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