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The biphasic regioselective hydrogenation of benzo[b]thiophene and quinoline catalyzed by Ru(II) species, deriving from the water soluble phosphine TPPTS (tris-*meta*-sulfonato-phenylphosphine) and stabilized by nitrogen donor ligands

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Abstract

The regioselective catalytic hydrogenation of benzo[b]thiophene (BT) and quinoline (Q) were carried out in a biphasic (water/decalin) medium using two ruthenium(II) complexes as catalyst precursors. These water soluble complexes were of the type $RuHCl(TPPTS)_2(L)_2$, (where L = 1,2,3,4-tetrahydroquinoline [THQ], **1**, or Aniline [An], **2**). The catalytic results from these precursors were compared with their analogue derivates from TPPMS (*meta*-sulfonato-phenyldiphenylphosphine in its sodium salt form) $RuHCl(TPPMS)_2(L)_2$ (L = THQ, **3** and An, **4**). In the biphasic hydrogenation of BT, the type of nitrogen donor ligand, as well as the type of phosphine, has an influence on the catalytic activity. This effect was not observed during the hydrogenation of quinoline. The only products detected during the hydrogenation of BT and Q were 2,3-dihydrobenzo[b]thiophene (DHBT) and 1,2,3,4-tetrahydroquinoline (THQ), respectively. No evidence of C–S or C–N bond cleavage were detected. In all the reactions, the catalyst precursors remained in the aqueous phase.

Keywords: Aqueous-biphasic catalysis; Hydrogenation; Ruthenium; Quinoline; Benzo[b]thiophene; Nitrogen donor ligands

1. Introduction

The reduction of nitrogen and sulfur containing aromatics is a reaction of great interest, because of the enormous application that it has in refining process. It is well known that benzo[b]thiophene (BT), together with thiophene (T) and some of their derivatives account for about 90% of the sulfur content in petroleum-derived fuels, such as naphtha and diesel [1]. Aromatic nitrogen-containing compounds are found in less quantity in fuels. However, this little amount can cause enormous problems. Nitrogen severely reduces the activity of a large number of refining processes, such as reforming, cracking, hydrocracking, hydrodesulfurization (HDS), hydrogenation and isomerization, besides creating problems attempting with the stability and quality of the fuels as well as being responsible for the production of atmospheric NO_x [2].

The removal of unwanted sulfur and nitrogen compounds in carried out industrially through the use of hydrotreating processes. However, conventional HDS

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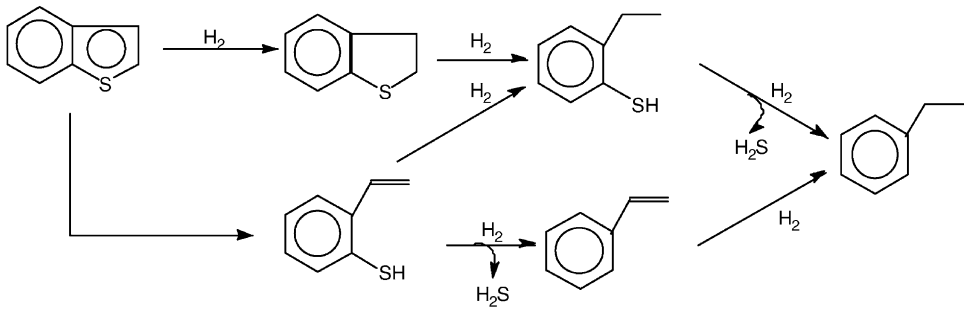

Scheme 1. Proposed mechanism for the desulfurization process of BT via heterogeneous catalysis [3].

and hydrodesnitrogenation (HDN) generally occurred together with many other reactions, such as aromatic saturation, olefin hydrogenation, hydrocracking, etc. [1]. These additional reactions tend to affect product quality by reducing octane and cetane number in the fuel [1].

