Synthesis and characterization of [HRu(CO)(CH₃CN)(TPPTS)₃]BF₄ Catalytic properties in the aqueous-biphasic hydroformylation of olefins

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Abstract

The new water soluble complex [HRu(CO)(CH₃CN)(TPPTS)₃]BF₄ (TPPTS = tris[[(m-sulfonated)phenyl]phosphine P(m-C₆H₄SO₃Na)₃) has been synthesized by ligand exchange techniques from the corresponding PPh₃ derivative in a methoxyethanol–water mixture. The new complex was characterized by FTIR, UV–vis, and ¹H NMR and ³¹P {¹H} NMR spectroscopy and used as catalyst precursor for the aqueous biphasic hydroformylation of several olefins and their mixtures under moderate reaction conditions. The catalytic activity order found was: 1-hexene > allylbenzene > 2,3-dimethyl-1-butene > styrene > cyclohexene. The sulphur tolerance of this complex was also investigated using thiophene as a model molecule; it was found that the new complex maintains its activity when the thiophene concentration is below 500 ppm. The mercury test in independent experiments showed no interference of the Hg at all with the evolution of the reaction, demonstrating that the catalysis is performed by molecular species. The recyclable nature of the complex was demonstrated during 1-hexene hydroformylation where at the end of each catalytic reaction all the metal remains in the aqueous phase.
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1. Introduction

Aqueous biphasic catalysis has been a center of attention during the last years. The possibility of recovering and recycling the catalytic precursor from the reaction mixture brings the opportunity of the continuous use of the biphasic catalysis in industrial processes [1–4]. A considerable amount of work has been reported by several groups in this fascinating research area [5–9]. Recently a wide variety of water-soluble

tertiary phosphines has been prepared and used in aqueous hydrogenation. For example Toth and Joó [10] reported ruthenium complexes such as RuCl₂(TPPMS)₂, RuHCl(TPPMS)₃ and RuH(OAc)(TPPMS)₃ as catalyst precursors for the hydrogenation of 1-hexene and styrene under similar conditions with slower rate than RhCl(TPPMS)₃. Andriollo et al. [11] synthesized and characterized RuHCl(CO)(TPPMS)₃ and used it as the catalyst for the hydrogenation of styrene in a water/decaline mixture with 86% conversion. Nomura [12] reported the selective hydrogenation of the C=C double bond of α,β unsaturated ketones by using [RuCl(μCl)(TPPMS)₂]₂ in water. Sánchez-Delgado et al. [13], studied the synthesis and characterization of [RuHCl(TPPMS)₂]₂ and it was tested in the hydrogenation of olefins in homogeneous and biphasic system, in which the latest system showed better yield and selectivity. Recently, Joó et al. [14] reported the synthesis and characterization of a new ruthenium complex using the m-sulfonated phenyldiphenylphosphine sodium salt; this complex proved useful in the hydrogenation of

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different substrates in biphasic conditions. According to the literature, rhodium complexes have been studied mainly in the hydrogenation of C=C, C=O, C=S, and C=N bonds [13,15–18]. However, very few reports about biphasic hydroformylation reactions using ruthenium complexes are found in the literature, most of what is published deals with rhodium complexes. Recently, Gao et al. [19] reported the use of a stable ruthenium cluster $Ru_3(CO)_9(TPPMS)_3$ in the hydrogenation of acrylic acid and styrene and also for the hydroformylation of ethylene and propylene.

In industry, hydroformylation is usually carried out homogenously, resulting in complex and expensive separation processes. New technologies have emerged to overcome these difficulties, of special interest is the Ruhrchemie/Rhone-Poulenc process in which biphasic hydroformylation is applied to propylene using a water soluble Rh-derived catalyst with TPPTS ligands [1,2].

