

Synthesis, characterization and catalytic applications in aqueous-biphase system of a new tungsten complex

$W(CO)_3(CH_3CN)(TPPTS)_2$

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Abstract

A new water soluble complex, $W(CO)_3(CH_3CN)(TPPTS)_2$, has been synthesized by the reaction of the water soluble ligand tris-*meta*-sulfonato-phenylphosphine (TPPTS) with the tungsten precursor $W(CO)_3(CH_3CN)_3$ and characterized using spectroscopic techniques. The new complex shows high solubility and stability in water demonstrated by UV–VIS studies. This complex is an effective catalyst precursor for the liquid-biphase hydrogenation of the double bond in the presence of surface active agent like cetyltrimethylammonium chloride (CTAC) of various alkenes such as 1-hexene, 1-decene, allylbenzene, styrene, 1-cyclohexene and 1-methyl-1-cyclohexene. The activity of this complex has an influence depending of the type substrate used and with this ligand, it remains as a molecular complex, independently of the reaction condition used. At the end of the reaction, all the metal remains in the aqueous phase without indication of partition of the complex towards the organic phase. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalysis in water or in aqueous-biphase systems is a continuous research area due that it considered the technique of the future, for the production of commodities, specialties and fine chemicals [1]. The main feature about this type of catalysis involve that the catalytic active specie is immobilized in water due the presence of ligand capable to maintain the catalyst in this phase, while the reactants and products are maintained in the other phase. Consequently, increasing

research efforts are being paid to the design of appropriate water-soluble ligands among which tertiary phosphine play a major role in terms of both versatility of coordination and industrial application [1,2].

Since the discovery of the water soluble ligands tris(sodium-*m*-trisulphonated-triphenylphosphine [$P(m-C_6H_4SO_3Na)_3$] by Kuntz in 1975 [3,4] the two phase hydroformylation process, using a water-soluble rhodium catalyst, has increased the interest in the use of this type of ligand for other application. The crucial advantages of aqueous two-phase catalysis are the easy separation of the catalyst from water immiscible products, the possibility of using 18 electron complexes that could dissociate in water to give aqua species, capable of acting as intermediates

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in the generation of the catalytic active moiety [5–7].

In this sense, most of the water soluble complexes has been synthesized using late transition metal and different applications are disclosed [8] and references cited therein). This aspect prompt to us to study, the synthesis characterization of new water soluble complexes, this time with transition metal of the VI group and explore the possible catalytic application. As a result of this investigation, promising results were founded with $W(CO)_3(CH_3CN)(TPPMS)_2$, recently reported from part of our group [9] were this complex can be used as a catalyst precursor for the biphasic hydrogenation of different substrate and were depending of the reaction condition, an unprecedented transformation of this complex into a hybrid catalyst (homogeneous–heterogeneous) can be achieved [9].

This interesting results prompted us to explore the possibility to prepare the analog complex, with the water soluble ligand TPPTS and verify if the nature of the water soluble ligand can makes a difference on the structure as well as on the catalytic behavior. A brief account of the catalytic activity of the new complex in the hydrogenation of various alkenes such as 1-hexene, 1-decene, allylbenzene, styrene, cyclohexene and methyl-1-cyclohexene in H_2O -*n*-heptane is also reported.

2. Experimental

2.1. Experimental procedure

All reactions and manipulations were carried out under a nitrogen atmosphere [10]. Solvents were dried and deoxygenated prior to use. The ligand TPPTS [3,11] and the complex $W(CO)_3(CH_3CN)_3$ [12] were prepared according to literature procedures. High-pressure, -temperature reactions under a controlled pressure of H_2 were performed with a stainless steel 300 ml Parr reactor. FABMS analyses were carried out using a VG-ZAB-2SEQ mass spectrometer (*m*-nitrobenzyl alcohol, matrix) at 35 kV and at a mass resolution high enough to resolve peaks at one mass unit apart. GC–MS analyses were performed with 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 (Megabore type capillary column,

15 m; DB-5 phase; 1.5 μ m FT, J&W Scientific). Quantification was achieved by using the internal standard method. 1H and ^{31}P { 1H } NMR spectra were recorded on Bruker 500 MHz spectrometers, 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 with a Perkin-Elmer 5000 instrument.

