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On the synthesis and characterization of two ruthenium water-soluble complexes: preliminary results on the hydrogenation of cinnamaldehyde in a biphasic system. Surface activity of the ligands TPPMS and TPPTS

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Abstract

The synthesis, characterization and preliminary hydrogenation studies, on the reduction of an aldehyde to alcohol, of two water-soluble ruthenium complexes are being reported. The complexes $[HRuCl(CO)P_3^*]$ were prepared by ligand exchange in a biphasic medium. P^* corresponds to the water soluble phosphines: TPPMS (**I**), the sodium salt of *m*-monosulfonated triphenyl phosphine, $[Ph_2P(C_6H_4SO_3Na)\cdot 2H_2O]$, and TPPTS (**II**), the trisodium salt of *m*-trisulfonated triphenyl phosphine, $[P(C_6H_4SO_3Na)_3\cdot nH_2O]$. Spectroscopy investigations have shown that in solution complexes **I** and **II** have the same structures as their organosoluble analog $[HRuCl(CO)(PPh_3)_3]$. Critical micellar concentration (CMC) studies and surface tension measurements showed that the water-soluble ligand TPPTS is a poor surface active agent as compared with the TPPMS ligand. Preliminary results on the hydrogenation of *trans*-cinnamaldehyde (CNA) with complexes **I** and **II** were carried out. The reduction of CNA proceeds through two parallel routes in both cases. Effect of the pressure and temperature is observed in the hydrogenation of CNA with **I** and **II**.

1. Introduction

The introduction, in 1985, of the industrial hydroformylation (Rhône-Poulenc/Ruhrchemie) in a biphasic (water/organic) medium has increased the interest in such water-soluble organometallic systems [1–3]. The advantages of using biphasic catalytic systems may include the ease of products separation, the recuperation of the catalyst, and the possibility of using 18 electron complexes that could dissociate in water to give 'aqua' species, capable of acting as intermediates in the generation of the catalytic active moiety [4].

A problem with this area of catalysis has been the lack of water-soluble ligands that could permit the solubility and stabilization of the organometallic moiety in the aqueous media. However, considerable efforts are being made in the synthesis and characterization of new water-soluble ligands in recent years [5].

Among the most common and useful hydrosoluble ligands, used in biphasic systems, are the sodium salts of mono- and trisulfonated triphenyl phosphine. The TPPTS is the trisodium salt of the *m*-trisulfonated triphenyl phosphine,

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$[P(m\text{-}C_6H_4SO_3Na)_3]$ [1,2], and TPPMS is the sodium salt of the *m*-monosulfonated triphenyl phosphine, $[Ph_2P(m\text{-}C_6H_4SO_3Na)]$ [6–8].

The TPPTS ligand is of interest because of the high water solubility of its metal complexes, and its involvement in biphasic catalytic processes of commercial importance [9]. Recent publications on TPPTS deal with its adequate synthesis [10], purification [10,11], characterization [12], mechanistic aspects of CO dissociation [13] and some catalytic reactions related to several processes on hydrogenation and hydroformylation [4,5,14]. Most organometallic aqueous soluble complexes with the TPPTS ligand involve transition metals from the groups 8, 9, 10 and 11 of the periodic table of the elements [5,15,16]. For early transition metals only four complexes have been reported, belonging to molybdenum and tungsten [13,17].

The TPPMS ligand is less soluble in water than the TPPTS; this is probably one reason for the lesser number of publications on the synthesis and catalytic aspects of TPPMS water-soluble complexes [6–8,18]. One aspect of interest regarding the TPPMS ligand is its surface active property, which may be of interest to produce micro emulsions and micellar catalytic systems (vide infra). In contrast to the use of TPPTS, in the synthesis of water-soluble organometallic complexes, TPPMS offers less publications. The few so far known are from the late elements of the periodic table [7].

There are two major routes to the synthesis of water-soluble complexes: (i) direct reaction of the metal halides with the sulfonated phosphine, and (ii) ligand substitutions of the organo-soluble phosphines by the water-soluble ones [8]. Procedure ii offers compounds with higher purity for catalytic purposes.