A different industrial application of hydroformylation involves the treatment of refinery naphtha (the basis of gasoline) in which nearly 50% of the volume belongs to the C6–C8 cut. The final product specification only allows for a maximum of 12%, thus it is an interesting possibility to hydroformylate naphtha to lower its C6–C8 content, and meet the required percentage, by converting them to oxygenated species (aldehydes and alcohols). To pursue this goal we are studying a ruthenium catalyst that is cheaper than the rhodium one, which could expands to alkenes longer than propylene and also is sulphur-tolerant.

Recently, our group [20] reported the synthesis and characterization of the new water-soluble dihydride ruthenium complex $H_2Ru(CO)(TPPMS)_3$ and its catalytic behavior in the biphasic hydroformylation of 1-hexene, cyclohexene, 2,3-dimethyl-1-butene and their mixtures. We also reported the new water soluble complex $[HRu(CO)(CH_3CN)(TPPMS)_3][BF_4]$ and its use in the hydrogenation reaction of allylbenzene, 1-decene, styrene and 1-methylcyclohexene [27]. In this article we report the synthesis and characterization of the new water-soluble hydride complex $[HRu(CO)(CH_3CN)(TPPTS)_3][BF_4]$ and its catalytic behavior in the hydroformylation of 1-hexene, 2,3-dimethyl-1-butene, styrene, allylbenzene and cyclohexene and their mixtures.

2. Experimental

2.1. General procedures

All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques [21]. Solvents were purified by distillation and saturated with nitrogen prior to use. The infrared spectra were recorded in a Perkin-Elmer Spectrum 1000 FT-IR using samples as KBr disks. ^1H and ^{31}P {^1H} NMR spectra were recorded on a Bruker 500 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). 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 UV–vis spectra were taken in a diode array Hewlett-Packard 8452 spectrometer. Atomic absorption analyses were performed in a Perkin-Elmer 5000 instrument. $RuCl_3 \cdot 3H_2O$, styrene, allylbenzene, hex-1-ene, cyclohexene, 2,3-dimethyl-1-butene, tri-isooctylamine, and triphenylphosphine were obtained from Aldrich Chemical. All gases were purchased from Venezuela AGA Gases. TPPTS was prepared according to the literature procedure [22,23].

2.2. Synthesis of $[HRu(CO)(CH_3CN)(TPPTS)_3]BF_4$

The complex $[HRu(CO)(CH_3CN)(TPPTS)_3]BF_4$ was synthesized according to the modified method reported by Sánchez-Delgado et al. [24] for the analog organosoluble complex. To a solution of the complex $[HRu(CO)(Cl)(TPPTS)_3]$ (3.00 g, 1.64 mmol) prepared according to the literature procedure [15] in 100 mL of acetonitrile, was added $NaBF_4$ (0.176 g, 1.60 mmol) in 100 mL of acetonitrile. The mixture was gently refluxed during 1 h. After cooling, the resulting yellow complex was filtered via canula and dried under vacuum; to yield 2.97 g, 88%. FT-IR (KBr): 2355 cm^{-1} (w, ν_{CN}), 2025 cm^{-1} (w, ν_{Ru-H}), 1936 cm^{-1} (s, ν_{CO}). ^1H NMR (D_2O): 6.99–7.74 ppm (m), −6.89 ppm; −7.35 ppm (dt). ^{31}P NMR (D_2O): 42.85 ppm (d); 24.82 ppm (t), ($J_{P-P} = 14.7$ Hz).

2.3. Catalytic hydroformylation

In a typical experiment, an aqueous solution of the ruthenium catalyst precursor (0.027 g; 0.014 mmol) in 8.0 mL of water and the olefin (1-hexene, allylbenzene, 2,3-dimethyl-1-butene, styrene or cyclohexene) (0.16 mmol) in 8.0 mL of n-heptane, were introduced into a glass-lined stainless steel autoclave (Parr, 25 mL) fitted with internal mechanical stirring, temperature control unit and a sampling valve. The solution was purged four times with syngas (CO/H_2, 1:1); then, charged to 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. The samples were cooled, the phases separated and the organic phase analyzed by GC–MS. The reaction temperature varied from 333 to 393 K; syngas pressure varied from 4192.6 to 6987.6 kPa; the substrate/catalyst ratio varied from 25/1 to 200/1 and the stirring rate was kept constant at 760 rpm. The best reaction conditions were: pressure of syngas = 6288.8 kPa, temperature = 353 K, substrate/catalyst ratio = 100, and reaction time = 24 h.

