

# Synthesis, characterization and catalytic activity of the water-soluble tungsten complex $[W(CO)_3(MeCN)(TPPMS)_2]$ , $TPPMS = (C_6H_5)_2P(m-C_6H_4SO_3Na) \cdot 2H_2O$ : the unprecedented transformation of the complex into a hybrid (homogeneous/heterogeneous) catalyst precursor during two-phase catalytic hydrogenation upon changes in reaction conditions

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## Abstract

The water-soluble tungsten complex:  $[W(CO)_3(MeCN)(TPPMS)_2]$ , where  $TPPMS = (C_6H_5)_2P(m-C_6H_4SO_3Na \cdot 2H_2O)$ , was prepared and characterized using spectroscopic techniques. The complex is soluble and stable in water for long periods as demonstrated by UV–VIS studies. When this water-soluble tungsten complex was used as a catalyst precursor during the two-phase catalytic hydrogenation of small olefins and aromatic molecules (1-hexene, styrene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene and benzene) the expected selectivity for a homogeneous catalyst precursor was not obtained. Under the chosen reaction conditions, the hydrogenation of benzene proceeded at a much faster rate (benzene: 2.1; 1-hexene: 1.2; styrene: 1.3; 2,3-dimethyl-1-butene: 1.5 and 2,3-dimethyl-2-butene:  $1.6 \text{ mol}(\text{mol W})^{-1} \text{ h}^{-1}$ ). The Hg test, carried out in another set of experiments, showed inability of the system for catalytic hydrogenation. Upon changes in the pH of the catalytic solution, the hydrogenation proceeded either homogeneously or heterogeneously. At  $\text{pH} < 6$ , the catalysis proceeds heterogeneously, while at  $\text{pH} > 6$  the process is homogeneous (Scheme 1). Hydrogen pressure also facilitates this transition. Temperature, substrate to catalyst ratio (S/C) and stirring do not affect the heterogeneous nature of the system. The heterogeneous catalytic solution is blue while the homogeneous one remained yellow. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Tungsten; Water-soluble; Hybrid catalyst; Hydrogenation

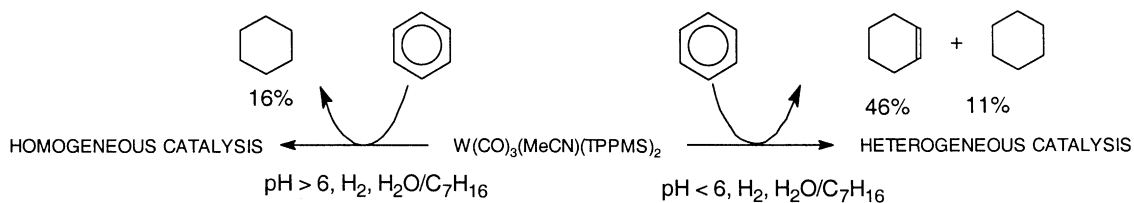
## 1. Introduction

Biphasic catalysis has been the center of attention for the last 15 years, thanks to the unprecedented commercial push given by the Rhone–Poulenc/Ruhrchemie (RP/RC) process for the hydroformylation of propane to butylaldehyde [1]. With the advent of this

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Scheme 1.

accomplishment, other biphasic commercial processes have been developed (e.g. hydroisomerization (Kuraray) [2,3], alkylation to geranylacetone (RP) [3], etc.).

Three major factors make biphasic catalysis appealing to the entrepreneur mind: namely, simple separation and recycle capacity of the organometallic catalytic precursors; ease for reducing pressure and reaction temperature, which translates into a more economical process and the environmental friendliness of water soluble compounds [4,5].

One consideration that has always bothered researchers is the capacity of water-soluble phosphines for transforming molecular systems into stabilized colloidal species in solution [6]. These species tend to be catalytically active, the hydrosoluble phosphine ligands are transformed into their inactive oxides [6,7]. This tendency has risen doubts on whether it is possible to maintain the real capacity of hydrosoluble phosphine biphasic systems for extensive periods of time. These doubts made the RP/RC process to upgrade the simple TPPTS ligand into a more complex and highly bulky analog, which is more resistant to self-destruction [8]. Another aspect of interest, regarding some organometallic salts in the presence of hydrosoluble ligands, relates to their capacity to shift between a “homogeneous” or a “heterogeneous” system, which are difficult to distinguish by simple spectroscopic techniques. The identification of these systems requires the collaborative use of a large array of physical methods and tests in order to distinguish characteristics of complex and highly bulky compounds with possible hybrid (homogeneous/heterogeneous) features [9].

There are very few water-soluble complexes of group six that have been used in homogeneous or in two-phase catalysis. So far, only one paper have reported the synthesis and two-phase catalytic activity

of several seven-coordinate complexes of the type  $[\text{MXY}(\text{CO})_3(\text{MeCN})_2]$  ( $\text{M} = \text{W}$  and  $\text{Mo}$ ) [10].

