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Ruthenium carbonyls as benzo[b]thiophene hydrodesulfurization catalysts in homogeneous phase

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Abstract

The catalytic activity of mononuclear and polynuclear ruthenium complexes in the benzo[b]thiophene (BT) hydrodesulfurization (HDS) has been tested in the temperature range between 150 and 170°C under 100 bar of hydrogen. The ruthenium complexes tested are shown to be catalytically active in the hydrogenation of BT to 2,3-dihydrobenzo[b]thiophene (DHBT) and 2-ethylthiophenol. The best performance was provided by $H_4Ru_4(CO)_8(PPh_3)_4$ when working at 170°C: In these conditions BT is hydrogenated to DHBT with a conversion of 38.2% after 96 h or 81.2% after 384 h. Ethylbenzene (conversion 4.9%) is also formed confirming that a complete HDS of the substrate (even if in a low amount) may be obtained. The addition of a strong base (^{t}BuOK) as a co-catalyst changes the chemioselectivity of the reaction. The mononuclear complexes are less active than the cluster ones. BT is in fact converted to DHBT up to 19.5% in the presence of $Ru(CO)_3(PPh_3)_2$ under the same conditions. These data show that this reaction is promoted by the cooperation of several metal atoms in the catalytic intermediates.

Keywords: Hydrodesulfurization; Ruthenium carbonyl; Homogeneous catalysts; Benzo[b]thiophene complexes; Phosphine substituted

1. Introduction

Gasoline hydrodesulfurization (HDS) is a unavoidable pre-treatment of petroleum feedstocks that have to be submitted to catalytic reforming to prevent deactivation of the catalyst, or in general to transform gasoline in a fuel with reduced SO_x pollutant emission. HDS is usually carried out industrially in heteregeneous phase using several catalysts based on Mo and W sulphides containing also other metals such as Co, Rh, Ir, Ru, Ni, Os as activators [1].

With the aim of studying the role played by the above metals used as promoters and to individuate more efficient catalysts leading to the lower sulfur content that will be required in the next generation of fuel, we have investigated the catalytic HDS process in homogeneous phase. Up to now, Ir and Rh [2] complexes have been investigated as catalysts in homogeneous phase in this reaction while the role played by Ru complexes is scarcely known [3], even if this metal has been reported as one of the most active co-catalysts in this reaction in heterogeneous phase [4]. Very recently Bianchini [5] reported a very efficient ruthenium catalyst for the hydrogenation of benzo[b]thiophene (BT) to 2,3-dihydrobenzo[b]thiophene (DHBT) in homogeneous phase.

We have now tested as BT hydrodesulfurization catalysts several ruthenium complexes that are catalytically active in the hydrogenation of organic unsaturated substrates [6]. These compounds are mononuclear or cluster carbonyl and hydrocarbonyl complexes of Ru(0), Ru(I), and Ru(II), containing phosphinic ligands such as PBu_3 or PPh_3.

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BT has been chosen as substrate to correlate our results with those reported in the literature on this compound and because it is one of the most difficult products to eliminate through the HDS process.

The reaction of BT with hydrogen leads through hydrogenation to DHBT or through hydrogenolysis to vinylthiophenol (VTP) as reported in Scheme 1 [2b]. These products may give further reactions in the course of the process, up to the formation of ethylbenzene (EB) and H_2S, that is the HDS reaction.

2. Results

2.1. Mononuclear ruthenium complexes

The mononuclear ruthenium complexes tested were $Ru(CO)_3(PPh_3)_2$ (**1**), $Ru(CO)_3(PBu_3)_2$ (**2**), $H_2Ru(CO)_2(PPh_3)_2$ (**3**), $H_2Ru(CO)_2(PBu_3)_2$ (**4**). The results for the HDS of BT are reported in Table 1.

The hydrogenation of BT in the presence of the above ruthenium complexes gives DHBT as the main product, while 2-ethylthiophenol (ETP) is formed in a very low yield (less than 1% conversion, Table 1).

At 150°C after 212 h the hydrido ruthenium complex **3** gives the best result among the mononuclear catalysts tested with a conversion of 14.0%. At 170°C after 106 h an higher conversion (19.5%) has been obtained working in the presence of **1**.

The mononuclear ruthenium complexes containing PBu_3 as ligand are usually less active than the corresponding complexes with PPh_3. A conversion of 2.7% has been achieved in the presence of **4** after 106 h at 150°C while in the presence of **3** the conversion reached is 7.6%.