2.2. Synthesis of $W(CO)_3(CH_3CN)(TPPTS)_2$ (1)

The complex $W(CO)_3(CH_3CN)_3$ (0.5 g, 1.14 mmol) was dissolved in 2-methoxyethanol (25 ml) and placed into a 250 ml round-bottomed flask. Then TPPTS (1.6 g, 2.8 mmol) in 2-methoxyethanol (50 ml) was added to the solution. The resulting solution was stirred for 6 h at 60 °C. After cooling to room temperature, the yellow powder, which had separated, was filtered off, washed with 2-methoxyethanol and then dried in vacuo. Yield: 1.3 g (52%). Complex (1) is air-stable and soluble in CH_3CN , MeOH, and DMF, hot water–methanol mixtures (1:1, v:v). ^{31}P { 1H } NMR (20 °C, D_2O): δ 31.6 (s), 1H NMR (20 °C, D_2O): δ 7.70–7.50 ppm (m), 12H (aromatic ring), δ 3.30 ppm (s), 3H (CH_3CN), IR (KBr): 2359.9 cm^{-1} w (νCN), 1874, 1895 and 1995 cm^{-1} s (νCO), 1201 cm^{-1} m ($-\text{SO}_3$). FABMS: calcd. For *m/z* which, on the basis of the isotopic distribution of the elements, particularly of tungsten, are assigned to the ions $[M]^+$, $[M - Na]^+$, $[M - Na - HSO_3]^+$, $[M - TPPTS - Na]^+$ $[M - CO]^+$, respectively.

2.3. Catalytic runs

In a 300 ml stainless steel vessel of a Parr autoclave containing 12 ml of water were placed (1) (0.02 mmol), 1 ml of aqueous solution (25% w/w) of cetyltrimethylammonium chloride (CTAC). The substrate (0.2 mmol) and naphthalene (0.1 mmol) as the internal standard were placed in *n*-heptane (12 ml). After pressurizing with 69 atm of H_2 , the reactor was heated to 100 °C with stirring (600 rpm). After the 8 h, the reactor was cooled to room temperature and the two phases were separated were and the organic phase analyzed by GC and GC–MS for the determination of conversion and selectivity. After all the organic solvent was removed under reduced pressure, and analyzed by atomic absorption which showed the

absence of tungsten in this phase. All the experiments were carried out into a glass-lined stainless steel autoclave in order to avoid the possible catalytic activity of the walls of the autoclave.

3. Results and discussion

3.1. Synthesis and characterization

The complex (**1**) is obtained as yellow microcrystal by reacting $W(CO)_3(CH_3CN)_3$ with two equivalent of TPPTS in warm 2-methoxyethanol. The compound

is air stable, soluble in polar solvents, including methanol–water mixtures. This complex was purified by recrystallization in water–ethanol mixture and the TPPTS used as starting material have between 80 and 90% of purity. The solubility in water is high as is expected due the presence of the TPPTS ligand [3] and the stability of this complex was measured by UV–VIS analysis for a period of 96 h, as is shown in the Fig. 1.

The UV–VIS analysis reveal that after 96 h at room temperature, the intense absorption peak at 232 nm remain constant, which is a prove of the stability in water, where no indication of possible changes in the nature of the complex is demonstrated. This fact