One aim of the present work is to explore further the use of group six water-soluble complexes in homogeneous (two-phase) catalysis. Herein is reported, the unprecedented transformation of the water-soluble tungsten complex,  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]$  into a heterogeneous–homogeneous catalyst system under reductive conditions. This tungsten complex, which is yellow, converts into a catalytically active heterogeneous blue species. This blue species do not show activity under excess mercury [12]. The blue catalytic solution, on standing at standard pressure and temperature, changes back to yellow. Further work is being carried out to identify the real structures of the yellow and blue species, and will be reported elsewhere. The observed catalytic behavior of the initial complex and the influence of the reaction conditions, including the serendipitous capacity of the pH of the solution to turn the tungsten–TPPMS complex into a catalytic hybrid system (homogeneous/heterogeneous) are reported.

## 2. Experimental

### 2.1. General comments

All manipulations were carried out using standard Schlenk techniques under dry nitrogen. Organic solvents were of commercial origin and purified by distillation. The olefins, their respective saturated products and benzene were reagent grade (Aldrich) and stored under nitrogen. Water was deionized and treated with nitrogen prior to use. TPPMS was prepared according to reported procedures and recrystallized in methanol [12]. In general, the ligand TPPMS is obtained in its dihydrate form [13]. Tungsten hexacarbonyl (reagent

grade, Aldrich) was purified by sublimation. Quinoline (reagent grade, Aldrich) was purified by distillation under reduced pressure. Tetrahydroquinoline (reagent grade, Aldrich) was used without further purification.

FT-IR spectra were recorded on a Perkin-Elmer 1000 spectrometer, using KBr disks. NMR spectra were recorded on a Bruker AM 300 spectrometer. Mass spectra were obtained with a Kratos ZAB BEQO spectrometer with EI and FAB (glycerol matrix), 12 eV. GC analyses were performed on a Hewlett-Packard 5890 Series II with FID coupled to a HP integrator; GC column was HP, ultra 2, 5% phenyl-methyl-silicone, 25 m  $\times$  0.32 mm. Naphthalene was used as internal standard. UV spectra were recorded on a double beam HP UV-VIS 8452 spectrometer with a temperature controller 89090A.

## 2.2. Synthesis of the complex

### $[W(CO)_3(MeCN)(TPPMS)_2]$

The homogeneous, air sensitive  $[W(CO)_3(MeCN)_3]$  complex was prepared and characterized according to literature procedures [14–16].  $[W(CO)_3(MeCN)_3]$  (0.5 g, 1.14 mmol) was dissolved in dry ethanol (25 ml), under inert atmosphere, to which a solution of TPPMS (0.9 g, 2.47 mmol, 20 ml) dissolved in EtOH was added. This solution was set to reflux with continuing stirring, and after 6 h, a cream precipitate was obtained. The cream solid was filtered off and washed with cold ethanol, after drying, it gave a product in 75% yield. The FT-IR showed the characteristic bands of the TPPMS ligand, as well as three prominent bands observed at 1887, 1845 and 1823  $cm^{-1}$ , corresponding to the  $\nu CO$  vibrations. A sharp and small band at 2018  $cm^{-1}$  was assigned to the  $\nu CN$  of acetonitrile coordinated to a metal center. The  $^1H$ -NMR ( $D_2O$ ) showed a singlet at 1.9 ppm assigned to the  $CH_3$  in acetonitrile and the characteristic set of peaks for the aromatic hydrogen in the region between 7.10 and 8.10 ppm. The  $^{31}P$ -NMR ( $D_2O$ ) shows only one singlet at 35.89 ppm. The mayor peak observed in the FAB-MS corresponded to a  $Z/e$  of 1108 a.u.  $[W(CO)_3(TPPMS)_2(MeCN) \cdot 4H_2O + H]^+$ ; 1081  $[W(CO)_2(TPPMS)_2(MeCN) \cdot 4H_2O + H]^+$ ; 1063  $[W(CO)_2(TPPMS)_2(MeCN) \cdot 3H_2O + H]^+$ ; 1026  $[W(CO)_2(TPPMS)_2(MeCN) \cdot H_2O + H]^+$ ; 1008  $[W(CO)_2(TPPMS)_2(MeCN) + H]^+$ . From these spectroscopic evidences, it was assigned a structure with

six ligands surrounding the tungsten and the two TPPMS ligands having the same chemical environment. The four water molecules may be closed to the sulfonated moieties, given the structural formula as  $[W(CO)_3(MeCN)(TPPMS)_2]$ , where TPPMS =  $(C_6H_5)_2P(m-C_6H_4SO_3Na \cdot 2H_2O)$  [13].