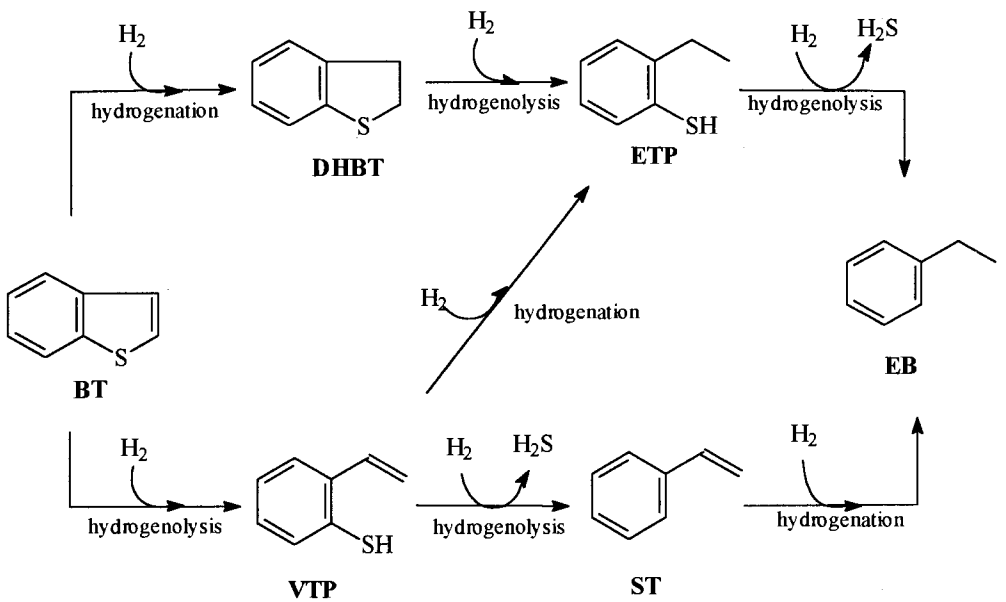
The PBu_3-containing complexes are also less selective because along with the hydrogenation product DHBT the compound of hydrogenolysis ETP is formed, even if the HDS product EB is never present in the tests reported (Table 1).

2.1.1. Identification of the ruthenium complexes present in the reaction crude

The solution collected at the end of the hydrogenation of BT in the presence of **2**, (reaction time 5 h, reaction temperature 150°C) was distilled at reduced pressure to eliminate the solvent. The residue was dissolved in C_6D_6 and analyzed by ^{1}H- and ^{31}P-NMR. In the ^{31}P-NMR spectrum three singlets are present. The singlet of low intensity at δ 33.9 ppm is attributed to the starting complex **2**, the second singlet of high intensity at δ 33.3 ppm is assigned to **4** and the third resonance of low intensity at 23.8 ppm may be tentatively attributed to $Ru(CO)_2(O_2)(PBu_3)_2$. This product may be formed in the working up of the solution in agreement with the formation of $Ru(CO)_2(O_2)(PPh_3)_2$ [7]. Another weak signal at δ 25.5 ppm is also present but it was not possible to attribute it. The presence of **4** was confirmed by a triplet at δ −7.73 ppm (J_{HP} 24.3 Hz) in the hydride region of the ^{1}H-NMR spectrum.

2.2. Polynuclear ruthenium complexes

The complexes tested as catalytic precursors are the trinuclear compound $Ru_3(CO)_9(PPh_3)_3$ (**5**) and the tetranuclear ruthenium hydrides $H_4Ru_4(CO)_8(PPh_3)_4$ (**6**), and $H_4Ru_4(CO)_8(PBu_3)_4$ (**7**). The results of the HDS of BT are reported in Table 2.



Scheme 1.

Table 1
Hydrogenation of BT to DHBT and ETP in the presence of mononuclear Ru(0) and Ru(II) complexes[a]

Complex	Code	T/°C	BT conversion (%) after											
			29 h			53 h			106 h			212 h		
			DHBT	ETP	Sel[b]	DHBT	ETP	Sel[b]	DHBT	ETP	Sel[b]	DHBT	ETP	Sel[b]
$Ru(CO)_3(PPh_3)_2$	**1**	150	n.d.	n.d.		1.0	–	> 99	4.6	–	>99	6.6	–	>99
$Ru(CO)_3(PPh_3)_2$	**1**	170	1.7[c]	0.3[c]	85.0[c]	12.3	0.7	94.6	19.5	0.8	96.1	n.d.	n.d.	
$Ru(CO)_3(PBu_3)_2$	**2**	150	0.5	0.2	71.4	0.6	0.3	66.7	2.5	0.4	86.2	4.3	0.6	87.7
$H_2Ru(CO)_2(PPh_3)_2$	**3**	150	3.5	–	>99	4.3	–	>99	7.6[d]	<0.1[d]	98.7[d]	14.0[e]	<0.1[e]	>99[e]
$H_2Ru(CO)_2(PBu_3)_2$	**4**	150	n.d.	n.d.		n.d.	n.d.		2.7[d]	0.3[d]	90.0	n.d.	n.d.	

[a] Benzene 10 ml. Catalyst (mol of Ru); 5.85×10^{-5}. BT/Ru: 100:1 molar ratio. pH_2: 100 bar. BT, benzo[b]thiophene; DHBT, 2,3-Dihydrobenzo[b]thiophene; ETP, 2-Ethylthiophenol; n.d., not determined.
[b] Sel = Selectivity (%) = DHBT*100/(DHBT + ETP).
[c] 31 h.
[d] 96 h.
[e] 192 h.

The hydridoruthenium clusters are more active than the mononuclear complexes. At 150°C **6** has the highest activity. Furthermore at 170°C after 384 h, in the presence of **6**, BT is converted into DHBT by an 81.2% conversion that is with a turn-over frequency of 21 h^{-1}. EB is also formed (4.9% conversion, turnover frequency of 1 h^{-1}), corresponding to the HDS of the substrate.