3. Results and discussion

3.1. Synthesis and characterization of $[HRu(CO)(CH_3CN)(TPPTS)_3]BF_4$

The new water soluble complex $[HRu(CO)(CH_3CN)$ $(TPPTS)_3]BF_4$ was obtained as a yellow air stable powder by reacting $[HRu(CO)(Cl)(TPPTS)_3]$ with $NaBF_4$ and acetoni-

Table 1
Spectroscopy data for the complex [HRu(CO)(CH₃CN)(TPPTS)₃]BF₄

Spectroscopy analysis	Assignment
FT-IR (cm^{-1})	3452 (ν(O–H)), 2355 (ν(C=N)), 1936 (ν(C=O)), 1399 (ν(ArC–H)), 1639 (ν(ArC–H)), 1197 (ν(SO₃)), 690 (ν(SO₃))
^{1}H NMR (ppm)	6.99–7.74 m, Ar–(H), 1.44 s, CH₃CN–(H), −7.23 dt, (H)
^{31}P {^{1}H} NMR (ppm)	42.85 d, (P_a) 24.82 t, (P_b), $J_{P–P} = 14.7$ Hz

Ar: aromatic, m: multiplet, s: singlet, t: triplet, d: doublet, dt: doublet of triplets.

Fig. 2. Structure proposed for the complex [HRu(CO)(CH₃CN)(TFFTS)₃]BF₄.

trile. The complex is soluble in water, methanol and ethanol. The UV–vis spectrum showed one adsorption band at 230 nm assigned to LMCT characteristics of Ru(II) center coordinated with a phosphorus ligand [25]. This band remains constant after 72 h at room temperature, which is a good indication of the stability of the complex in water.

This complex can be used as a catalyst precursor in aqueous catalysis. The FT-IR spectrum of the complex showed a band at 3452 cm^{-1} assigned to the –OH groups of water present in TPPTS, and a band at 2355 cm^{-1} corresponding to the –CN stretching of the acetonitrile present in the complex. Also the spectrum shows a strong band at 1936 cm^{-1} assigned to the ν_{CO} stretching of the carbonyl bonded to the ruthenium center and one band at 1197 cm^{-1} assigned to SO₃ group.

The ^{1}H NMR spectrum (D₂O) of the complex (Table 1) shows two groups of signals in the region between $\delta = 6.99$ and 7.74 ppm, assigned to the aromatic protons of the TPPTS ligand. One singlet at $\delta = 1.44$ ppm corresponds to the methyl group of the CH₃CN coordinated to the ruthenium center. Under our reaction conditions, and according to the ^{1}H and ^{31}P {^{1}H} NMR signals, we were unable to observe the formation of stereoisomers for the water soluble complex [HRu(CO)(CH₃CN)(TPPTS)₃][BF₄] that are reported by Sánchez-Delgado et al. for the organosoluble analog [HRu(CO)(CH₃CN)(TPP)₃][BF₄] [24], probably due to the different reaction conditions.

The signal observed in the high field region, a doublet of triplets centered at −7.23 ppm with $J_1 = 90$, $J_2 = 31$ Hz, is assigned to the hydride group and it is the result of the coupling of this hydride with one phosphorus atom in a *trans* position and with two phosphorus atoms in a *cis* position, as can be seen in Fig. 1.