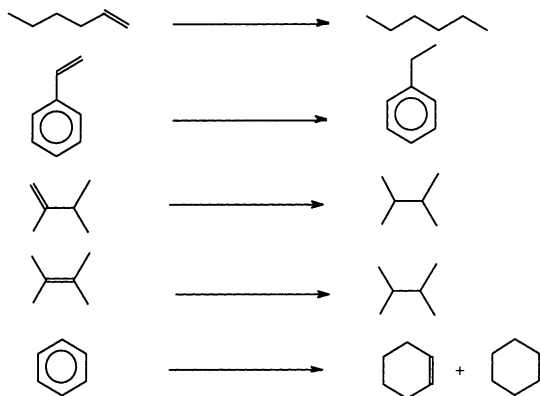
## 2.3. Catalytic hydrogenation

In a typical experiment, an aqueous solution of the tungsten catalytic precursor (50 ml,  $5.8 \times 10^{-3} M$ ) and a heptane solution of the substrate (50 ml,  $2.9 \times 10^{-1} M$ ) were introduced into a glass-lined stainless steel autoclave (Parr, 300 ml) fitted with internal stirring and a sampler valve. The solution was purged with hydrogen (three times) and then charged with the required hydrogen pressure and heated to the desired temperature with stirring at 600 rpm. When the temperature was at equilibrium (time 0), samples of the reaction mixture were periodically extracted through the sample valve and the system total pressure was adjusted via a high pressure reservoir. The initial rate velocity, defined as  $mol(mol W)^{-1} h^{-1}$ , was obtained at the beginning of the hydrogenation profile, up to 10% conversion. After the reaction, the samples were cooled, the phases separated and the organic phase analyzed. initial reaction conditions for the hydrogenation of olefins were: temperature, 100°C; pressure, 1000 psi; stirring, 600 rpm; S/C, 50; water/heptane, 80 ml, 1:1 (v/v); time, 18 h. Previous to each catalytic reaction a control or blank experiment without the catalyst was carried out and negative catalytic results obtained.

## 3. Results and discussion

The complex  $[W(CO)_3(MeCN)(TPPMS)_2]$  is soluble in water and also in warm methanol, ethanol, acetonitrile and tetrahydrofuran. In the latter solvent the complex tends to decompose slowly. The four water molecules observed in the FAB-MS may be closed to the sulfonated moieties of the TPPMS ligand. This ligand usually crystallizes with two waters of crystallization, given the formula  $(C_6H_5)_2P(m-C_6H_4SO_3Na \cdot 2H_2O)$  [13].

When  $[W(CO)_3(MeCN)(TPPMS)_2]$  is used as a catalyst precursor in the two-phase hydrogenation of



Scheme 2.

some olefins (1-hexene, styrene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene and benzene) surprisingly the initial rate velocities for the monosubstituted olefins were lower than that observed for the most sterically crowded ones (1-hexene: 1.2, styrene: 1.3, 2,3-dimethyl-1-butene: 1.5 and 2,3-dimethyl-2-butene: 1.6 mol(mol W)<sup>-1</sup> h<sup>-1</sup>). Inclusively, benzene presented a higher initial rate velocity compared to the olefins (benzene: 2.1 mol(mol W)<sup>-1</sup> h<sup>-1</sup>). Scheme 2 shows the substrates together with their respective products according to GC–MS studies and the reaction profiles for each substrate are presented in Fig. 1.

The above results are unexpected because in homogeneous catalysis the hydrogenation rate for different alkenes change in the order: monosubstituted > disubstituted > trisubstituted > tetrasubstituted ≫ aromatics [17,18].

The biphasic hydrogenation of benzene gave cyclohexane as major product. A GC–MS of the organic phase showed that the conversion to cyclohexene was 46%, while cyclohexane amounted to 11% (PH<sub>2</sub> 1000; 100°C, S/C = 50, 20 h). The catalytic profile for the hydrogenation of benzene shown in Fig. 1 is the sum of both products. The selective hydrogenation of benzene has been a major target of industrial research because the oxidation of cyclohexene to adipic acid may proceed more cleanly than the current cyclohexane oxidation [19]. Although, ruthenium is the most important catalyst precursor for this reaction via homogeneous catalysis, under biphasic conditions the hydrogenation proceeds to the fully hydrogenated product [20,21]. In regard to tungsten there are no

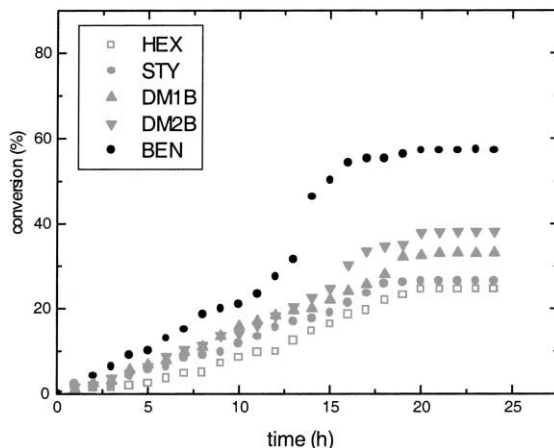


Fig. 1. Reaction profiles for the biphasic hydrogenation of the olefins and benzene using the catalyst precursor [W(CO)<sub>3</sub>(MeCN)(TPPMS)<sub>2</sub>] (100°C, 1000 psi, 600 rpm, S/C 50:1, 1:1 (v/v) water/heptane 80 ml, 24 h; HEX = 1-hexene, STY = styrene, DM1B = dimethyl-1-butene; DM2B = dimethyl-2-butene and BEN = benzene).

precedents in the literature in the use of water-soluble tungsten complexes for this interesting reaction.