In order to understand the actual mechanistic details in hydrotreating, one proposal is the study of the selective hydrogenation and hydrogenolysis of heteroaromatic compounds in a homogeneous medium [1,3]. This study may lead to relevant information for further understanding HDS and HDN mechanisms and give detailed information on chemical reaction pathways. A point of interest is to investigate whether the rupture of the C–S and C–N bonds (hydrogenolysis) occurs prior or subsequent to the hydrogenation of the heterocyclic rings on solid catalysts. While this information is not known, it is believed that is much easier to remove sulfur and nitrogen once the aromatic rings have been reduced via hydrogenation (Scheme 1) [3].

One way to study the hydrogenation of heteroaromatic compounds is through the use of transition metal complexes; because, they allow the use of spectroscopic techniques which are much easier to comprehend and handle [3]. A number of late transition metal complexes are known to catalyze the regioselective homogeneous hydrogenation of BT to DHBT and that of Q to THQ, and the mechanisms of such reactions have been investigated in detail [4,5]. Nevertheless, the separation problems commonly encountered in homogeneous processes [6,7] make this approach unattractive for application in petroleum-derived fuels. A possible way to overcome this problem, in the selective hydrogenation step, would be by using liquid-biphasic catalysis [8]. In this type of catalysis, the active species is immobilized in one of the two liquid phases (e.g. water) while the reactants and products are maintained in the other (naphtha), thus allowing a continuous flow process design and better understanding of the different steps involved [9].

We have previously reported the first example of the regioselective two-phase hydrogenation of BT to DHBT and Q to THQ. This hydrogenation was carried out by using an in situ mixture of $RuCl_3{\cdot}3H_2O$ with a six-fold excess of TPPMS (the sodium salt of *meta*-sulfonatophenyl-diphenylphosphine) in a water/decalin medium, together with a study of the influence of some organic nitrogen bases [9,10]. In this paper, we reported the regioselective hydrogenation of Q and BT in a two-phase liquid system catalyzed by the complexes $RuHCl(P)_2L_2$ where P is TPPMS or TPPTS, and L being THQ or An, as nitrogen donor ligands. Ru(II) species were observed as the main catalyst precursors in the in situ hydrogenation of heteroaromatic compounds [9,10].

2. Experimental section

2.1. General

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were dried and deoxygenated prior to use. The complexes $RuHCl(TPPMS)_2(THQ)_2$ (**3**), $RuHCl(TPPMS)_2(An)_2$ (**4**) $[RuHCl(TPPMS)_2]_2$, (**5**) were prepared according to literature procedure [10,11]. Mass spectrometry (MS) was recorded in ZAB BEQQ equipment, with EI and FAB (glycerol matrix) mode of ionization at

70 and 12 eV. The GC–MS analyses were done with a HP 5890 system (HP-1 column, 50 M; split injection of 1:50; $T_i = 60\,^{\circ}C$, time of 2 min for organic compounds, program of 10 °C/min; $T_f = 120\,^{\circ}C$). GC chromatograms were run on a Varian 3400 with FI detector (megabore type capillary column, 15 m; DB-5 phase; 1.5 u FT, J&W Scientific). Quantification was achieved by using the method of internal standard (cyclo-octane); the peaks were identified by comparison with authentic samples by GC–MS. NMR were run in a Bruker 300 and 400 MHz spectrometers, using deuterated solvents. H_3PO_4 and TMS were used as external standards. Atomic absorption analyses were performed with a Perkin-Elmer 5000 instrument.