The amount of ETP formed, in the presence of cluster ruthenium catalysts, was always lower than 0.1%.

The PPh_3 substituted hydridoruthenium clusters are catalytically more active than those containing PBu_3 as in the case of the mononuclear ruthenium complexes.

The higher activity displayed by cluster ruthenium catalysts if compared with that of the mononuclear complexes is in line with the hypothesis, reported for heterogeneous catalysis, that the HDS process is promoted by a cooperative effect of several metal atoms.

2.3. Polynuclear ruthenium complexes in the presence of a strong base

A strong base present as co-catalyst in this reaction can change to a large extent the catalytic activity of the ruthenium complexes. In fact the base may react with the reaction products or it may lead to the formation of a different specie from the catalytic precursor.

When the tetranuclear ruthenium clusters **6** or **7** have been employed in the presence of potassium *tert*-butoxide (^{t}BuOK) as co-catalyst, the chemioselectivity of the reaction has been completely modified, the main reaction product being ETP instead of DHBT. Furthermore, in the conditions adopted the PBu_3 containing complex showed a higher catalytic activity than the corresponding PPh_3 derivative, contrary to the results obtained in the absence of the co-catalyst. Several factors seem to play a role in this reaction. In fact the strong base may act for opening the saturated ring of DHBT through a base-assisted process [5] or the increasing reactivity of **7** may be attributed to the formation of an anionic species such as $[H_3Ru_4(CO)_8(PBu_3)_4]^-$.

2.4. Synthesis and reactivity of some ruthenium complexes

Mononuclear ruthenium complexes containing BT as ligand were synthesized and reacted with hydrogen to investigate their eventual role in the hydrogenation of BT itself (Table 3).

2.4.1. Synthesis of $Ru(CO)_2(BT)(PPh_3)_2$ (**8**)

2.4.1.1. From $Ru(CO)_2(CH_2{=}CHCN)(PPh_3)_2$ and BT. $Ru(CO)_2(CH_2{=}CHCN)(PPh_3)_2$, prepared as reported in the literature [7], was dissolved in benzene and BT (molar ratio BT:Ru = 3:1) was added. The solution was kept at room temperature for 18 h. The product formed was precipitated using pentane and characterized by spectroscopic methods. In the IR spectrum two strong bands are present in the carbonyl stretching region. Only one resonance is present in the ^{31}P-NMR spectrum in agreement with equivalent phosphine ligands. In the ^{13}C-NMR spectrum a triplet at δ 200.1 ppm may be attributed to the coupling of the carbonyl groups with two equivalent phosphine ligands. According to these data it is possible to attribute to this complex a structure having the two carbonyl groups in *cis* and the two phosphines in *trans* position. BT is found to be coordinated to the ruthenium center through its sulfur atom. In fact

Table 2
Hydrogenation of BT to DHBT and ETP in the presence of cluster ruthenium complexes[a]

Complex	Code	T/°C	BT conversion (%) after											
			24 h			96 h			192 h			384 h		
			DHBT	ETP	Sel[b]	DHBT	ETP	Sel[b]	DHBT	ETP	EB	Sel[b]	DHBT	ETP	EB	Sel[b]
$Ru_3(CO)_9(PPh_3)_3$	**5**	150	0.3	–	100	10.9	<0.1	>99	20.1	<0.1	–	>99	n.d.	n.d.	n.d.	
$H_4Ru_4(CO)_8(PPh_3)_4$	**6**	150	4.2	<0.1	>98	8.2	<0.1	98.8	23.5	<0.1	–	>99	42.8	<0.1	–	>99
$H_4Ru_4(CO)_8(PPh_3)_4$	**6**	170	4.7	<0.1	>98	38.2	<0.1	>99	54.6	<0.1	1.4	97.3	81.2	<0.1	4.9	94.2
$H_4Ru_4(CO)_8(PBu_3)_4$	**7**	150	2.6	<0.1	>96	5.7	<0.1	98.3	8.2	<0.1	–	98.8	n.d.	n.d.	n.d.	

[a] Benzene 10 ml. Catalyst (mol of Ru): 5.85×10^{-5}. BT/Ru: 100:1 molar ratio. pH_2: 100 bar. BT, benzo[b]thiophene; DHBT, 2,3-dihydrobenzo[b]thiophene; ETP, 2-ethylthiophenol; EB, ethylbenzene; n.d., not determined.
[b] Sel = Selectivity (%) = DHBT*100/(DHBT + ETP + EB).

small differences in the ^{1}H- and ^{13}C-NMR chemical shifts of coordinated and free BT are found.

*2.4.1.2. From $H_2Ru(CO)_2(PPh_3)_2$ (**3**) and BT.* To a benzene solution of **3**, prepared as previously reported [8], BT (molar ratio BT:Ru = 3:1) was added and the solution kept at room temperature for 20 h. After the addition of pentane a residue was separated which provided the same spectroscopic data of the compound **8** described above.