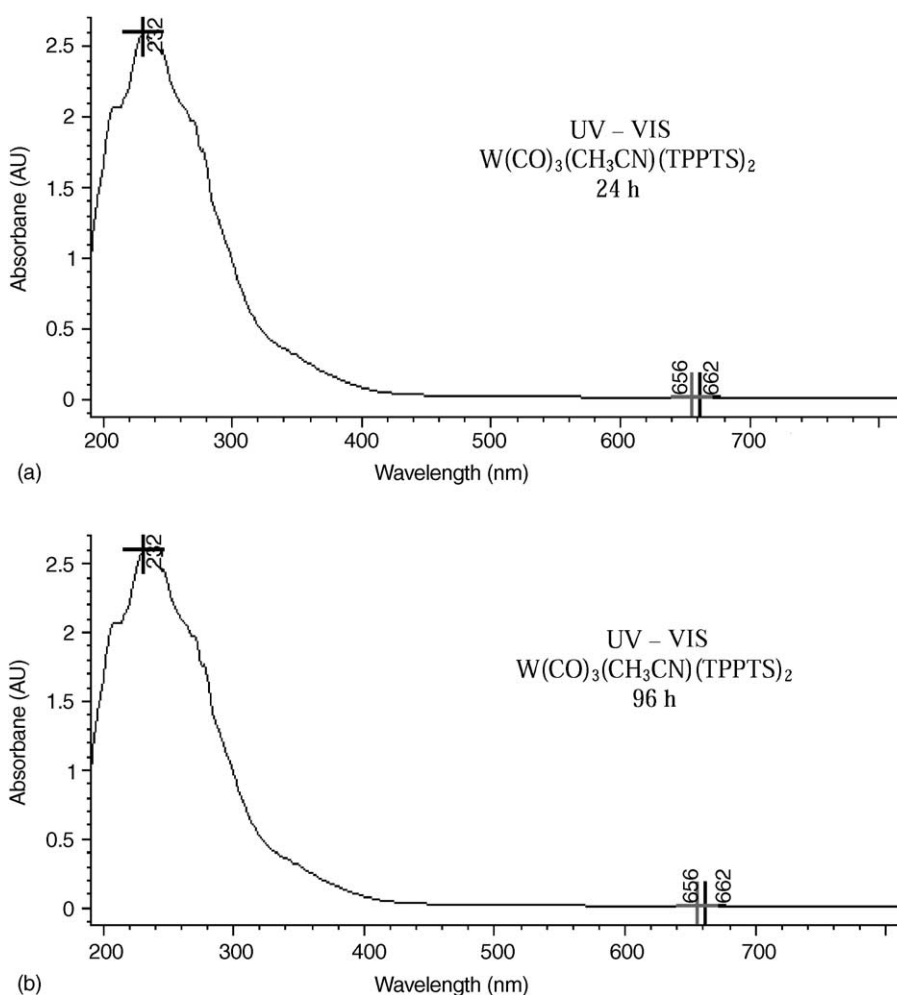


Fig. 1. Study of the stability in water of the complex $W(CO)_3(CH_3CN)(TPPTS)_2$ by UV–VIS: (a) aqueous solution at 24 h; (b) aqueous solution at 96 h.

confirm that $W(CO)_3(CH_3CN)(TPPTS)_2$ can be used in water safely. The IR spectrum shows a band at 2359.9 cm^{-1} corresponding to the CN stretching of the acetonitrile present in the complex, three strong bands observed at 1874 , 1895 and 1995 cm^{-1} , corresponding to the ν_{CO} vibrations which are in concordance with the observed bands in the similar complex [9] reported before and one band at 1201 cm^{-1} corresponding to a SO_3^- stretching.

The 1H NMR shows the aromatics protons related to the ligand TPPTS and one singlet centered at 3.36 ppm corresponding to a CH_3CN coordinated to the tungsten. An comparative analysis of the area corresponding to the of the protons located in the aromatic region with the singlet centered at 3.36 ppm , permit to conclude that *only one* CH_3CN is coordinated to the W center. The $^{31}P\{^1H\}$ NMR spectrum of (**1**) consists of a temperature-invariant and intense singlet centered at $\delta\ 31.6$ in D_2O corresponding to two phosphorus atoms in *trans* position. The analysis of the $^{31}P\{^1H\}$ allows to calculate the purity of this compound, where the complex was achieved with 85%, good for using in catalytic experiment. The other signal observed are related to the TPPTS oxide and the free ligand, normally founded in this type of synthesis [13].