Careful visual observation of the aqueous catalytic solutions show that the original light yellow color has turned turbid blue with an acidic character (pH between 3 and 4). The experiments were all reproducible with almost similar hydrogenation results.

Mercury (Hg) is a well-known poison for heterogeneous catalysts due to amalgam formation with the metal catalyst [9,11] and the Hg test is one of the most popular and easiest to use “homogeneous versus heterogeneous” test [9,11]. When a set of experiments were carried out under the Hg test, the catalytic hydrogenation experiments were all inhibited. This implies that the biphasic catalytic precursor does not work homogeneously. That is, the catalysis is carried out heterogeneously, under the initial experimental conditions used in these experiments. This may be the reason why the initial rate velocities were different than expected for a homogeneous hydrogenation reaction (see above) [17,18].

In virtue of these unexpected results, some changes in reaction conditions were studied and thus, the effect of the temperature, substrate to catalyst ratio, pressure, stirring rate and pH were investigated, using the hydrogenation of styrene to ethylbenzene as example.

Table 1

Effect of increasing temperature in the biphasic hydrogenation of styrene, using as catalyst precursor the complex  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]^a$

Time (h)	Conversion of styrene to ethylbenzene (%)				
	$T = 80^\circ\text{C}$	$T = 100^\circ\text{C}$	$T = 110^\circ\text{C}$	$T = 120^\circ\text{C}$	$T = 140^\circ\text{C}$
5	4	4	6	6	7
9	7	7	8	10	21
13	10	12	19	24	31
17	13	21	30	35	41

<sup>a</sup> 1000 psi, S/C = 50:1, heptane/water 80 ml, 600 rpm.

### 3.1. The effect of temperature and substrate to catalyst ratio

When the biphasic hydrogenation of styrene was carried out using the complex  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]$  as catalyst precursor in studying the effect of temperature (the study was carried out from 80 to  $140^\circ\text{C}$ , in steps of  $20^\circ$ , keeping other reaction conditions constant), only a small increase in conversion was observed with incrementing temperature (See Table 1). In the same manner, the catalytic conversion of styrene to ethylbenzene was also slow when the substrate to catalyst ratio was increased (Table 2).

As it was observed during the first set of experiments in Fig. 1, in these experiments all catalytic solutions were blue after the catalysis with a pH between 3 and 4. In the case of the temperature profiles, there were induction periods of almost 3 h. Long induction period during hydrogenation reactions have been suggested as indication of a possible heterogeneous catalytic process [9]. At  $140^\circ\text{C}$  no decomposition of the catalytic solution was observed. The Hg test was

Table 2

Effect of increasing substrate to catalyst ratio (S/C) in the biphasic hydrogenation of styrene, using as catalyst precursor the complex  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]^a$

Time (h)	Conversion of styrene to ethylbenzene (%)		
	S/C = 25	S/C = 50	S/C = 100
0	0	0	0
5	10	12	16
10	15	26	32
15	27	36	42
20	44	53	57

<sup>a</sup> 1000 psi, S/C = 50:1, heptane/water 80 ml, 600 rpm,  $T = 100^\circ\text{C}$ .

carried out in a set of independent experiments showing that the biphasic catalysis is not homogeneous because the hydrogenation is inhibited under these conditions [9,11]. In all the experiments using the Hg test, reaction products were not detected by GC and GC-MS. The catalysis proceeds heterogeneously but it is difficult to determine if a colloid or a nanocluster is the responsible catalytic moiety. Also, traces of metal particles, indicating decomposition of the catalyst, were not observed in any of the experiments.

### 3.2. Pressure effect on the hydrogenation

When a study was carried out varying the hydrogen pressure from 600 up to 1200 psi (in steps of 200 psi, The reaction temperature for all these experiments was  $140^\circ\text{C}$ ), interesting results were observed (Fig. 2).

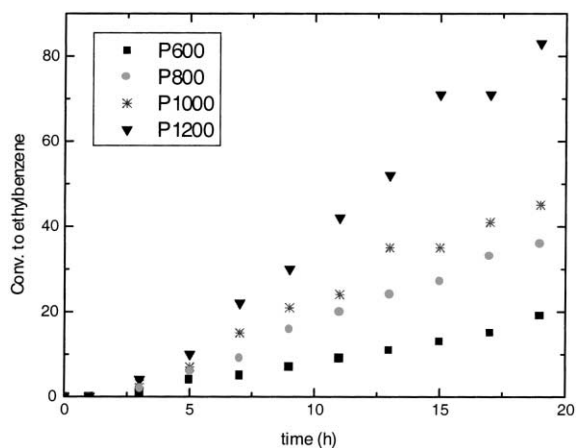


Fig. 2. Reaction profiles for the biphasic hydrogenation of styrene to ethylbenzene as a function of pressure ( $P = \text{psi}$ ), using the catalyst precursor  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]$ , ( $140^\circ\text{C}$ , 600 rpm, S/C 50, water/heptane 80 ml, 20 h).