*2.4.2. Synthesis of $Ru(CO)_2(BT)(PBu_3)_2$ (**9**)*

BT was added to a benzene solution of $H_2Ru(CO)_2(PBu_3)_2$ (**4**) (molar ratio BT:Ru = 3:1), prepared as reported in the literature [6a], and kept at room temperature for 120 h. The solvent was then evaporated to dryness and the residue analyzed by spectroscopic methods. According to these data, consistent with those described for **8** and reported in Section 4, the product $Ru(CO)_2(BT)(PBu_3)_2$ (**9**) has a structure analogous to that attributed to $Ru(CO)_2(BT)(PPh_3)_2$ (**8**).

*2.4.3. Reaction of $Ru(CO)_2(BT)(PPh_3)_2$ (**8**) with H_2*

A benzene solution of **8** was kept under hydrogen (5 atm) at 50°C for 18 h. A partial transformation of **8** into the dihydridoruthenium complex **3** and BT was noticed indicating the existence of an equilibrium (Eq. (1)):

$$Ru(CO)_2(BT)(PPh_3)_2 + H_2 \rightleftharpoons H_2Ru(CO)_2(PPh_3)_2 + BT \quad (1)$$

Reaction of $Ru_3(CO)_9(PPh_3)_3$ (**5**) with BT

A benzene solution of $Ru_3(CO)_9(PPh_3)_3$ (**5**) [9] and BT (molar ratio BT:Ru = 5:1) was heated at reflux temperature for 24 h. A red product, among others, was isolated and characterized but it was the known complex $Ru_3(CO)_7(\mu^3\text{-}C_6H_4)(\mu\text{-}PPh_2)_2$ [10].

3. Discussion and conclusions

In all the experiments performed, the benzene ring of BT is not hydrogenated in the catalytic process. Also the benzene used as solvent is recovered unaltered at the end of the reaction. This is an interesting observation, by an industrial point of view, because the HDS process is generally performed as a pre-treatment of the catalytic reforming. Reforming is carried out to increase the octane number of gasoline and therefore the preservation of the aromatic content of the feed in the HDS pre-treatment is important to maintain high this parameter. Furthermore hydrogen is saved if the hydrogenation of aromatics does not take place.

A reaction mechanism is suggested for the mononuclear ruthenium complexes (Scheme 2) in consideration of the following data:

Table 3
Hydrogenation of BT to DHBT and ETP in the presence of cluster ruthenium complexes and ^{t}BuOK[a]

Complex	Code	T/°C	BT conversion (%) after			
			24 h	48 h		96 h
			ETP	DHBT	ETP	ETP
$H_4Ru_4(CO)_8(PPh_3)_4$	**6**	150	3.3	–	7.6	8.5
$H_4Ru_4(CO)_8(PBu_3)_4$	**7**	150	n.d.	2.2	43.1	n.d.

[a] Benzene 10 ml. Catalyst (mol of Ru): 5.85×10^{-5}. BT/Ru: 100:1 molar ratio. ^{t}BuOK/BT: 1:1 molar ratio. pH_2: 100 bar. BT, benzo[b]thiophene; DHBT, 2,3-dihydrobenzo[b]thiophene; ETP, 2-ethylthiophenol; n.d., not determined.

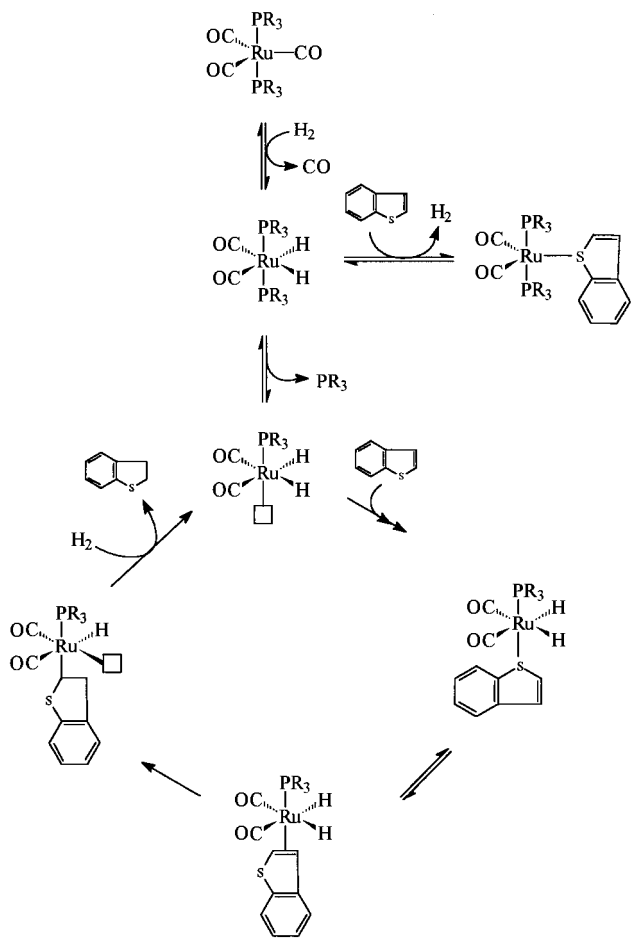
- $H_2Ru(CO)_2(PBu_3)_2$ (**4**) is present in the reaction mixture obtained when $Ru(CO)_3(PBu_3)_2$ (**2**) is used as catalytic precursor.
- $Ru(CO)_2(BT)(PPh_3)_2$ (**8**), which has been synthesized separately, reacts with hydrogen restoring the dihydrido complex $H_2Ru(CO)_2(PPh_3)_2$ (**3**) and BT. An analogous behavior was shown by the PBu_3 derivatives. Complexes like **8** therefore seem not to be involved in the catalytic cycle of the HDS reaction.
- The catalytic activity of $Ru(CO)_3(PPh_3)_2$ (**1**) is lower than that of $H_2Ru(CO)_2(PPh_3)_2$ (**3**).
- The higher activity of the PPh_3 containing complexes is in agreement with the more easy displacement of the less basic phosphine ligand.