On the basis of the $^{31}P\{^1H\}$, 1H NMR, IR and FABMS spectra, (**1**) is safely assigned a structure in which the tungsten center contains *two* P atoms located *trans* each other with three CO ligand; two *trans* one *cis* with one CH_3CN ligand which complete the coordination of the metal center, according to the Fig. 2, where the complex (**1**) has the same structure of its analogue TPPMS complex reported recently by Baricelli et al. [9].

3.2. Catalytic activity

Once that this complex was fully characterized, the catalytic activity for the liquid-biphasic hydrogenation

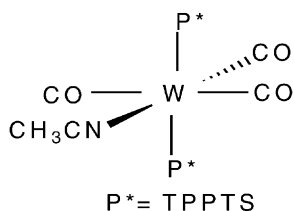


Fig. 2. Structure proposed for the complex **1**.

of some alkenes was investigated using as a starting reaction condition $100\text{ }^\circ\text{C}$ and 1000 psi of H_2 in a mixture of water–*n*-heptane. Initially, a series of experiment using 1-hexene as a substrate, were performed in order to get information about the activity of this complex as a function of the reaction condition.

One aspect that we founded at the beginning, concern with the fact that no activity is obtained in absence of a surface active agent. This aspect is possible if is taking account that the TPPTS ligand act more like electrolyte in comparison with the TPPMS ligand that shows interfacial properties [14]. Thus, with the TPPTS ligand, the complex is located distant from the interface, the zone were the catalysis take place, which mean that poor or in some cases no contact with the substrate is efficiently achieved. To overpass this situation, the use of surface active agent has been used previously by other authors [15,16] in the hydrogenation of 1-hexene. For this reason, several surface active reagent were tested, which cetyltrimethylammonium chloride (CTAC) resulted the best agent for the hydrogenation of 1-hexene in biphasic condition with this catalyst precursor.

After founded good catalytic activity, the effect of the reaction condition in the behavior of this catalyst precursor was evaluated. Thus, the influence of reaction temperature was choice as a first parameter to evaluate were the results are shown in Table 1.

As can be seen in Table 1, activity of this complex is sensitive with temperature, were the high conversion is obtained at temperature around to $100\text{ }^\circ\text{C}$. However, were the temperature is increased, a dropping of the activity is obtained, inducing to us to believe that probably the stability of this complex, may be affected with the temperature. In this sense, the catalytic aqueous phase was analyzed by UV–VIS, were the analysis

Table 1
Hydrogenation of 1-hexene as a function of the temperature

Temperature ($^\circ\text{C}$)	Conversion (%)
60	25.6
80	57.0
100	89.9
120	30.3

Condition: catalyst precursor, 0.02 mmol ; CTAC, 1 ml of aqueous solution (25% w/w); 1-hexene, 0.2 mmol ; naphthalene, 0.1 mmol ; *n*-heptane, 12 ml ; water, 12 ml ; $[H_2]$, 1000 psi ; S/C , 100 ; H_2 , 1000 psi ; time, 6 h .