The profiles of Fig. 2 show that as the hydrogen pressure increases from 600 to 1200 psi, a great improvement in the conversion of styrene to ethylbenzene is obtained. In the experiments done with hydrogen pressure between 600 up to 1000 psi, the catalytic solutions were all blue. In another set of experiments carried out using the Hg test [9,11], total inactivity of the catalyst was observed. All aqueous solutions showed acidic pH (pH varied between 3 and 4). In the pressure range from 600 to 1000 psi, the conversion to ethylbenzene did not surpass 45%; however at 1200 psi, the catalytic solution keeps its original yellow color and showed almost neutral pH (pH 6.5). The conversion reached a maximum of 90%. The Hg test conducted in another experiment did not inhibit the catalysis (1200 psi, 140°C, 600 rpm) [9,11]. This was the first experiment in which the Hg test gave a negative result and indicates that the reaction is carried out via homogeneous catalysis [9,11].

In order to test the condition of homogeneity observed at 1200 psi, two experiments were designed using a heptane solution consisting of a mixture of benzene and styrene. In the first experiment the following reaction conditions were used: 1000 psi H<sub>2</sub>, 140°C, 600 rpm, S/C 50:1, 1:1 (v/v) water/heptane, 80 ml total volume. The reaction profiles are depicted in Fig. 3.

Under these conditions, benzene is hydrogenated preferably over styrene. The aqueous solution was blue

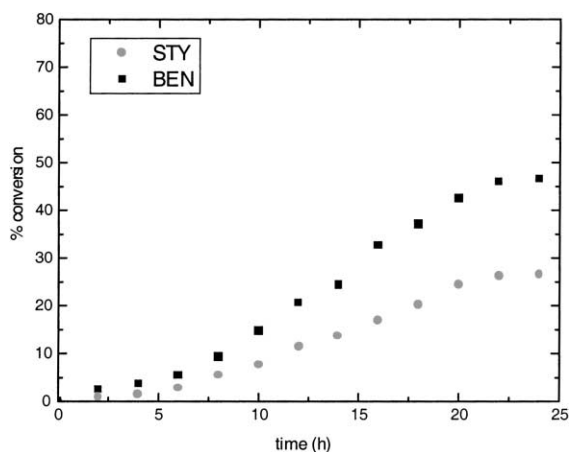


Fig. 3. Reaction profiles for the biphasic hydrogenation of a mixture of styrene and benzene, using as catalyst precursor the complex  $[W(CO)_3(MeCN)(TPPMS)_2]$ , (1000 psi, 140°C, 600 rpm, S/C 50, water/heptane 80 ml, 20 h).

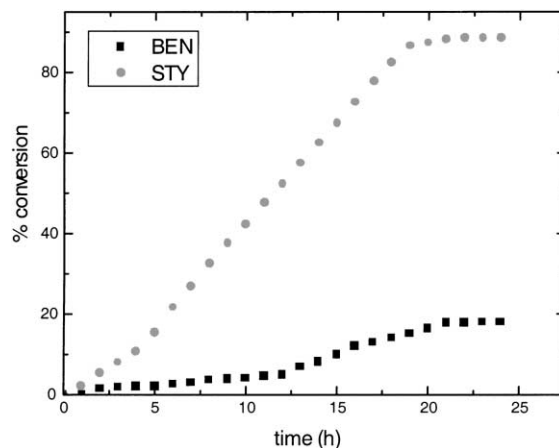


Fig. 4. Reaction profiles for the biphasic hydrogenation of styrene and benzene, using the catalyst precursor  $[W(CO)_3(MeCN)(TPPMS)_2]$ , (1200 psi, 140°C, 600 rpm, S/C 50, water/heptane 80 ml, 20 h).

and acidic. The Hg test [9,11] gave total inactivity of the catalytic solution. The second experiment was done using the same reaction conditions as in Fig. 3, except that the reaction pressure was 1200 psi (Fig. 4).

Under these reaction conditions, the color of the aqueous solution remained yellow and the pH was neutral. The Hg test carried out in another set of experiments do not show catalytic inhibition, confirming the homogeneity of the hydrogenation experiment [9,11]. From these observations, it is possible to presume that the biphasic system, conformed by the tungsten aqueous solution and the heptane/substrate solution, correspond to a HYBRID catalytic precursor. This catalyst precursor acts homogeneously or heterogeneously depending upon the pressure of the reaction. Below 1200 psi, the catalysis is carried out heterogeneously (all aqueous solutions are blue and acidic). Above 1200 psi, the catalyst precursor behaves homogeneously (aqueous solution remains yellow and insensitive to excess mercury added to the reaction medium) [9,11].

### 3.3. Effect of pH in the hydrogenation of styrene

One relevant observation obtained from the previous experiments refers to the effect of the pH on the catalysis. When the solution turned blue, the pH was always acidic. All yellow aqueous solutions were pH neutral.