The stereochemistry of the complex is confirmed with the analysis of the ^{31}P NMR (D₂O) spectrum, which showed a doublet at $\delta = 42.85$ ppm and a triplet at $\delta = 24.82$ ppm with a $J_{P–P} = 14.7$ Hz, indicating a clear AX₂ pattern. This observation and all information obtained from UV–vis, FT-IR, ^{1}H NMR, are in accordance with the results reported for the similar organosoluble and hydrosoluble hexacoordinated ruthenium complexes whose arrangement is analogous to that displayed in Fig. 2 [26,27]. These features are also similar to those of the PPh₃ analogue, and the structure of this complex can be confidently assigned as in (**1**).

3.2. Aqueous biphasic hydroformylation of alkenes

The complex [HRu(CO)(CH₃CN)(TPPTS)₃]BF₄ is an efficient catalyst precursor for the hydroformylation of various olefins, namely 1-hexene, allylbenzene, 2,3-dimethyl-1-butene, styrene and cyclohexene.
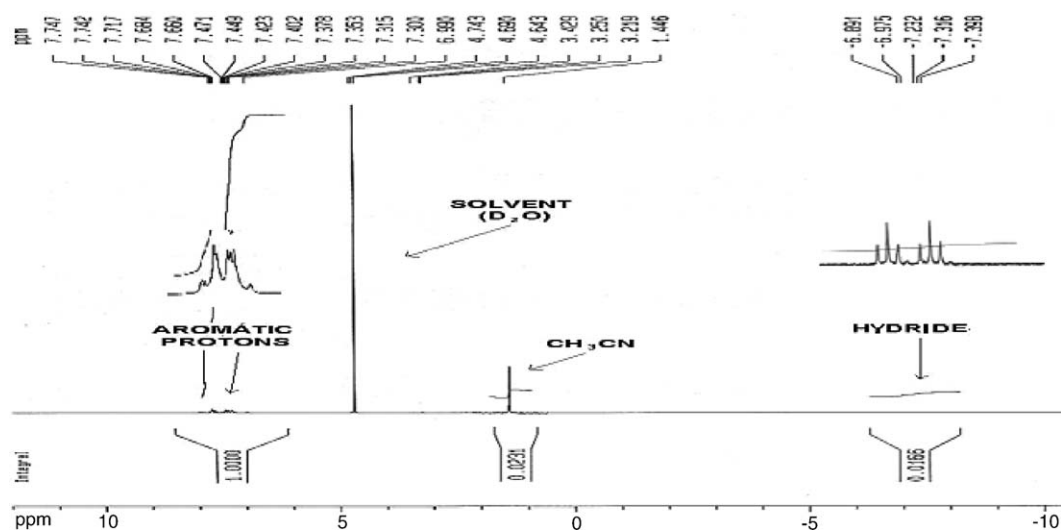

Fig. 1. ^{1}H NMR spectrum in the high field for the complex [HRu(CO)(CH₃CN)(TFFTS)₃]BF₄.

Table 2
Aqueous biphasic hydroformylation of alkenes by use of [HRu(CO)(CH$_3$CN)(TPPTS)$_3$]BF$_4$[a]

Substrate	Products	Product distribution (%)	Aldehydes (%)	n/i Ratio
1-Hexene	Heptanal	54		
	2-Methylhexanal	27	81	2
	Hex-2-ene	20		
Allylbenzene	3-Phenyl-2-methylpropanal	4		
	4-Phenylbutanal	28	32	7
2,3-Dimethyl-1-butene	3,4-Dimethylpentanal	17		
	2,3-Dimethyl-2-butene	0.6	17	N/A
Styrene	2-Phenylpropanal	2		
	3-Phenylpropanal	8	10	4
Cyclohexene	Cyclohexanecarboxaldehyde	3	3	N/A

Total conversion based on the disappearance of the alkenes. N/A = ratio does not apply.

[a] P(H$_2$/CO) = 6288.8 kPa, 353 K, [Subst]/[Cat] = 100, 24 h.