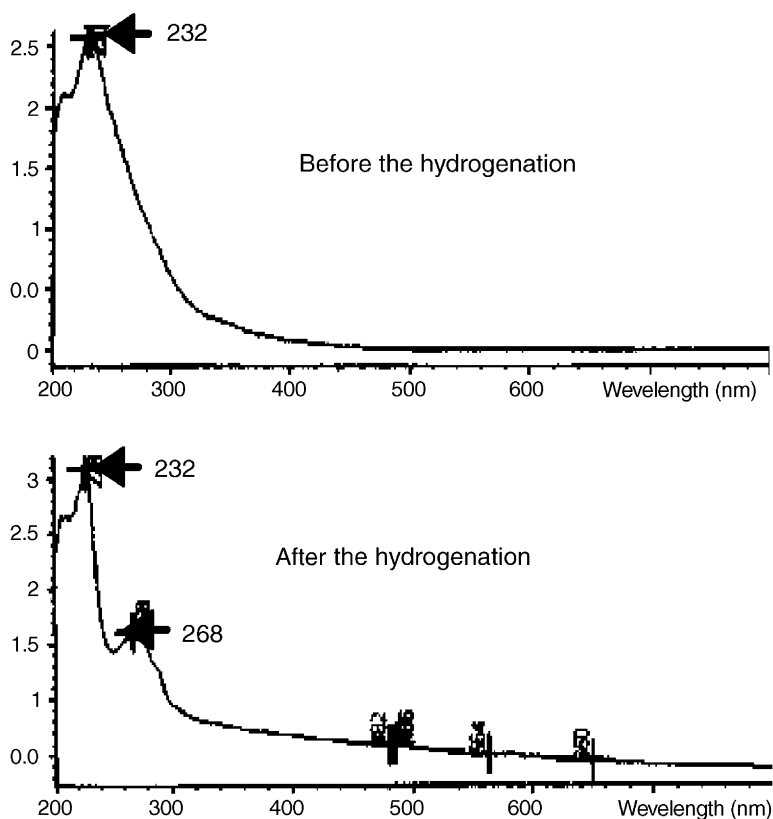


Fig. 3. Analysis by UV–VIS of the catalytic in the hydrogenation of 1-hexene at 120 °C.

shows the presence of a new specie, different of the initial catalyst precursor, as can be observed in Fig. 3.

Accordingly to the UV–VIS spectra, at the end of the reaction is detected a new band at 268 nm, indicating the presence of new specie, that it may be responsible for the lower activity obtained at this temperature. Another interesting point is related about the behavior of this complex as a function of the temperature, when it is compared with the analogue W-TPPMS. The TPPMS analogue complex shows a possible hybrid behavior as at high temperature. This result were not detected in this case, which indicate that the nature of the water soluble ligand induce some different characteristic in this type of complexes. Further experiment regarded to identify clearly this new specie, are currently going on and the result will be present in a next communication.

The effect of the H₂ pressure on the activity of this catalyst precursor, was also investigated. For this

purpose, a range of H₂ pressure starting from 600 to 1200 psi [9] was covered, were the result are summarized in Table 2.

The data reported in Table 2, plainly shows that the activity is also sensitive with the H₂ pressure, reaching maximum value at 1000 psi, with a little bit drop at 1200 psi. However, not alteration on the aqueous

Table 2
Hydrogenation of 1-hexene as a function of the H₂ pressure

H ₂ pressure (psi)	Conversion (%)
600	0
800	59
1000	90
1200	83

Condition: catalyst precursor, 0.02 mmol; CTAC, 1 ml of aqueous solution (25% w/w); 1-hexene, 0.2 mmol; naphthalene, 0.1 mmol; *n*-heptane, 12 ml; water, 12 ml; temperature, 100 °C; S/C, 100; H₂, 1000 psi; time, 6 h.

Table 3
Alkene hydrogenation reactions catalyzed by complex (1)

Substrate (% conversion)	Product (% selectivity)
1-Hexene (87)	<i>n</i> -Hexane (100)
1-Decene (54)	<i>n</i> -Decane (100)
Styrene (28)	Ethylbenzene (100)
Allylbenzene (39)	Propylbenzene (100)
Cyclohexene (22)	Cyclohexane (100)
Methyl-1-cyclohexene (10)	Methyl-1-cyclohexane (100)

Condition: catalyst precursor, 0.02 mmol; CTAC, 1 ml of aqueous solution (25% w/w); 1-hexene, 0.2 mmol; naphthalene, 0.1 mmol; *n*-heptane, 12 ml; water, 12 ml; temperature, 100 °C; H₂, 1000 psi; time, 6 h.

phase at the end of the reaction is detected; the initial yellow solution remains unchanged after the catalysis, an aspect not observed with the analogue W-TPPMS, where this complex showed changes in the color depending of the H₂ pressure, a fact that was correlated with the character homogeneous–heterogeneous displayed for this complex with this variable condition [9].

The effect of the substrate:catalyst ratio during the hydrogenation of 1-hexene was also studied. As is present in Table 3, this catalyst precursor shows high activity at substrate:catalyst ratio between 50 and 100 (Fig. 4).