In order to investigate the effect that a change in pH can have in the biphasic hydrogenation of styrene, a set of experiments were performed at two different pH conditions. In a first experiment, the hydrogenation of styrene was carried out under the following conditions: HCl, 0.1 M, pH 2, 1000 psi, 140°C, 20 h, S/C 50:1, heptane/water 1:1, 80 ml. Under these conditions, the catalysis proceeded with 86% conversion to ethylbenzene. The aqueous solution was blue and the pH of the solution after the catalysis was 3. Another experiment was carried out under the Hg test showing not catalysis at all. The biphasic system shows a heterogeneous catalytic behavior at acidic pH (that is at pH below 6).

In the second experiment, a heptane solution containing equimolar amounts of styrene and quinoline (quinoline,  $P_{kb} = 9.1$ ) was hydrogenated. The reaction conditions were the same as the previous HCl experiment. The products obtained from the biphasic hydrogenation were 1,2,3,4-tetrahydroquinoline (THQ, 100% conversion) and trace amount of ethylbenzene. The pH of the yellow aqueous solution, after the hydrogenation, was 8.3. When the same reaction was repeated under the Hg test (with an additional increase in reaction time, 10 h more), the result obtained was that quinoline converted to THQ (100%) and styrene to ethylbenzene in 10%. Again, the yellow aqueous solution showed a pH of 8.5. These results demonstrated that the catalytic precursor  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]$  acts homogeneously above pH 6.

In this last experiment, the organic nitrogen base (quinoline) interfered with the hydrogenation of the olefin; for this reason, another experiment was carried out, using exactly the same reaction conditions, but changing the base from quinoline to diethylamine,  $[(\text{CH}_3\text{CH}_2)_2\text{NH}]$ . The individual reaction profiles for the hydrogenation of each of the olefins and for benzene, in the presence of diethylamine, is depicted in Fig. 5.

In these experiments, the hydrogenation reactions for the olefins were faster than the one obtained under acidic conditions. The Hg test [9,11], done in another set of experiments gave excellent hydrogenation profiles, confirming the homogeneity of the reaction under basic pH. All aqueous solutions were yellow. The order of hydrogenation is typical for a homogeneous catalytic reaction (1-hexene  $\geq$  styrene  $>$  2,3-dimethyl-1-butene  $>$  2,3-dimethyl-2-butene  $>$  benzene; Fig. 5) [17,18].

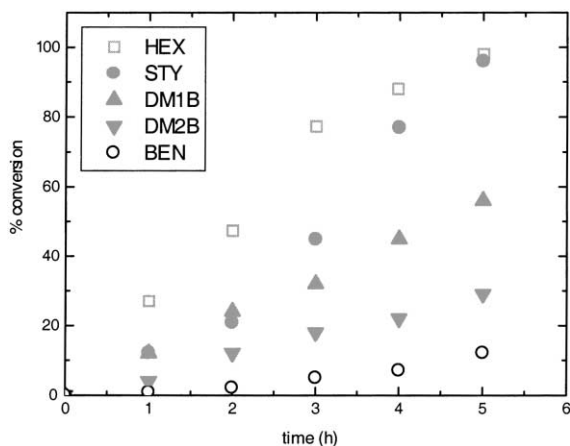


Fig. 5. Reaction profiles for the biphasic hydrogenation of some olefins and benzene, using diethylamine as organic base and  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]$ , as catalyst precursor (1000 psi, 140°C, 5 h, S/C 50:1, heptane/water 1:1, 80 ml; HEX = 1-hexene, STY = styrene, DM1B = dimethyl-1-butene; DM2B = dimethyl-2-butene and BEN = benzene).

### 3.4. The effect of stirring on the hydrogenation

Increasing the stirring rate tends to increase the conversion of styrene to ethylbenzene, as shown in Table 3. All these experiments were carried out under the following reaction conditions: 140°C, 1000 psi, 1:1 heptane/water, 80 ml, S/C 50:1; no additive (acid or base) was added.

In all these experiments, the aqueous solutions were blue. The Hg test showed inhibition of the catalysis [9,11]; indicating the heterogeneous nature of the blue catalyst system (600 and 1000 rpm) [9]. Although, the catalysis is carried out heterogeneously, the positive effect of the stirring is a consequence of the

Table 3

Effect of increasing agitation in the biphasic hydrogenation of styrene, using as catalyst precursor the complex  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]^a$

Revolutions per minute (rpm)	Conversion to Eb (%)
200	17
400	41
600	62
800	78
1000	99

<sup>a</sup> 140°C, 1000 psi, S/C = 50:1, heptane/water 80 ml.