The data in Table 2 shows that 1-hexene is converted to aldehydes at a higher rate than allylbenzene, 2,3-dimethyl-1-butene, styrene and cyclohexene according to the relative order 1-hexene ≫ allylbenzene > 2,3-dimethyl-1-butene > styrene > cyclohexene. The analysis of the reaction mixture revealed that 1-hexene was transformed to linear aldehyde (heptanal) and the corresponding isomer (2-methylhexanal) with an n/i ratio of 2. The formation of 2-ethylpentanal was not detected presumably because the formation of the linear aldehyde is faster than the isomerization to 2-hexene (Scheme 1).

Allylbenzene produces selectively the linear aldehyde 4-phenyl-butanal with an n/i ratio of 7; 2,3-dimethyl-1-butene is converted to a least branched aldehyde 3,4-dimethyl-pentanal and the branched isomer 2,2,3-trimethyl-butanal is not observed due to steric repulsions that hinder the formation of the corresponding alkyl intermediate [28,29]. Styrene is converted prefer-
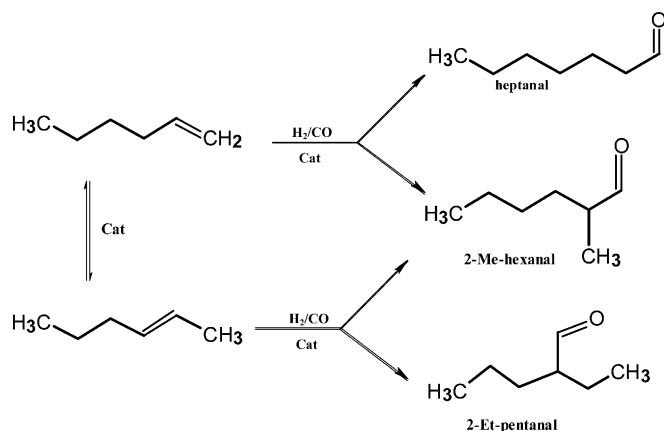
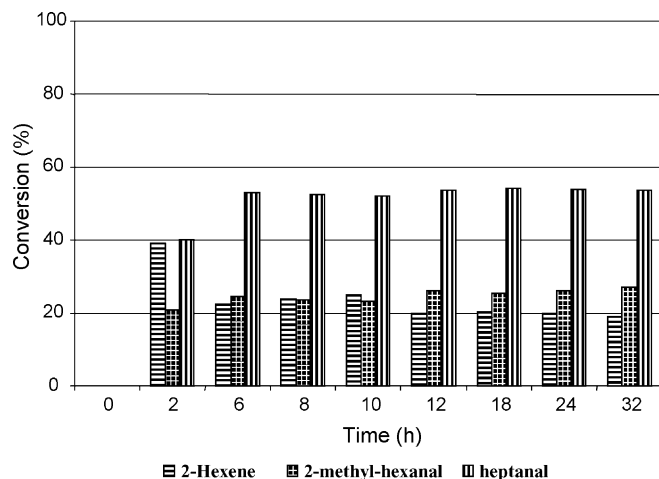Scheme 1. Hydroformylation of 1-hexene.

Fig. 3. Product distribution in the aqueous biphasic hydroformylation of 1-hexene at 353 K, 6288.8 kPa of CO/H$_2$. In all cases heptane–water (1:1, v/v).

ably to the linear isomer 3-phenyl-propanal and the branched isomer 2-phenyl-propanal with a n/i ratio of 4; and cyclohexene can only generate cyclohexanecarboxaldehyde as the unique product.

The hydroformylation of 1-hexene was carried out at 6288.8 kPa of syngas and 353 K. The analysis of the product distribution displayed in Fig. 3 reveals that in about 6 h, the conversion to aldehydes is completed. The linear product (n-heptanal) was obtained in 54% yield while the branched isomers formed in about 27% yield. The isomerization product 2-hexene was formed in 20% yield. 2-Ethylpentanal was not observed in the final reaction mixture [29]. This product distribution remained constant for 32 h without formation of hydrogenation products, which indicated the high selectivity towards the production of aldehydes.