The hydrogenation of α,β-unsaturated aldehydes has been described using ruthenium [19,20] and rhodium [19,21] water-soluble complexes as well as supported aqueous phase catalysts [22,23]. Water solubility of the organometallic catalyst improves the recuperation, recycling and selectivity to unsaturated alcohol, of main interest to the chemistry of fragrances. The selective reduction of the aldehyde moiety to produce allylic alcohols is an attractive way of producing reductions with respect to economical and industrial process considerations [21]. From the water-soluble complex point of view, rhodium transforms cinnamaldehyde selectively by reducing the corresponding carbon–carbon double bond, while in the case of ruthenium, the transformation occurs by reducing the carbonyl moiety. Supported aqueous phase catalysts tend to produce aldehyde reduction to alcohols, but the reactions need to be carried out in an organic (non-polar) solvent [22].

In order to investigate the catalytic potential of the selective hydrogenation of *trans*-cinnamaldehyde to cinnamyl alcohol, the aqueous transition metal complexes, $[HRu(CO)Cl(TPPMS)_3]$ (**I**) and $[HRu(CO)Cl(TPPTS)_3]$ (**II**) have been prepared and characterized. It is expected that complex **I**, being an interfacial catalyst precursor, will carry out the reduction by parallel routes, while complex **II**, being a water catalyst precursor, will reduce mainly at the carbonyl.

2. Experimental

All manipulations were carried out using standard Schlenck techniques [24] under dry argon or nitrogen. Solvents were purified by conventional procedures. Mass spectrometry was carried out with ZAB BEQQ equipment, with the EI and FAB (glycerol matrix) modes of ionization at 70 eV and 12 eV. The GC-MS analyses were done with a HP 5890 system (HP-1 column, 50 m; split injection of 1:50; $T_i = 60°C$, two minutes for organic compounds, program of 10°C/min, $T_f = 120°C$). GC chromatograms were run on a Varian 3400 with an FI detector (Megabore type capillary column, 15 m; DB-5 phase; 1.5 u FT, J and W Scientific). Quantification was achieved by using the internal standard (cyclooctane) method; the

peaks were identified by comparison with authentic samples analyzed by CG-MS. Infrareds were taken in a Perkin-Elmer 1600 FTIR, coupled to a Digital Computer DEC Station 316SX and an HP color pro printer, using KBr. NMRs were run in Bruker 200 and 400 MHz spectrometers, using deuterated solvents. H_3PO_4 and TMS were used as external standards.

$RuCl_3 \cdot nH_2O$ (Aldrich) and triphenylphosphine (Strem) were used without further purification. 2-methoxyethanol, toluene, *trans*-cinnamaldehyde, cinnamyl alcohol, hydrocynnamaldehyde, phenyl propanol and diethyl ether were obtained from Aldrich Chemical.

The TPPMS and TPPTS ligands were prepared according to literature procedures [6,12]. Purification was achieved by recrystallization in water and ethanol until the ^{31}P NMR showed only one singlet (relative to phosphoric acid) at -5.99 (TPPMS) and -4.16 ppm (TPPTS). $HRu(CO)Cl(PPh_3)_3$ was prepared according to published procedures [25].

Catalytic runs were done according to the following conditions. The reactor was an autoclave from Parr Instruments (300 ml, 316SS, Glass Liner) with mechanical stirring and a temperature controlled unit. The reaction temperature was varied from 80 to 120°C (353 to 393 K); hydrogen pressure varied from 100 psi (7 bar) to 450 psi (31 bar); the stirring rate was set at 630 rpm for 8 h. Samples of the reactions were taken periodically via a sampling valve; layers were separated, and the organic phases were immediately analyzed by gas chromatography. The gas chromatograph was calibrated in order to calculate concentrations on a mol percentage basis. The total volume of the mixture was 100 ml (1:1 toluene/water); the concentration ratio of substrate to catalyst was 50:1. The amounts of complexes **I** and **II** present in the mixture of **I**/**II** + free TPPMS/TPPTS + OTPPMS/OTPPTS, was obtained from integration of ^{31}P-NMR spectra. The turnover frequency (TOF) was obtained from the ratio of substrate consumed to catalyst present per unit of time.