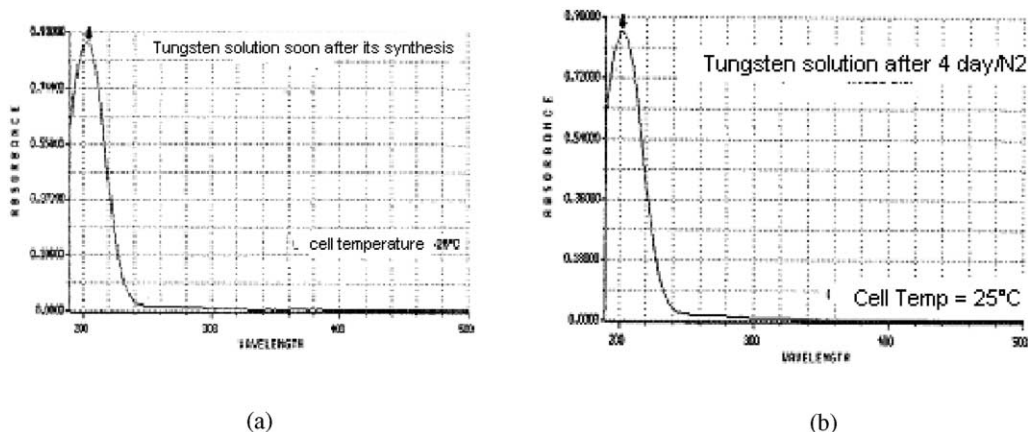


Fig. 6. UV–VIS spectrum of the catalyst precursor  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]$ : (a) aqueous solution soon after preparation; (b) aqueous solution 4 days later.

tensoactivity properties of the TPPMS ligand. The smaller the droplets of the catalytic and organic layers, the better the interaction at the interface and the more efficient the hydrogenation becomes [22].

To recap from all the experimental details given: If the hydrogenation of olefin molecules or benzene is carried out at a hydrogen pressure below 1200 psi and/or under an acidic pH ( $\text{pH} < 6$ ) the catalyst precursor  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]$  acts forming an heterogeneous catalytically active species. This catalyst system tends to hydrogenate benzene at a much faster initial rate velocity than olefins. If the reaction pressure is above 1200 psi or if the pH of the catalyst solution is basic ( $\text{pH} > 6$ ), then the tungsten catalyst precursor behaves homogeneously; as confirmed by the homogeneity test using excess mercury [9,11]. If the aqueous catalyst solution is acidified the system works heterogeneously, even if the pressure is 1200 psi.

There are precedents in the literature indicating that some organometallic catalyst precursors are capable, in the presence of water-soluble phosphines, of forming colloids or nanoclusters [6,7,23–25]. These colloids are better prepared from organometallic precursors in an organic medium and in the presence of triphenylphosphine and derivatives [7,24].

Initial studies of the blue solid, isolated after one of the catalytic experiments, has shown, via transmission electron microscopy (TEM), that the tungsten complex forms a colloid of narrow size particle distribution.

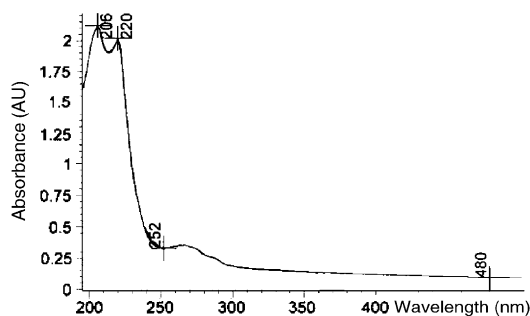


Fig. 7. UV–VIS spectrum of the blue solution soon after the catalysis.

However, more detailed analyses are needed in order to asseverate the real nature of the heterogeneous system. One group is looking carefully at this issue and will report results somewhere else<sup>1</sup>.

Studies using UV–VIS spectroscopy shows that the initial yellow complex,  $[\text{W}(\text{CO})_3(\text{MeCN})(\text{TPPMS})_2]$ , is stable in water for prolonged period of time (Fig. 6).

The blue solution has a different UV–VIS spectrum than the observed for the molecular yellow complex (Fig. 7). On standing at room temperature and under normal atmosphere conditions, the blue solution turned yellow with time. In almost 1 h the yellow color returned back. The UV–VIS spectrum of this yellow solution, after the catalysis, is given in Fig. 8.

<sup>1</sup> Samples have been sent to a solid state laboratory for obtaining the required information.



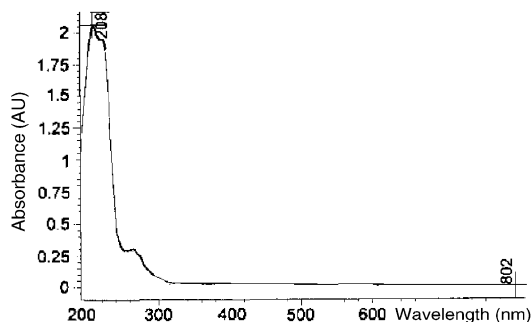


Fig. 8. UV–VIS spectrum of the yellow product obtained hours later after the catalysis letting the solution to turn from blue to yellow on standing.

Analyses of the yellow solids obtained before and after the catalysis are being carried out in order to determine whether or not the system returns back to the original molecular state<sup>1</sup>.