2.2. Synthesis of $RuHCl(TPPTS)_2L_2$, where L = THQ (**1**), or An (**2**)

In a typical experiment, a water solution of $RuCl_3{\cdot}3H_2O$ (100 ml, 1.91 mmol) is placed in a Schlenk flask and a water solution of TPPTS (100 ml, 9.5 mmol) is added to the solution with constant stirring. Then L is added (THQ or An 1.6 mmol). The solution is kept under reflux for 6 h, under anaerobic conditions. After cooling, the resulted solution is evaporated to dryness and the solid dissolved in dry methanol. The alcoholic solution is filtered through celite and the solvent evaporated. The solid is washed with toluene (2×20 ml) giving a light green or brown precipitate in 75% yield. Data for complex $RuHCl(TPPTS)_2(THQ)_2$ (**1**): ^1H NMR (CD_3OD), THQ: 6.32 (t, $J = 5.8$ Hz, H_2), 4.44 (t, $J = 6.6$ Hz, H_3), 5.25 (t, $J = 5.7$ Hz, H_4), 8.30 (s, H_5), 8.33 (s, H_6), 8.51 (s, H_7), 8.55 (s, H_8), −11.30 (t, $J_{H-P} = 36$ Hz, Ru–H), 8.11–7.10 (M, TPPTS). $^{31}P\{^1H\}$ NMR (CD_3OD) AM system δ_A: 61.70; δ_M: 58.80 ($J_{p-p} = 35$ Hz). IR (Nujol mulls): 1193 cm^{-1}, br, m, $–SO_3$. FAB–MS (*m*-nitrobenzyl alcohol) (*z*/*e*): 1648 $[RuHCl(TPPTS)_2(THQ)_2 + H]^+$; 1515 $[RuHCl(TPPTS)_2(THQ) + H]^+$; 1382 $[RuHCl(TPPTS)_2 + H]^+$; 1346 $[Ru(TPPTS)_2 + H]^+$; 622; $[TPPTS\text{-}Na\ 2H_2O]^+$.

Data for complex $RuHCl(TPPTS)_2(An)_2$ (**2**): ^1H NMR (CD_3OD), 8.45 (m, aniline), 5.89 (t, $J = 6$ Hz, NH_2), −10.30 (t, $J_{H-P} = 37$ Hz, Ru–H), 8.11–7.10 (m, TPPTS). $^{31}P\{^1H\}$ NMR: 59.5 (s). IR (Nujol mulls): 1195 cm^{-1}, br, m, $–SO_3$. FAB–MS (*m*-nitrobenzyl alcohol) (*z*/*e*): 1565 $[RuHCl(TPPTS)_2(An)_2 + H]^+$; 1474 $[RuHCl(TPPTS)_2(An) + H]^+$; 1383 $[RuHCl(TPPTS)_2 + H]^+$; 1345 $[Ru(TPPTS)_2 + H]^+$; 622 $[TPPTS\text{-}Na\ 2H_2O]^+$.

2.3. Hydrogenation of BT and Q

In a typical experiment, a catalyst solution containing the complexes $RuHCl(P)_2(L)_2$ (6×10^{-3} M) in water (50 ml), and a decalin solution of BT or Q (50 ml, 0.15 M) were introduced into a glass-lined stainless steel autoclave (300 ml) from a PARR instrument, equipped with internal mechanical stirring, temperature control unit and a sampling valve. The reactor was purged with H_2 and then charged and heated to the desired pressure and temperature with constant stirring at 600 rpm. Samples of the reaction mixture were extracted periodically and analyzed by GC, using cyclo-octane as the internal standard, or by GC–MS.

3. Results and discussion

3.1. Synthesis of the complexes $RuHCl(TPPTS)_2(L)_2$ L = THQ (**1**), An (**2**)

The complexes $RuHCl(TPPTS)_2L_2$ are straightforwardly obtained as brown (THQ) and light green (An) powders by reacting $RuCl_3{\cdot}3H_2O$ with five-fold excess amount of TPPTS and the corresponding nitrogen donor ligand (THQ or An) in water, under refluxing conditions. The resulting compounds are air-stable and soluble in water and methanol. This solubility in water facilitates the easy use as catalytic precursors in aqueous catalysis.

The ^1H NMR spectrum of the $RuHCl(TPPTS)_2(THQ)_2$ (**1**) showed the signals characteristic of the THQ coordinate in the region between 4.3 and 8.5 ppm; the hydride signal is observed as a triplet centered at −11.30 ppm ($J_{H-P} = 36$ Hz) corresponding to a proton *cis* to two phosphorus atoms. The $^{31}P\{^1H\}$ NMR is represented by an AM system centered at 59.58 ppm (δ_A: 61.70; δ_M: 58.80; $J_{p-p} = 35$ Hz) for two phosphorus atoms *cis* to each other.