2.1. $HRu(CO)Cl(TPPMS)_3$ (*I*)

A warm solution of $HRu(CO)Cl(PPh_3)_3$ (1.00 g, 1.05 mmol) in toluene (60 ml) was filtered and transferred, via cannula, to a 250 ml R.B. flask containing a warm solution of TPPMS (2.52 g, 6.30 mmol) in water (60 ml). The resulting two-layer system was set to reflux (4 h) with vigorous stirring. During the reaction, the color of the aqueous layer changed from white to pale brown. After cooling, the layers are set to separate (1 h) and decanted in an inert atmosphere. The organic layer is discarded, and the water-soluble layer is filtered warm, using celite, cooled down to room temperature and filtered again in order to remove the excess TPPMS. This procedure is repeated until a cream solution is obtained. The filtrate is dried in vacuo and the cream product is kept under argon. The product is stable in air and soluble in water, ethanol and methanol. Yield: 0.93 g (70%). Anal. Calcd (exp.): C, 51.02 (51.68); H, 3.63 (4.30). XPS gives qualitative information of the elements present in the solid, except hydrogen, in %: Na, 1.85; O, 19.63; C, 72.25; Cl, 0.32; S, 2.79; Ru, 0.8, oxidation state II; P, 2.38. The XPS values for carbon and oxygen are always higher due to the presence of adventitious carbon and traces of oxygen present within the compartment of the XPS apparatus. The oxidation state for ruthenium was taken from the kinetic energy of a secondary line, $Ru(3P_{3/2})$ because the primary line ($Ru(_{2P})$) is interfered by the strong carbon line. This secondary line has an energy of 461.6 eV, which correlates well with other energies found for ruthenium complexes with similar oxidation: $HRu(Ph_3P)_3Cl$ (462.2 eV) and $HRu(Ph_3P)_3I$ (461.8 eV) [26]. IR (KBr, cm^{-1}): 2010.0 (w, νH–Ru), 1924 (s, νCO). ^{1}H-NMR: (CD_3OD) -7.06 (triplet) and -7.41 ppm (triplet) (H–RuP_3). The pattern observed in the ^{1}H-NMR corresponds to a doublet of triplets (see discussion). ^{31}P NMR (ppm): 15.28 (triplet, $J_{PPtrans}$: 14.8 Hz), 41.60 (doublet; J_{PPcis}: 14.2 Hz). The most abundant fragments corresponding to the

FAB mass spectrometry are (Z/e; relative abundance, %): $[HRuCl(CO)[Ph_2P(m\text{-}C_6H_4SO_3Na)]_3^+$ (1258, 100), $RuCl(CO)[Ph_2P(m\text{-}C_6H_4SO_3Na)]_3^+$ (1257, 92), $[RuCl(CO)[Ph_2P(m\text{-}C_6H_4SO_3Na)]_2[Ph_2P(m\text{-}C_6H_3SO_3Na)]^+$ (1256, 40), etc.

2.2. $HRu(CO)Cl(TPPTS)_3$ (II)

A solution of $HRu(CO)Cl(PPh_3)_3$ (0.50 g, 0.525 mmol) in toluene (50 ml) was placed in a 250 ml R.B. flask containing TPPTS (2.64 g, 2.97 mmol, 70% purity) in 2-methoxyethanol (50 ml). The resulting one layer system was set to reflux (18 h) with vigorous stirring. A precipitate is formed upon cooling. The organic layer is discarded by filtering and the solid obtained was washed several times with toluene (2 × 25 ml) and ether (2 × 25 ml). The beige solid was dried in vacuo. The product is stable in air and highly soluble in water, ethanol and methanol. Yield 1.60 g (44%, purity 30%). IR (KBr, cm^{-1}): 2020 (w, νH–Ru), 1941 (s, νCO). ^{1}H-NMR: (D_2O) −7.07 (triplet) and −7.41 ppm (triplet) (H–RuP_3). The pattern observed in the ^{1}H-NMR corresponds to a doublet of triplets (see discussion). ^{31}P NMR (ppm): 23.85 (triplet; $J_{PPtrans}$: 15.4 Hz), 41.96 (doublet; J_{PPcis}: 18.8 Hz).