In order to confirm that the hydroformylation reaction proceeds in a homogeneous phase, the well-known mercury test [30,31] was carried out in several independent experiments and the results showed no interference at all with the evolution of the reaction (Fig. 4). The metal content in the organic phase was determined by atomic absorption analysis in each run and the results show that <5 ppm was detected in the organic phase, indicating that practically all of the metal remains in the aqueous phase.

3.3. Aqueous hydroformylation of olefin mixtures

We tested the performance of the new catalyst [HRu(CO)(CH$_3$CN)(TPPTS)$_3$]BF$_4$ in the hydroformylation reaction of a simulation of naphtha. To simulate a C6–C8 cut of refined naphtha we mixed equimolar quantities of the possible pairs of five representative olefins: 1-hexene (a linear olefin), allylbenzene (allylic olefin), 2,3-dimethyl-1-butene (branched olefin), styrene (aromatic olefin) and cyclohexene (cyclic olefin) as well as the corresponding five component mixture to simulate the quantities in a real naphtha. The mixtures were subjected to the hydroformylation reaction according to the best operational parameters found for the pure alkenes.
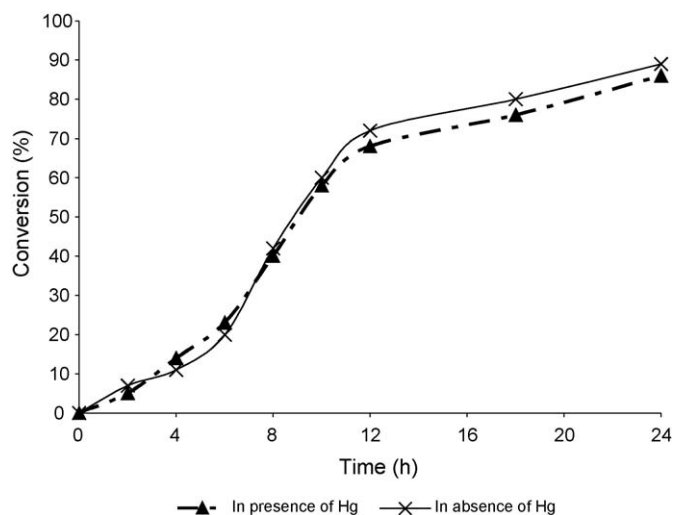
Fig. 4. Mercury test. Hydroformylation of 1-hexene with the complex $[HRu(CO)(CH_3CN)(TFFTS)_3]BF_4$.

In all cases, hydroformylation was efficiently achieved and the conversion for each olefin in the mixture decreased moderately with respect to the values found for individual substrates. The results for the mixture of the five alkenes are collected in Table 3, where it is observed that the total conversion of olefin in equimolar mixture (entry **1**) decreased drastically for all olefins from pure to mixture quantities as follows: 1-hexene (99–24%), allylbenzene (33–10%), 2,3-dimethyl-1-butene (17–9%), styrene (10–7%) and cyclohexene (3–0%).

This behavior is due to the competition for the active center presumably originated from the dissociation of one phosphine ligand from the precursor ruthenium complex, simultaneously with the steric repulsions between the olefins in the mixture [28–32]. Also in Table 3 it is very interesting to observe that when a mixture (entry **2**) is prepared in which the concentrations of the olefins are similar to the real quantities found in naphtha cuts (1-hexene 32.8%, allylbenzene 25.1%, cyclohexene 18.7%, 2,3-dimethyl-1-butene 17.2%, and styrene 6.2%),

Table 3

Aqueous biphasic hydroformylation of alkenes mixtures by use $[HRu(CO)(CH_3CN)(TPPTS)_3]BF_4$[a]

Alkene	Total conversion (%)[b]	Aldehydes (%)
(1)		
1-Hexene	22	48
Allylbenzene	10	
2,3-Dimethyl-1-butene	9	
Styrene	7	
Cyclohexene	0	
(2)		
1-Hexene	54	82
Allylbenzene	22	
2,3-Dimethyl-1-butene	6	
Styrene	0	
Cyclohexene	0	

(**1**) Equimolar mixture; (**2**) real quantities present in naphtha cuts.