In Scheme 2 a phosphine ligand is displaced in **3** or **4** with formation of a coordination vacancy at the ruthenium atom. An alternative pathway involving the loss of dihydrogen was ruled out in consideration of the results above reported using pure samples of **8** and **9**. The BT may approach the metal using either the sulfur atom or the C2–C3 double bond [2b,2c,11]. The η^2-metal complex undergoes stepwise selective hydrogenation of the C2=C3 double bond through a hydrido-benzothienyl complex that reacts with hydrogen to give DHBT and restore the dihydridoruthenium complex. A similar hypothesis has been reported by Herrera et al. [12]. An alternative pathway that involves the insertion of the metal into the C–S bond of BT is not in agreement with the results that only DHBT is the main reaction product. Furthermore the insertion of the metal into the C–S bond is never observed for d^6 metal ions such as Ru(II).

Regarding the catalytic activity of the cluster complexes we can not formulate any hypothesis at this time. A benzene solution of $Ru_3(CO)_9(PPh_3)_3$ (**5**) was heated at reflux temperature in the presence of BT but complexes containing BT were not identified among the reaction products. Heating a solution of BT and $Ru_3(CO)_9(PPh_3)_3$ (**5**) the ruthenium cluster $Ru_3(CO)_7(\mu^3\text{-}C_6H_4)[\mu\text{-}P(C_6H_5)_2]_2$ [10] was isolated and characterized. Instead of that, heating the $Ru_3(CO)_9(PPh_3)_3$ (**5**) solution at 100°C in the presence of hydrogen $H_4Ru_4(CO)_{10}(PPh_3)_2$ and $H_4Ru_4(CO)_9(PPh_3)_3$ were formed [13]. Further work is necessary to identify the ruthenium complexes involved in these reactions.

When the HDS reaction is performed in the presence of cluster ruthenium hydrides and a strong base, ETP is formed as the main product: no EB was found. Two possible ways may be involved:

- Hydrogenation of BT to DHBT and a subsequent opening of the heterocycle ring by the strong base [14].



Scheme 2.

- Modification of the ruthenium complex to form a different catalyst having a different behavior.
- In our opinion the second process is the most likely to occur, considering that:
- An higher catalytic activity is shown by the tributylphosphine derivative if compared with the triphenylphosphine complex;
- if the strong base would act on the heterocycle ring, an appreciable amount of the unreacted DHBT might be present among the products.

A possible way is the reaction of the ruthenium hydride with the strong base to form an anionic ruthenium complex such as $[H_3Ru_4(CO)_8(PPh_3)_4]^-$ (Eq. (2)). An analogous compound $[H_3Ru_4(CO)_{12}]^-$ was obtained from $H_4Ru_4(CO)_{12}$ and KOH [15]. Some anionic complexes are reported to be very efficient catalyst in the hydrogenation of carboxylic acid esters [16].

$$H_4Ru_4(CO)_8(PR_3)_4 + {}^tBuO^- \rightleftarrows H_3Ru_4(CO)_8(PR_3)_4^- + {}^tBuOH \quad (2)$$

This new complex may react with the BT substrate (Scheme 3) to give an η^1-S complex. The complex involving the same or a different ruthenium atom may lead to a ruthenium insertion into the C–S bond to give a η^2-benzothiophene derivative that undergoes hydrogenation of the C=C bond to produce an ETP salt and restore the starting hydridoruthenium complex. The formation of an η^2-alkylthioderivative of osmium has been reported by Spera and Harman from an Os(II) η^2-thiophene complex [17]. An analogous mechanism has been recently reported for an anionic mononuclear ruthenium complex [18].

4. Experimental

Quantitative analyses of the reaction products were performed by GC using a Perkin–Elmer model 1022, Autosystem Gas-Chromatograph, equipped with a FFAP column (i.d. 1/8'', length 2 m). In consideration of the analogy of the products examined, no correction factors were introduced. The identity of the products was confirmed by GC-MS using a Shimadzu apparatus having a GC14A capillary column chromatograph and a QP2000 system mass detector. The chromatograph was equipped with a CP-Sil8 50 m capillary column. A Perkin–Elmer SCIEX API 365 having a turbo ion spray system was employed to obtain the MS spectra of the ruthenium complexes. Elemental analyses were performed using a Perkin–Elmer model 2400 Series II elemental analyzer.

IR spectra were recorded with a Perkin–Elmer 1760-X FT-IR spectrometer.