3. Results and discussion

3.1. Characterization of the water-soluble ruthenium hydride complexes (I) and (II)

The pale-yellow complex $[HRu(CO)Cl(TPPMS)_3]\cdot 2H_2O$ (**I**) and the TPPTS beige analog $[HRu(CO)Cl(TPPTS)_3]$ (**II**) have being obtained by ligand exchange reaction in a biphasic medium. When $HRu(CO)Cl(PPh_3)_3$ (**III**) is refluxed with the corresponding water-soluble ligand, TPPMS (toluene/water) or TPPTS (toluene/2-methoxyethanol), products **I** and **II** have being obtained in 70 and 40% yield, respectively; yields are determined based on ruthenium. Previous attempts to obtain complex **I** by a known, direct route, using $RuCl_3\cdot 3H_2O$ and the TPPMS ligand yielded a mixture of at least two compounds, which were difficult to separate [7]. Complex **II** has also been obtained using a toluene/water mixture, but in poor yields.

Contaminants encountered from the reaction of **III** with the corresponding water-soluble phosphines were the TPPMS/TPPTS free ligands and their respective oxide derivatives (OTPPMS/OTPPTS). Purification of both hydrosoluble complexes in water and in ethanol reduces the content of the free ligands and their oxides to a minimum; however, trace amounts will always remain (^{31}P-NMR (singlets): TPPMS, −5.99 ppm; OTPPMS: 33.22 ppm **I**; TPPTS, −4.22 ppm; OTPPTS: 34.60 ppm **II**). Elemental analysis and MS (FAB) indicated the presence of two water molecules in **I**.

Some characteristic IR absorption frequencies for **I** and **II** are shown in Table 1; these frequencies are compared with those of their organosoluble analog $[HRu(CO)Cl(PPh_3)_3]$ (**III**). Table 2 shows the characteristic M–CO and M–H frequencies for some known TPPMS and TPPTS complexes and organo-soluble analogs (in brackets).

The molecular geometry for **I** and **II** can be inferred, as it is the case for its organosoluble

Table 1
Some characteristic IR frequencies for complexes **I**, **II** and **III**

Complex	ν(CO) cm^{-1}	ν(M–H) cm^{-1}	ν(C–H) cm^{-1}	ν(O–H) cm^{-1}	δ(OH) cm^{-1}
I	1923, st	2010, m	3052, sh	3452, br, st	1631, m
II	1941, st	2020, w	3071, sh	3485, br, st	1636, m
III	1928, v st	2013, m	3052, sh		

IR values for **III** were taken from Refs. [27,28].

Table 2
Characteristic IR bands for some water-soluble complexes with TPPMS and TPPTS ligands (organosoluble analog in brackets)

Complex	νCO	νM–H	Ref.
$HRh(CO)(TPPMS)_3$	1910 (1918)	2000 (2041)	[8,6]
trans-$RuCl_2(CO)_2(TPPMS)_2$	2005		[7]
cis-$RuCl_2(CO)_2(TPPMS)_2$	2000		[28]
$HRuCl(CO)(TPPMS)_3$	1900 (1903)	2060 (2020)	[7,6]
cis-$HRuCl(CO)_2(TPPMS)_2$	1941	1997	[7]
$HRuCl(TPPMS)_3$		2025 (2020)	[8]
$HRu(OAc)(TPPMS)_3$		1996	[7]
$HRuCl(CO)(TPPMS)_3$	1924 (1926)	2010 (2013)	this work [6,28]
$HRuCl(CO)(TPPTS)_3$	1941 (1903)	2020 (2020)	this work [6,28]
$RuCl_2(CO)_2(TPPTS)_2$	1998/2062		[4]
$[RuCl_2(CO)_2(TPP)_2]$	(1991/2056)		[6,28]
$HIr(CO)(TPPTS)_3$	1927		[4]