The coordination of the THQ to the Ru center was confirmed by NMR analysis of the patron observed for this complex because, the results obtained in this work are comparable with the results obtained earlier by Fish and co-workers [5d] for

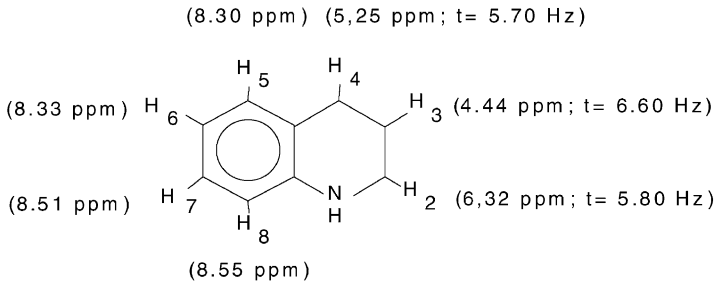

Fig. 1. ^{1}H NMR for the coordinated 1,2,3,4-THQ for the complex **1**.

Ru cyclopentadienyl complexes derivates of quinoline and 1,2,3,4-tetrahydroquinoline. They observed that the coordination of heterocycle THQ molecule is achieved via η^1-N, according to the signal displayed in the region between 4.4 and 6.4 ppm, characteristic for the heteroaromatic ring coordinated to a metal center [5d]. The signals corresponding to the THQ coordinated to complex **1** are shown in Fig. 1

On the basis of the ^{31}P{^{1}H}, ^{1}H NMR, FAB–MS analysis and the data reported for the analogue complex with TPPMS, RuHCl(TPPMS)$_2$(THQ)$_2$ [10], the complex RuHCl(TPPTS)$_2$(THQ)$_2$ (**1**) can be assigned the structure shown in Fig. 2. The Ru center has two phosphine and one THQ *cis* to the hydride while the other THQ is *trans* to hydride ligand. The fundamental of this structure is also supported according to earlier reports from the coordination chemistry of Ru(II) complexes involved in catalytic hydrogenation, where the catalytic cycles involve species close to the structure proposed for complex **1** [12,13].

Besides the AM system detected by ^{31}P NMR, corresponding to the main product, others signals were also observed; one for the oxide, OTPPTS (34.3 ppm) and another unidentified yet (28.8 ppm) both as very minor products.

For complex **2**, RuHCl(TPPTS)$_2$(An)$_2$, the ^{1}H NMR spectrum showed the characteristic signals of the An at 5.9 ppm which corresponds to the NH_2 moiety and at 8.5 ppm assigned to one protons from the aromatic ring of the aniline, respectively. The hydride signal is observed as a triplet centered at -10.30 ppm (J_{H-P} = 36 Hz) corresponding to a proton *cis* to two phosphorus atoms. The ^{31}P{^{1}H} NMR spectrum of RuHCl(TPPTS)$_2$(An)$_2$ (**2**), consists of a temperature-invariant singlet at d = 59.5 in D_2O and is quite coincident with the spectrum of the RuHCl(TPPMS)$_2$(An)$_2$ reported for us previously (singlet at 57.9 ppm in CD_3OD) [10]. Taking into account the ^{31}P{^{1}H} and ^{1}H NMR as well as the FAB–MS spectra, the complex RuHCl(TPPTS)$_2$(An)$_2$ (**2**) is assigned the structure shown in Fig. 3. In this drawing the Ru(II) center contains two phosphine *cis* to the hydride and both An ligands *cis* to the TPPTS ligands. Again, the basis of this postulation is in accordance to earlier reports concerning Ru(II) species present in previous catalytic hydrogenation studies [12,13].

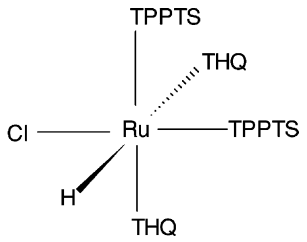

Fig. 2. Proposed structure for complex **1**.

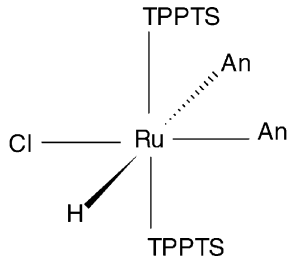

Fig. 3. Proposed structure for complex **2**.