^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra were recorded using a Varian VXR300 spectrometer operating at 299.987 MHz for ^{1}H, at 75.429 MHz for ^{13}C and at 121.421 MHz for ^{31}P-NMR, using solutions in $CDCl_3$, CD_2Cl_2 or C_6D_6; $SiMe_4$ was used as external standard for ^{1}H-NMR and ^{13}C-NMR, H_3PO_4 (85%) for ^{31}P-NMR (signals reported as positive downfield of the standard).

Solvents (benzene, diethyl ether, cyclohexane) were dried according to Vogel [19]. Benzo[b]thiophene: the Aldrich product was crystallized from cooled pentane; the product had mp 32°C.

Other reagents were commercial products and used without further purification.

The following catalysts were prepared according to the reported method, their spectroscopic characteristics were in agreement with the data reported: $Ru(CO)_3(PPh_3)_2$ [9] (**1**), $Ru(CO)_3(PBu_3)_2$ [20] (**2**), $H_2Ru(CO)_2(PPh_3)_2$ [8] (**3**), $H_2Ru(CO)_2(PBu_3)_2$ [6a] (**4**), $Ru_3(CO)_9(PPh_3)_3$ [9] (**5**), $H_4Ru_4(CO)_8(PPh_3)_4$ [13] (**6**), $H_4Ru_4(CO)_8(PBu_3)_4$ [13] (**7**), $Ru(CO)_2(CH_2{=}CHCN)(PPh_3)_2$ [7].

4.1. Catalytic tests

4.1.1. General procedure

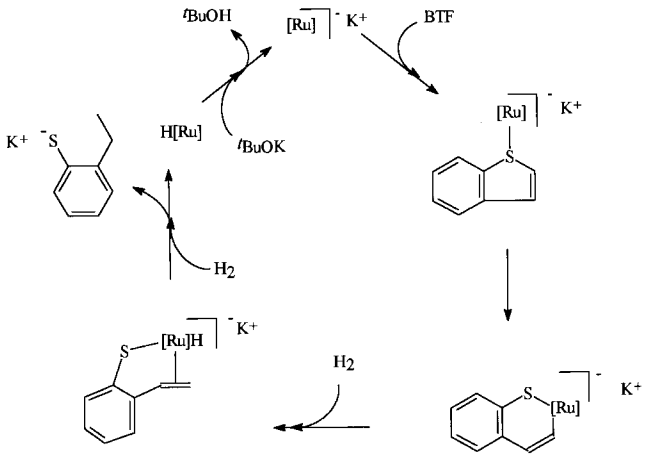
As an example of the general procedure used, the hydrogenation in the presence of **6** at 170°C is reported.

In a glass vial 24.70 mg (0.0588 mmol Ru) of **6** and 0.7844 g (5.84 mmol) of BT were introduced. The vial was placed in a stainless steel autoclave in which a nitrogen atmosphere was present. Anhydrous benzene (10 ml) was added, the autoclave was sealed and pressurized with hydrogen up to 100 bar at room temperature. The apparatus was placed in an oil bath heated at 170°C and mixed by swinging. Samples of the solution were collected after 24, 72, 96, 192 and 384 h. On each sample a GC analysis was performed using a FFAP column in the following conditions: 40°C for 15 min then heated up to 70°C at a rate of 10°C min^{-1} and kept at this temperature for 15 min then heated up to 180°C at a rate 10°C min^{-1} and kept at this temperature for 15 min. On the same solution a GC-MS analysis were performed to confirm the identity of the products, using the CP-SIL8 capillary column in the following conditions: kept at 40°C for 15 min then heated up to 70°C at a rate of 5°C min^{-1} and kept at this temperature for 15 min then heated up to 180°C at a rate of 10°C min^{-1} and kept at this temperature for 15 min.

DHBT, ETP, and unreacted BT were present in the solution. In the samples, collected after a reaction time of 192 and 384 h, EB was also present.

4.1.2. DHBT identification

MS m/z (%): 136 (79) $[M]^+$, 135 (100) $[M-H]^+$, 91 (11) $[C_7H_7]^+$, 77(5) $[C_6H_5]^+$ according to the data reported [21].



Scheme 3.

^{1}H-NMR (C_6D_6 as solvent) δ 7.15–6.80 (m, 4H, H_{arom}), 2.7767, 2.7760, 2.7080, 2.7079 (AA′BB′ pattern, 4H, CH_2, $J_{AA'} = J_{BB'} = 0.1$ Hz, $J_{AB} = J_{A'B'} = 8.0$ Hz, $J_{AB'} = J_{A'B} = 8.1$ Hz; through simulation) ppm.

4.1.3. EB identification

MS m/z (%): 106 (35) $[M]^+$, 105 (5) $[M-H]^+$, 104 (4) $[M-H_2]^+$, 91 (100) $[C_7H_7]^+$, 78 (10) $[C_6H_6]^+$, 77 (10) $[C_6H_5]^+$, 65 (5) $[C_5H_5]^+$, 51 (20) $[C_4H_3]^+$, 39 (15) $[C_3H_3]^+$ according to the data reported [22].