analog, by their identical signals observed in their ^1H and ^{31}P-NMR. Apart from the signals observed between 7.0 and 8.3 ppm, assigned to the aromatic protons in the phenyl rings, the only other signal observed was a doublet of triplets, centered at −7.27 ppm (−7.06 and −7.41 ppm, $J_{HPtrans}$: 103 Hz, J_{HPcis} (ave.): 25.0 Hz, 20°C, D_2O) and −7.20 ppm (−7.07 and −7.41 ppm, $J_{HPtrans}$: 104 Hz, J_{HPcis} (ave.): 24.0 Hz, 25°C, D_2O) for complexes **I** and **II**, respectively. An identical pattern was observed for the organosoluble analog, **III**, centered at −7.24 ppm (−7.04 and −7.39 ppm, −20°C, $CDCl_3$) as reported by Sánchez et al. [27,28].

The ^{31}P-NMR spectra of **I** and **II** show two signals, consisting of one doublet (equatorial P: 41.65 ppm, J_{PPcis}: 14.2 Hz for **I**; 41.96 ppm, J_{PPcis}: 14.8 Hz for **II**) and one triplet (axial P: 15.28 ppm, $J_{PPtrans}$: 14.8 Hz for **I**; 23.85 ppm, $J_{PPtrans}$: 15.4 Hz for **II**) relative to phosphoric acid. In the ^{31}P-NMR of **I** and **II** the signals corresponding to the free water-soluble ligand (TPPMS: −5.99 ppm; TPPTS: −4.05 ppm) as well as the sulfonated phosphine oxide (OTP-

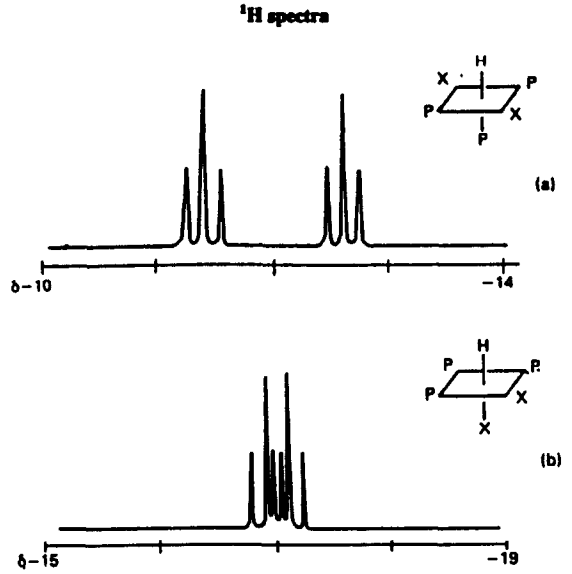


Fig. 1. Simulated spectra for the interaction between one hydride and three phosphorus atoms in an octahedral transition metal complex. Taken from Ref. [30].

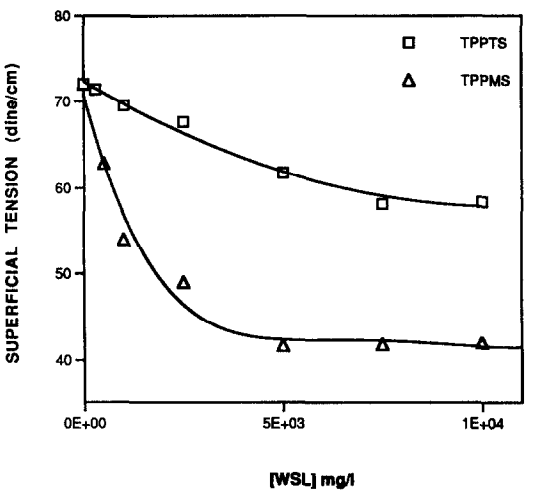


Fig. 2. Critical micellar concentration studies for the ligands TPPMS and TPPTS in an aqueous solution.

Table 3
Determination of the surface tension for TPPMS and TPPTS on a biphasic (water/toluene) system

	Tension (dinas/cm)
Toluene/water	48.69
TPPTS	51.23
TPPMS	15.05

PMS: 33.22 ppm; OTPPTS: 34.62 ppms) have been observed.