Table 1
Benzo[b]thiophene hydrogenation catalyzed by the complexes $RuHCl(P_2)_2(L)_2$ P = TPPMS, TPPTS with L = THQ, An

Entry	Catalyst precursor	2,3-Dihydrobenzo[b] thiophene (% conversion)
1	$RuHCl(TPPTS)_2(THQ)_2$ (**1**)	46
2	$RuHCl(TPPTS)_2(An)_2$ (**2**)	61
3	$RuHCl(TPPMS)_2(THQ)_2$ (**3**)	84
4	$RuHCl(TPPMS)_2(An)_2$ (**4**)	98

Conditions: $T = 136\,^{\circ}C$, 35 atm H_2, substrate/catalyst ratio = 25, time = 8 h, mixture water (50 ml) and decalin (50 ml), 613 rpm.

3.2. Hydrogenation of benzo[b]thiophene

The complexes **1** and **2**, and their analogues with TPPMS $RuHCl(TPPMS)_2(THQ)_2$ (**3**) and $RuHCl(TPPMS)_2(An)_2$ (**4**) [10], were used as a catalyst precursors in the liquid-biphase hydrogenation of benzo[b]thiophene. The initial catalyst conditions were: $T = 136\,^{\circ}C$, $P\ (H_2) = 35$ atm, 1:1 mixture of water/decalin (Table 1). Under the experimental conditions reported, all four complexes were capable of catalyzing regioselectively the hydrogenation of 25 equivalent of the substrate. The only product detected was 2,3-dihydrobenzothiophene (DHBT) without any evidence of product derived from the of C–S bond cleavage.

As shown in Table 1, the complexes containing aniline (An) as a donor ligand, are more active in hydrogenation (entries 2 and 4) compared with THQ (entries 1 and 3). One other observation is that even though in entries 1 and 2, the ruthenium center has a very similar environment (one hydride, one chloride and two TPPTS ligands) the catalytic results shows that the aniline produces a more active species, probably by a best stabilization of the metallic center in comparison with the THQ ligand [10]. Other experiments are under investigation to study the effect of different nitrogen molecules and the results will be present in a future report.

Another interesting observation relates to the effect of the water soluble ligands; the TPPMS tends to give a more active role to the ruthenium, as a catalyst precursor in the regioselective hydrogenation of BT, than the TPPTS. This observation is in accordance with a recent report indicating that the TPPMS ligand has surface-active properties that facilitates the contact between the catalyst precursor and the substrate, during the hydrogenation of α-β-unsaturated compounds [14]. Those complexes containing the TPPTS ligand, like **1** and **2**, behave more as an electrolyte (high water solubility) in comparison with their TPPMS analogue **3** and **4**. The high water solubility shown by the TPPTS complexes held the molecule quite far from the interface during the catalytic reaction, and the poor solubility of the benzo[b]thiophene in water do not permit a very integrated mixing of substrate and precursor concluding in a poor hydrogenation. For this reason, complexes **3** and **4** showed the best activity in the hydrogenation of sulfur-containing aromatic molecules.

After each catalytic reaction, the organic phase was analyzed by atomic absorption analysis, were the results confirm the *no presence* of metal in the organic phase (solubility in organic phases is less that 1 ppm) showing that the complex remains in the aqueous phase.

3.3. Hydrogenation of quinoline

The catalytic activities of all four complexes were also investigated in the hydrogenation of quinoline. The results are summarized in Table 2.