^{1}H-NMR ($CDCl_3$ as solvent) δ 7.30–7.10 (m, 5H, H_{arom}), 2.63 (q, 2H, CH_2CH_3, $J_{HH} = 7.5$ Hz), 1.23 (t, 3H, CH_2CH_3, $J_{HH} = 7.5$ Hz) ppm according to those reported [23].

^{13}C-NMR (CD_2Cl_2 as solvent) δ 144.2 (s, C_{ipso}), 128.3 (s, C_{arom}), 127.8 (s, C_{arom}), 125.5 (s, C_{arom}), 28.9 (s, CH_2CH_3), 15.6 (s, CH_2CH_3) ppm according to those reported [23].

4.2. BT hydrogenation in the presence of ^{t}BuOK

The reaction was carried out as reported in the previous paragraph, except for adding to the reaction mixture ^{t}BuOK (molar ratio BT/^{t}BuOK = 1:1). At the end of the reaction the gas was vented, the solution recovered was acidified with diluted H_2SO_4 (1:1) up to the dissolution of the solid present. The solution was extracted with diethyl ether (three times) and the organic phases collected together. The organic solution was analyzed by GC and GC-MS. With the aim to characterize ETP the solution was treated with a solution of NaOH (10%) up to pH 14 then extracted with diethyl ether. The aqueous solution was acidified with diluted H_2SO_4 (1:1) up to pH 0 and extracted with diethyl ether. After the distillation of the solvent the ETP was collected (bp 210°C [24]) and analyzed by GC, GC-MS, ^{1}H- and ^{13}C-NMR.

4.3. ETP identification

MS m/z (%): 138 (100) $[M]^+$, 123 (98) $[M-CH_3]^+$, 105 (49) $[M-SH]^+$, 77 (40) $[C_6H_5]^+$, 45 (33) $[CSH]^+$.

^{1}H-NMR (CD_2Cl_2 as solvent) δ 7.40–7.00 (m, 4H, H_{arom}), 3.45 (s, 1H, SH), 2.70 (q, 2H, CH_2CH_3, $J_{HH} = 7.5$ Hz), 1.25 (t, 3H, CH_2CH_3, $J_{HH} = 7.5$ Hz) ppm according to those reported [23].

^{13}C-NMR (CD_2Cl_2 as solvent) δ 142.7 (s, C2), 131.2 (s, C_{arom}), 131.1 (s, C1), 129.4 (s, C_{arom}), 127.3 (s, C_{arom}), 126.9 (s, C_{arom}), 28.3 (s, CH_2CH_3), 14.5 (s, CH_2CH_3) ppm in agreement with those reported [23].

4.4. Synthesis and reactivity of ruthenium complexes

4.4.1. Synthesis of $Ru(CO)_2(BT)(PPh_3)_2$ (**8**)

4.4.1.1. From $Ru(CO)_2(CH_2{=}CHCN)(PPh_3)_2$ and BT. To a benzene solution (20 ml) of $Ru(CO)_2(CH_2{=}CHCN)(PPh_3)_2$ (200 mg), BT (molar ratio BT/Ru = 3:1) was added. The solution was left at room temperature for 18 h. The addition of pentane to the solution caused the precipitation of $Ru(CO)_2(BT)(PPh_3)_2$. The residue was crystallized from benzene-pentane giving the product in 80% yield.

IR (benzene solution) in the 2200–1500 cm^{-1} region: 2007(s), 1942(vs) cm^{-1}; ^{31}P-NMR (C_6D_6 solution) a singlet at δ 38.0 ppm; ^{1}H-NMR (C_6D_6 solution) δ 7.90–7.70 (m, 26 H, H_{arom}), 7.30–6.90 (m, 10 H, H_{arom}) ppm; ^{13}C-NMR (CD_2Cl_2 solution) δ 199.5 (t, CO, $J_{CP} = 11.0$ Hz), 138.5(s, C-BT), 137.9 (s, C–BT), 134.5 (t, C_o–PPh_3, $J_{CP} = 5.5$ Hz), 132.4 (s, CH–BT), 132.3 (s, 2C, CH–BT), 131.5 (t, C_{ipso}–PPh_3, $J_{CP} = 23.5$ Hz), 130.8 (s, C_p–PPh_3), 129.0 (s, CH–BT), 128.8 (s, CH–BT), 128.6 (t, C_m–PPh_3, $J_{CP} = 5.0$ Hz) ppm. The PPh_3 resonances overlap the last CH–BT resonance.

MS m/z (%): 681 (90) $[M-BT]^+$, 653 (80) $[Ru(CO)(PPh_3)_2]^+$, 625 (100) $[Ru(PPh_3)_2]^+$, 548 (10) $[Ru(PPh_3)(PPh_2)]^+$ (centers of each ruthenium cluster peaks are reported). Elemental analysis, for $C_{46}H_{36}O_2P_2RuS$:% C 67.3 (67.72),% H 4.5 (4.45).

*4.4.1.2. From $H_2Ru(CO)_2(PPh_3)_2$ (**3**) and BT.* To a benzene solution (20 ml) of (**3**) (200 mg), BT (molar ratio BT:Ru = 3:1) was added and the solution left at room temperature for 20 h. After the addition of pentane a residue was separated, having the same spectroscopic data of the compound **8** described above.