In **I** and **II**, the large doublet and small triplet pattern observed in the ^{31}P-NMR directly establish two equivalent phosphorus atoms *cis* to the hydride and one phosphorus *trans*, such as the one observed in the simulated spectrum of Fig. 1 [29,30]. The identical resonance frequencies observed for **I**, **II** and **III**, indicate that the sulfonated phosphines do not exhibit any stereo-electronic peculiarities [11].

The behavior of the TPPMS and TPPTS ligands as surface active agents has been investigated. Determination of the critical micellar concentration (Fig. 2) showed that TPPMS has surface active properties, whereas TPPTS behaves more as an electrolyte. Table 3 shows the interfacial surface tension measured for the TPPMS and TPPTS ligands in a biphasic (water/toluene) system. The surface activity of TPPMS is evident. It is expected that complexes formed with the TPPMS ligand will act at the interface between two liquids in a biphasic system. On the contrary, complexes with the TPPTS ligand will not form emulsion, behaving as homogeneous catalyst precursors in an aqueous phase.

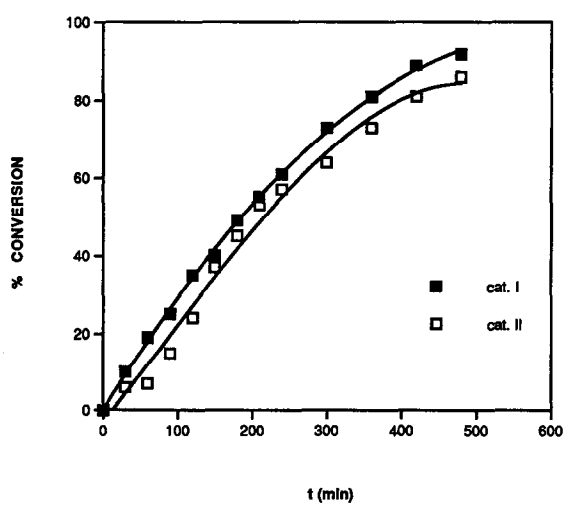


Fig. 3. Reaction profile for the hydrogenation of *trans*-cinnamaldehyde with complexes **I**, $[HRu(CO)Cl(TPPMS)_3]\cdot 2H_2O$, and **II**, $[HRu(CO)Cl(TPPTS)_3]$, in a biphasic medium.

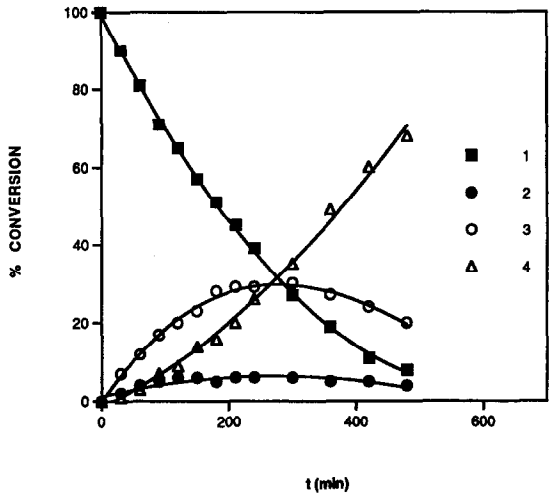


Fig. 4. Product distribution as a function of the reaction time (min) obtained during the hydrogenation of CNA with complex **I**, $[HRu(CO)Cl(TPPMS)_3]\cdot 2H_2O$.