After found the better reaction condition for the biphasic hydrogenation of 1-hexene which consist in a temperature: 100 °C, H₂ pressure: 1000 psi and substrate:catalyst ratio: 100, other substrate were hydro-

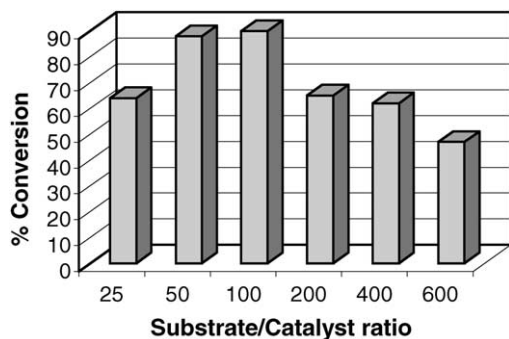
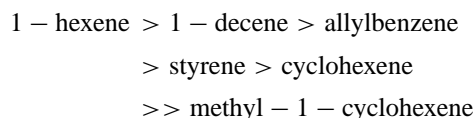


Fig. 4. Hydrogenation of 1-hexene as a function of the substrate:catalyst ratio. Condition: catalyst precursor, 0.02 mmol; CTAC, 1 ml of aqueous solution (25% w/w); 1-hexene, 0.2 mmol; naphthalene, 0.1 mmol; *n*-heptane, 12 ml; water, 12 ml; temperature, 100 °C; H₂, 1000 psi; time, 6 h.

genation at this reaction condition, were the results are present in Table 3. As can be seen in Table 3, for the case of 1-hexene and 1-decene, not appreciable isomerization was observed and allylbenzene is selectively converted to propylbenzene, cyclohexane to cyclohexane and styrene is hydrogenate to ethylbenzene. Methyl-1-cyclohexene is the hardest substrate to hydrogenate and only 10% is converted selectively to methyl-1-cyclohexane after 8 h of reaction.

At the end of each catalytic run, an efficient separation of the two phases is observed to give a colorless organic phase exclusively containing the organic products. No appreciable trace of tungsten species was detected by atomic absorption analysis of the organic phase.

The analysis of the results obtained, one may readily infer that the catalytic activity of (1) decreases in the order:



The results showed that this catalyst precursor is sensitive with the type of substrate employed. Consistently, 1-hexene and 1-decene are hydrogenated at different rates, which is commonly founded for the very hydrophobic 1-decene substrate even in the presence of a surfactant. In particular, it observed that the active specie should be more sterically congested than the catalyst generated by the analogue TPPMS complex which hydrogenates 1-hexene and 1-decene much faster than (1) [9].

This type of observation can be correlated with the rest of substrate. In the case the aryl olefin such as allylbenzene and styrene, the fact that the aryl substitute is close to the double bond may create a steric hindrance which allow some impediment for the coordination of the olefin to the tungsten center, which it is considered as a fundamental step for the hydrogenation process. This assumption is better observed when methyl-1-cyclohexene is used. This substrate has more steric congestion close to the double bond and this consideration can be take in account for the behavior observed in the catalysis. The results above confirm that steric demand close to the C=C bond has a remarkable influence on the activity of this catalyst precursor.

Finally, it is worth highlight the good hydrogenating activity exhibited by (**1**) towards different type of olefin. To the best of our knowledge, this is the first example of tungsten aqueous-biphasic hydrogenation of those substrates where this study opens a possibility to use this type of complex as a catalyst precursor for selective hydrogenation of different substrates.

4. Conclusions

The $W(CO)_3(CH_3CN)(TPPTS)_2$ behaves as an effective catalyst precursor for the aqueous-biphase hydrogenation of C=C double bonds of α -olefins in water-*n*-heptane mixture under moderate reaction conditions. The activity of this complex depends of the nature of the substrate; where steric effect has an influence on the behavior of this complex. Is demonstrated that the TPPTS ligand, maintain the molecular behavior in this complex, independently of the reaction condition used. The liquid-biphase character of the reactions allows one to easily separate the catalyst from the products.

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