Although there are examples in the literature that have reported the use of hybrid catalyst systems [9]; these organometallic compounds happened to be very bulky species that after formation of the colloid are capable of catalytic activities only under heterogeneous conditions [9]. The water-soluble tungsten complex reported herein can act homogeneously or heterogeneously depending upon the conditions of the medium. Thus, this is the only molecular complex, so far studied, that is capable of such hybrid (homogeneous/heterogeneous) behavior.

#### 4. Conclusions

The tungsten complex  $[W(CO)_3(MeCN)(TPPMS)_2]$  (TPPMS =  $(C_6H_5)_2P(m-C_6H_4SO_3Na \cdot 2H_2O)$ ), was prepared and characterized using spectroscopic techniques. The complex is soluble in water and stable in that medium for very long periods. When this water-soluble tungsten complex was used as a catalyst precursor in the biphasic hydrogenation of small olefin molecules and benzene, the expected order for initial rate velocities in homogeneous catalysis was not obtained. Benzene presented a higher initial rate in hydrogenation than any of the olefins. These olefins were hydrogenated with almost similar initial rates. Under the conditions initially studied, the yellow

aqueous solution turned into a blue one after the catalysis. This blue solution was catalytically inactive in the presence of excess mercury. However, if the pressure of the solution is incremented above 1200 psi or if the pH is basic ( $pH > 6$ ), the biphasic catalysis occurred homogeneously. The Hg test does not affect the initial hydrogenation rate under these two conditions ( $pH > 6$  and  $P > 1200$  psi). According to the experimental results the tungsten complex transforms into a hybrid (homogeneous/heterogeneous) system capable of catalytic activity.

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#### References

- [1] E.G. Kuntz, *Chemtechnology* 17 (1987) 570–575.
- [2] Y. Tokitoh, T. Higashi, K. Hino, M. Murasawa, N. Yoshimura, US Patent 5,118,885 (Kuraray) (1992).
- [3] M. Matsumoto, N. Yoshimura, M. Tamura, US Patent 4,510,332 (Kuraray) (1985).
- [4] G. Papadogianakis, R.A. Sheldon, *New J. Chem.* 20 (1996) 175–185.
- [5] D.E. Pérez, *Visión Technol.* 4 (1997) 147–164.
- [6] C. Larpent, R. Dabard, H. Patin, *New J. Chem.* 12 (1988) 907–913.
- [7] G. Schmid, *Chem. Rev.* 92 (1992) 1709–1727.
- [8] W.A. Herrmann, C.W. Kohlpaintner, R.B. Manetsberger, H. Bahrman, H. Kottman, *J. Mol. Catal.* 97 (1995) 65–72.
- [9] Y. Lin, R.G. Finke, *Inorg. Chem.* 33 (1994) 4891–4910.
- [10] M. Al-Jahdali, P.K. Baker, A.J. Lavery, M.M. Meeham, D.J. Muldoon, *J. Mol. Catal. A* 159 (2000) 51–62.
- [11] R. Crabtree, D.R. Anton, *Organometallics* 2 (1983) 855–859.
- [12] S. Ahrland, J. Chatt, N. Davies, A. Williams, *J. Chem. Soc.* 276 (1958) 276–288.
- [13] F. Joó, J. Kovács, A. Kathó, A. Bényei, T. Decuir, D. Darenbourg, *Inorg. Synth.* 32 (1998) 1–8.
- [14] D.P. Tate, W.R. Knipple, J.M. Augl, *Inorg. Chem.* 1 (1962) 433–434.
- [15] B.L. Ross, J.G. Grasselli, W.M. Ritchey, H. Kaesz, *Inorg. Chem.* 2 (1963) 1023–1030.

- [16] I.W. Stolz, G.R. Dobson, R.K. Sheline, *Inorg. Chem.* 2 (1963) 323–326.
- [17] R.H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 2nd Edition, Wiley/Interscience, New York, 1994, pp. 212–215.
- [18] B. Cornils, W.A. Herrmann (Eds.), *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1, VCH, Weinheim, 1996, pp. 204–206.
- [19] G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis. The Application and Chemistry of Catalysis by Soluble Transition Metal Complexes*, 2nd Edition, Wiley/Interscience, New York, 1982, pp. 180–183.
- [20] E. Garcia Fidalgo, L. Plasseraud, G. Süß-Fink, *J. Mol. Catal.* 132 (1998) 5–12.
- [21] L. Plasseraud, G. Süß-Fink, *J. Organomet. Chem.* 539 (1997) 163–170.
- [22] A. Andriollo, J. Carrasquel, F. López, J. Mariño, D.E. Páez, I. Rojas, N. Valencia, *J. Mol. Catal.* 116 (1997) 157–165.
- [23] C. Larpent, H. Patin, *J. Mol. Catal.* 44 (1988) 191–195.
- [24] W. Kläui, S. Klütze, *Book of Abstracts, XXXII ICC*, Florence, Italy, 30 August to 4 September 1998, p. 491.
- [25] D. Caro, de, H. Wally, C. Amiens, B. Chaudret, *J. Chem. Soc., Chem. Commun.* (1994) 1891–1892.