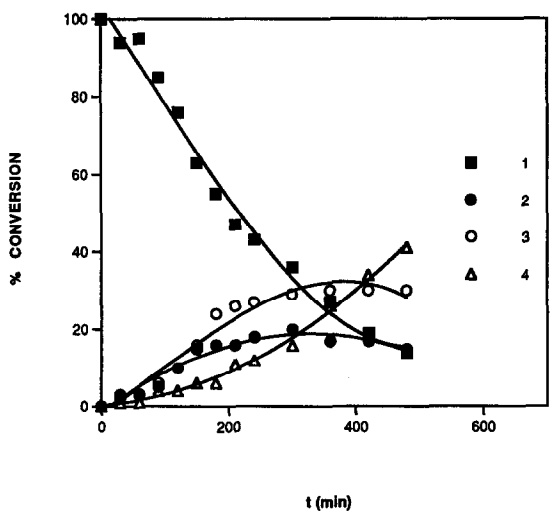
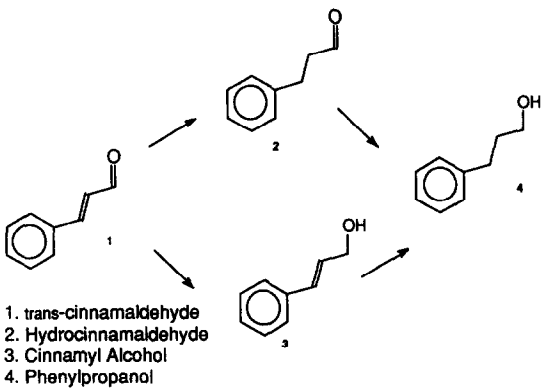


Fig. 5. Product distribution as a function of the reaction time (min) obtained during the hydrogenation of CNA with complex **II**, $[HRu(CO)Cl(TPPTS)_3]\cdot nH_2O$.



Scheme 1. 1. *trans*-cinnamaldehyde. 2. Hydrocinnamaldehyde. 3. Cinnamyl alcohol. 4. Phenylpropanol.

3.2. Hydrogenation of unsaturated aldehydes

The preliminary studies on the hydrogenation of unsaturated aldehydes (*trans*-cinnamaldehyde, CNA), in a biphasic (water/toluene, 1:1) system was followed using **I** and **II** as catalytic precursors. Under the same reaction conditions, **II** (Vi: 0.137) and **I** (Vi: 0.122) show similar activity (Fig. 3).

Figs. 4 and 5 show a typical product distribution as a function of time obtained during the hydrogenation of CNA. The reaction was found to proceed through two parallel routes leading to phenylpropanol (Scheme 1).

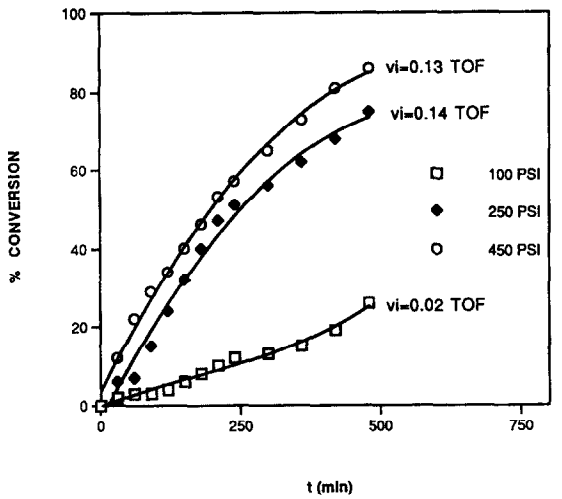


Fig. 7. Profile of the percentage conversion of CNA as a function of pressure (psi) with complex **II**.

With **I** (Fig. 4) the product distribution indicates that at high concentrations of CNA product 2 tends to be transformed to 4 very readily, while product 3 accumulates. As the concentration of CNA equals that of 3, there is a competition and the hydrogenation of 3 to 4 is observed. It seems that the reduction of CNA to phenylpropanol goes preferentially by the way of hydrocinnamaldehyde (2). The hydrogenation of CNA with **II** (Fig. 5) is carried out by

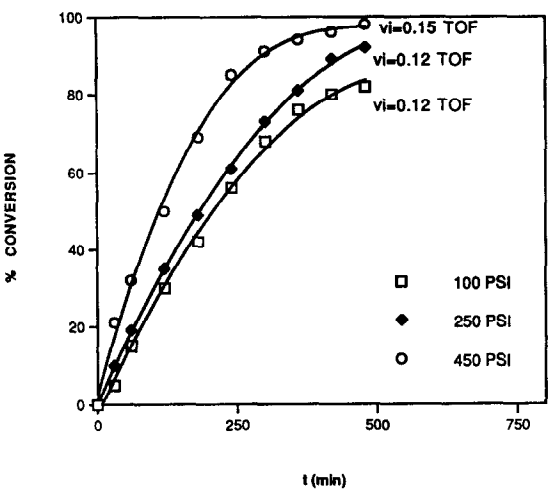


Fig. 6. Profile of the percentage conversion of CNA as a function of pressure (psi) with complex **I**.