4.4.2. Synthesis of $Ru(CO)_2(BT)(PBu_3)_2$ (**9**)

To a benzene solution (20 ml) of $H_2Ru(CO)_2(PBu_3)_2$ (**4**) (200 mg), BT (molar ratio BT:Ru = 3:1) was added at room temperature and the solution left stand for 120 h. The solvent was evaporated to dryness and the residue analyzed by spectroscopic methods.

IR (benzene solution) in the 2200–1500 cm^{-1} region: 1992(s), 1922(vs) cm^{-1}; ^{31}P-NMR (CD_2Cl_2 solution) a singlet at δ 22.0 ppm; ^{1}H-NMR (CD_2Cl_2 solution) δ 7.90–7.60 (m, 2 H, H_{arom}), 7.40–7.10 (m, 4 H, H_{arom}), 1.65 (s, 12 H, PCH_2), 1.35 (s, 24 H, $CH_2CH_2CH_3$), 0.90 (s, 18 H, CH_3), ppm; In the ^{13}C-NMR (CD_2Cl_2 solution) δ 199.5 (t, CO, $J_{CP} = 11.4$ Hz), 140.1 (s, C_{arom}), 140.0 (s, C_{arom}), 128.7 (s, CH_{arom}), 126.7 (s, CH_{arom}), 124.5 (s, CH_{arom}), 124.2 (s, CH_{arom}), 124.0 (s, CH_{arom}), 122.8 (s, CH_{arom}) ppm. The resonances of the PBu_3 ligand are present in the usual range between δ 30 and 14 ppm. These data are in agreement with the formulation $Ru(CO)_2(BT)(PBu_3)_2$ (**9**).

MS m/z (%): 696 (1) $[M]^+$, 668 (2) $[M-CO]^+$, 640 (2) $[M-2CO]^+$, 562 (50) $[M-BT]^+$, 534 (100) $[Ru(CO)(PBu_3)_2]^+$, 505 (20) $[Ru(PBu_3)_2]^+$, (centers of each ruthenium cluster peaks are reported).

*4.4.3. Reaction of $Ru(CO)_2(BT)(PPh_3)_2$ (**8**) with H_2*

A benzene solution (5 ml) of **8** (50 mg) was heated at 50°C in the presence of hydrogen (5 atm) for 18 h. The solution was analyzed by ^{31}P-NMR. A partial transformation (70%) of the starting complex into the dihydridoruthenium complex $H_2Ru(CO)_2(PPh_3)_2$ (**3**) was detected.

4.4.4. Identification of the ruthenium complexes in the reaction crude of a HDS experiment

Following the procedure above reported 34.5 mg (0.0585 mmol) of $Ru(CO)_3(PBu_3)_2$ (**2**), 0.7848 mg (5.85 mmol) of BT and 10 ml of benzene were introduced in the autoclave. The vessel was pressurized with hydrogen (100 bar) and heated at 150°C for 5 h. A sample of the solution was evaporated to dryness and the residue dissolved in C_6D_6 and analyzed by ^{1}H- and ^{31}P-NMR. In the ^{31}P-NMR spectrum singlets at δ 33.9, 33.3, 25.5, and 23.8 ppm were found. The signal at δ 33.9 ppm may be attributed to the starting complex (**2**), that at δ 33.3 ppm to $H_2Ru(CO)_2(PBu_3)_2$ (**4**), and that one at δ 23.8 ppm to $Ru(CO)_2(O_2)(PBu_3)_2$ formed in the working up of the solution. In the ^{1}H-NMR spectra a triplet at δ −7.9 ppm ($J_{HP} = 25$ Hz) may be attributed to the hydride complex **4**. The signal at δ 25.5 ppm may be attributed to a ruthenium complex containing BT, unfortunately in the ^{1}H-NMR is not possible to identify the corresponding signals.

*4.4.5. Reaction of $Ru_3(CO)_9(PPh_3)_3$ (**5**) with BT*

A benzene solution (20 ml) containing (**5**) (200 mg) and BT (100 mg) was heated at reflux temperature for 24 h. The solution was evaporated to dryness and the products separated by tlc using SiO_2 as stationary phase and hexane/benzene (2:1) as solvent. An orange product was separated and crystallized from CH_2Cl_2–pentane.

The IR spectrum (C_6H_{12} as solvent) showed the following carbonyl stretching frequencies: 2057(s), 2020(s), 2009(vs), 1998(s), 1968(s), 1955(s) cm^{-1}.

The ^{31}P-NMR spectrum (C_6D_6 as solvent) displayed δ 33.6 (s, 1P) and 15.4 (s, 1P) ppm; The ^{1}H-NMR spectrum ($CDCl_3$ as solvent) displayed δ 7.82 (m, 4H), 7.51 (m, 4H), 7.00 (t, 14H, $J_{HH} = 5.8$ Hz) and 6.25 (dd, 2H, $J_{HH} = 5.8$ Hz, $J_{HH} = 3.4$ Hz) ppm. The IR and ^{1}H-NMR data are in agreement with those reported by Bruce [10] for $Ru_3(CO)_7$ (μ^3-C_6H_4)(μ-PPh_2)$_2$.

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