[a] $P(H_2 + CO) = 6288.8$ kPa, 353 K, S/C = 100, $t = 24$ h.

[b] Total conversion based on the disappearance of alkenes.

Table 4

Product distribution of the aqueous biphasic hydroformylation of 1-hexene using $[HRu(CO)(CH_3CN)(TPPTS)_3]BF_4$[a]

Thiophene (ppm)	2-Hexene (%)	2-Methyl-hexanal (%)	Heptanal (%)
0	20	27	54
100	20	26	54
250	26	27	47
500	20	27	52
750	29	24	46
1500	31	21	47

Thiophene effect.

[a] $P(H_2 + CO) = 6288.8$ kPa, 353 K, S/C = 100, $t = 24$ h.

the total conversion decreases only slightly with respect to the pure olefins. This effect is explained because the steric repulsions are lower in the second mixture compared with the repulsions in the equimolar one.

3.4. Aqueous biphasic hydroformylation of 1-hexene in the presence of thiophene

In simulating naphtha we need to consider that refinery cuts usually contain small amounts (5–10 ppm) of organosulphur compounds that may act as poisons towards the catalyst. In order to model such a situation, 1-hexene was mixed with thiophene (100–1000 ppm) under the best operational conditions described above, to ascertain the sulphur tolerance of the ruthenium complex. The results are summarized in Table 4, where we can observe that the presence of thiophene in the hydroformylation of 1-hexene does not affect the total conversion until about 500 ppm which is a lot higher than the normal concentration of organosulphur compounds found in refined naphtha. From this value the total conversion decreases drastically probably by the formation of an inactive ruthenium-sulphur specie that is favorable under such conditions [33].

3.5. Catalyst recycling

One aspect that is very important in biphasic catalysis is the ability of reusing the catalyst precursor [34]. Taking this into account, a set of recycling experiments using the complex $[HRu(CO)(CH_3CN)(TPPTS)_3]BF_4$ during the hydroformylation of 1-hexene were carried out. In this sense, four consecutive experiments were run maintaining the same aqueous phase during the experiment and the organic phase was replaced for a fresh one containing 1-hexene every 24 h for 4 days. The results are summarized in Table 5. As shown therein, this complex effi-

Table 5

Recycling of the catalyst $[HRu(CO)(CH_3CN)(TPPTS)_3]BF_4$[a] in the biphasic hydroformylation of 1-hexene

Run	Total conversion (%)	Aldehyde selectivity (%)
1	100	89.44
2	100	83.65
3	99	86.09
4	99	85.64

[a] $P(H_2/CO) = 6288.8$ kPa, 353 K, [Subst]/[Cat] = 100, 24 h.

ciently catalyzed the hydroformylation of 1-hexene after four experiments without indications of dropping the activity.

4. Conclusion

The new water soluble ruthenium complex [HRu(CO)(CH$_3$CN)(TPPTS)$_3$]BF$_4$ was prepared and characterized using spectroscopic techniques. This complex is an efficient catalyst precursor for the aqueous biphasic hydroformylation of different olefins which showed the following hydroformylation order: 1-hexene > allylbenzene > 2,3-dimethyl-1-butene > styrene > cyclohexene. The presence of thiophene in the hydroformylation 1-hexene does not affect the activity of the catalytic precursor until greater than 500 ppm; from this observation we can infer that [HRu(CO)(CH$_3$CN)(TPPTS)$_3$]BF$_4$ is resistant to some possible sulphur poisons present in refinery cuts. Finally, this complex can be recycled without major indication of reduction of the activity.

Acknowledgements

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