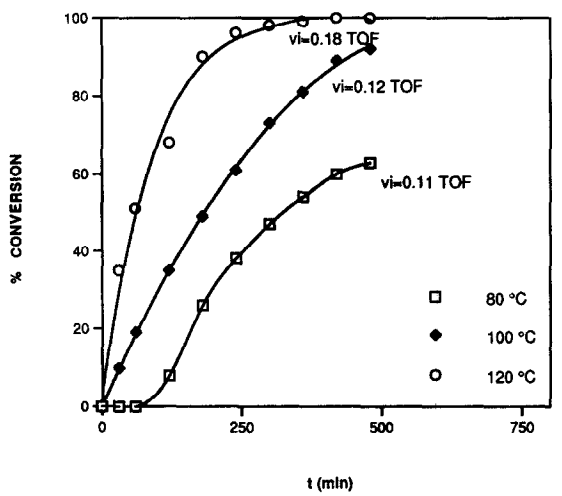


Fig. 8. Profile of the hydrogenation of CNA as a function of the temperature (°C) with **I**.

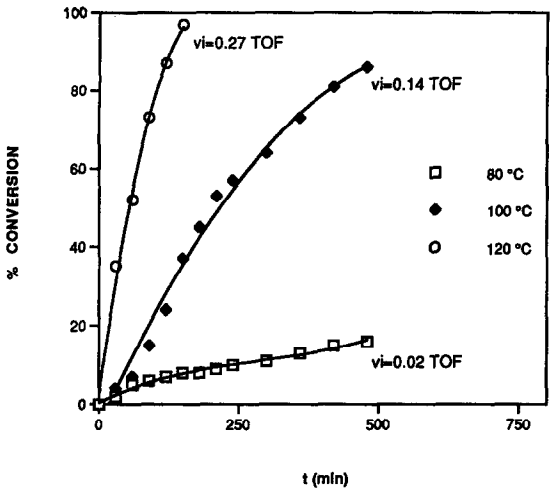


Fig. 9. Profile of the hydrogenation of CNA as a function of the temperature (°C) with **II**.

parallel routes, through 2 and 3, at high concentrations of CNA.

In the hydrogenation of CNA with **I** the pressure has little effect (Fig. 6) while with **II** there are some effects observed (Fig. 7).

Both catalyst precursors, **I** and **II**, showed a pronounced effect on the hydrogenation of CNA as a function of temperature (Figs. 8 and 9).

4. Conclusions

The synthesis, characterization and preliminary catalytic activities, in the hydrogenation of unsaturated aldehyde, were undertaken for two new water-soluble complexes: $[HRu(CO)Cl(TPPMS)_3] \cdot 2H_2O$ (**I**) and $[HRu(CO)Cl(TPPTS)_3]$ (**II**). Both complexes, **I** and **II**, were obtained using a ligand exchange reaction in a biphasic, water/toluene (**I**) and 2-methoxyethanol/toluene (**II**) route. The products were obtained as a mixture, with the free sulfonated phosphines and their respective oxides present as contaminants.

The hydrosoluble ligand TPPMS acts as a surface active agent, whereas the TPPTS behaves more like an electrolyte under similar conditions in a biphasic (water/toluene) system.

Complexes **I** and **II** are active in the hydrogenation of CNA. **I** prefers to reduce CNA to phenylpropanol by way of the hydrocinnamaldehyde. Complex **II** does the reduction using parallel routes. The hydrogenation of CNA with **I** and **II** showed a pronounced effect with temperature. The effect of pressure on the hydrogenation was only observed with **II**.

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