The results showed that all of the catalyst precursors are extremely active in the selective reduction of quinoline to 1,2,3,4-THQ. In fact, most of them completed the reaction after reaching 2 h. Because quinoline has a high solubility in water as temperature increases, this substrate can be located not only at the interface but also in high concentration in the catalysts phase, helping the hydrogenation process [14]. The GC–MS analysis of the organic phase showed that 1,2,3,4-THQ was the only product, without any

Table 2
Quinoline hydrogenation reactions catalyzed by the complexes $RuHCl(P_2)_2(L)_2$ P = TPPMS, TPPTS L = THQ, An

Entry	Catalyst precursor	1,2,3,4-Tetrahydroquinoline (% conversion)
1	$RuHCl(TPPTS)_2(THQ)_2$ (**1**)	90
2	$RuHCl(TPPTS)_2(An)_2$ (**2**)	71
3	$RuHCl(TPPMS)_2(THQ)_2$ (**3**)	93
4	$RuHCl(TPPMS)_2(An)_2$ (**4**)	100

Conditions: $136\,^{\circ}C$, 35 atm H_2, substrate to catalyst ratio = 25, time = 2 h, mixture water (50 ml) and decalin (50 ml), 613 rpm.

evidence of products derived from the cleavage of the C–N bond. Also, the analyses by atomic absorption of this phase confirmed that less than 2 ppm of ruthenium was detected, indicating again that most of the metal remains in the aqueous phase.

3.4. Catalysts recycle

One very important aspect in catalysis is the possibility for reusing the catalyst several times, without major changes in the nature and activity [15]. Taking into account this fact, it is necessary to obtain evidences about the recycling properties of the complexes used in this work. In this sense, a set of experiment studying the stability of the complexes during the hydrogenation of quinoline was carried out in order to demonstrate the ability of those complexes as a catalyst for this reaction. Complex **1** was chosen as the catalyst precursor for four consecutive hydrogenation experiment runs. In each run, the water phase was *maintained and only the organic phase, containing the quinoline, was changed*. The results obtained in each set of experiment can be seen in Table 3.

As is shown in Table 3, this complex efficiently catalyzed the quinoline hydrogenation after four runs without mayor indication of activity dropping. This experiment clearly shows the recycling capabilities of this type of catalyst precursor in the hydrogenation of quinoline under biphasic conditions. Furthermore, at the end off this experiment, the catalytic phase was dried and the resulting solid was analyzed by NMR and the results showed the presence of the signals corresponding to the complex $RuHCl(TPPTS)_2(THQ)_2$ (**1**); from $^{31}P\{^1H\}$ NMR, AM system centered at 59.58 ppm (δ_A: 61.70; δ_M: 58.80; $J_{p-p} = 35$ Hz), from ^1H NMR, $d = 4.3$ and 8.5 ppm with the hydride signal as a triplet centered at −11.30 ppm ($J_{H-P} = 36$ Hz)]. These experimental results point out that effectively, the structure proposed for complex **1** remains as main promoter of the catalyst precursor in the hydrogenation cycle. A set experiments related to the coordination chemistry of the quinoline hydrogenation by water soluble ruthenium complexes is currently in progress, using high pressure NMR, and the results will published approximately [16].

Table 3
Quinoline hydrogenation catalyzed by the complex $RuHCl(TPPTS)_2(THQ)_2$ (**1**)

Run	1,2,3,4-Tetrahydroquinoline (% conversion)
1	90
2	90
3	89
4	88

Conditions: $T = 136\,^{\circ}C$, 35 atm H_2, substrate/catalyst ratio = 25, time = 2 h, mixture water (50 ml) and decalin (50 ml), 613 rpm.

4. Conclusions

The complexes $RuHCl(TPPTS)_2(THQ)_2$ (**1**) and $RuHCl(TPPTS)_2(An)_2$ (**2**) are effective catalysts precursors for the aqueous-biphase hydrogenation of quinoline and benzo[b]thiophene in a water/decalin mixture under moderate reaction conditions. In the hydrogenation of benzo[b]thiophene with complexes **1**, **2**, **3** and **4**, the catalytic activity has a strong dependence on the type of water soluble ligand as well as, on the nature of the nitrogen donor ligand used. The TPPMS complexes show better catalytic activity in comparison with their TPPTS analogues. In fact, the tensoactive properties of the TPPMS ligand facilitates the catalyst reduction of benzo[b]thiophene. During the hydrogenation of quinoline, it was demonstrated that complex **1**, can be recycled several times without indication of loosing its catalytic activity. In both hydrogenation reactions, only the corresponding hydrogenate products at the heteroaromatic ring was observed, without any indication of C–N or C–S bond cleavage.

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