ELSEVIER

Journal of Molecular Catalysis A: Chemical 116 (1997) 131–146

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

Study of the hydrogenation of α,β-unsaturated carbonyl compounds catalyzed by water-soluble ruthenium–TPPTS complexes

Marc Hernandez, Philippe Kalck *

Laboratoire de Catalyse et de Chimie Fine, Ecole Nationale Supérieure de Chimie de Toulouse, Institut National Polytechnique, 118 route de Narbonne, 31077 Toulouse Cedex, France

Received 18 March 1996; revised 24 May 1996; accepted 10 June 1996

Abstract

Hydrogenation of cinnamaldehyde, crotonaldehyde, prenal, 2-butanone, cyclohexanone, benzylacetone, *trans*-4-hexen-3-one, and benzylideneacetone was carried out with various ruthenium complexes containing the water-soluble ligand tris(*m*-sulfonatophenyl)phosphine or TPPTS. The reactions were carried out at 40°C and 20 bar for the unsaturated aldehydes. As already reported in the literature the corresponding unsaturated alcohols were obtained with high selectivities. After one run, NMR analyses revealed that when using $RuCl_3 \cdot 3H_2O$–TPPTS systems, TPPTS gave the phosphonium salts by incorporation of the substrate in acidic conditions. The precursors $RuCl_3 \cdot 3H_2O$, $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$, $[Ru(H)(Cl)(TPPTS)_3]$, $[Ru(H)(OAc)(TPPTS)_3]$, $[Ru(H)_2(TPPTS)_4]$ were transformed into various species. Among them several are inactive, such as $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$. Hydrogenation of ketones was examined at 80°C and ca. 40 bar with $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$, $[Ru(H)(Cl)(TPPTS)_3]$ and $[Ru(H)_2(TPPTS)_4]$. The carbonyl function can be reduced to give the expected alcohol, especially with the latter complex. Transformation of the precursors was also observed. Finally, unsaturated ketones were hydrogenated with $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ and $[Ru(H)_2(TPPTS)_4]$; however in the best case, no more than 5% of the unsaturated alcohol was obtained, hydrogenation occurring mostly on the C=C bond. Complex $[Ru(H)_2(TPPTS)_4]$ appears to be the most interesting precursor, because it provides high activities and it is the only complex which was slowly transformed during catalysis.

Keywords: Hydrogenation; TPPTS complexes; Ruthenium

1. Introduction

It has been recently shown that ruthenium–TPPTS complexes, generated from ruthenium trichloride and tris(*m*-sulfonatophenyl)phosphine (TPPTS), are powerful catalysts to hydrogenate selectively the carbonyl function of α,β-unsaturated aldehydes [1]. Thus, not only does the catalyst reduce the carbonyl group, the carbon–carbon bond remaining untouched, but also the water-soluble ruthenium complex is easily separated from the organic products by a simple decantation. Several substrates have been examined, but if the catalytic cycle is considered to involve the coordination of the carbon–oxygen double bond, the presence of substituents on the carbon–carbon double bond should not affect the reactivity and the selectiv-

* Corresponding author. Tel.: +33-61175690; fax: +33-61175600.

PII S1381-1169(96)00233-6

ity of the reduction. The authors observed, however, significant effects induced by bulky groups on the C=C bond [1]. Although the formation of oxidized TPPTS was noted and a catalytic cycle was proposed, a study of the mechanism of the reaction was lacking.

This ruthenium system is especially interesting because iridium complexes issued from the addition of TPPTS to $[Ir_2(\mu\text{-}Cl)_2(COD)_2]$ show almost the same selectivity but at a ca. 70-fold lower activity, whereas rhodium–TPPTS complexes provide the saturated aldehydes with a remarkable selectivity [1]. The authors have also reported that in the presence of ethanol as cosolvent, the complex $[Ru(H)_2(TPPTS)_4]$ allows to hydrogenate *all-trans*-retinal into retinol [2].

Lau and Cheng have studied the *cis*-$[Ru(6,6'\text{-}Cl_2bipy)_2(OH_2)_2][CF_3SO_3]_2$ complex which is active in the hydrogenation of unsaturated aldehydes but with modest selectivities [3].

The carbonyl reduction involving a hydrogen transfer agent like sodium formate has also been explored. Using diphenyl(*m*-sulfonatophenyl)phosphine (or TPPMS) and the complex $[RuCl_2(TPPMS)_2]$, Joó and Bényei have obtained a full selectivity in unsaturated alcohols when converting crotonaldehyde, cinnamaldehyde and citronellal or citral [4,5]. Darensbourg et al. have used the ligand phosphatriazaadamantane (PTA) and the complex *cis*-$[Ru(Cl)_2(PTA)_4]$ [6]; here also the hydrogenation was fully selective. Grosselin et al. have shown that Ru–TPPTS systems are far more active than the two previous complexes for the selective hydrogenation of prenal using sodium formate [1].

Very recent work has been devoted to the anchoring of ruthenium–TPPTS complexes either in supported aqueous phase catalysis or using functionalized silicas [7]. Whereas a good selectivity was maintained along the recycling of the catalyst, the reactivity decreased significantly due to the leaching of the catalyst in polar media and a poisoning effect of the organic products on the silica supports.

Concerning the reduction of other carbonyl compounds in water, only a few studies have been reported. The complexes *cis*-$[Ru(6,6'\text{-}Cl_2bipy)_2(OH_2)_2][CF_3SO_3]_2$ and $[Ru(\eta^6\text{-}C_6H_6)(CH_3CN)_3][BF_4]_2$ were shown to hydrogenate, but with a low selectivity, the CO function of ketones or unsaturated ketones, whereas aldehydes are converted more easily [3,8]. Bipyridine- and phenanthroline-containing cationic ruthenium complexes can also hydrogenate ketones, provided high pressures of hydrogen are introduced [9]. In addition, ruthenium–TPPMS complexes were shown to be more active than rhodium–TPPMS complexes in the hydrogenation of keto-acids into the corresponding hydroxy-acids [10]. Among various TPPMS-containing ruthenium complexes [5], and even the precursor *cis*-$[Ru(Cl)_2(PTA)_4]$ [6], the species $[RuCl_2(TPPMS)_2]$ is the most active in the reduction of a series of substituted benzaldehydes with sodium formate [5].

Moreover, the direct hydrogenation of propanal in water by several ruthenium–TPPTS complexes was shown to be greatly enhanced by addition of salts, especially sodium iodide. Indeed, at 35°C, reaction rates were obtained which are rarely reached in organic solvents with the classical ruthenium–PPh_3 complexes. The complex $[Ru(H)(I)(TPPTS)_3]$ was proposed to be the actual precursor and the role of NaI was analyzed [11,12].

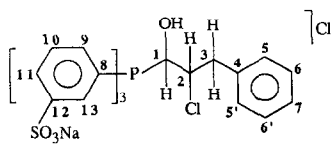
We were interested in the selective preparation of unsaturated alcohols by the direct catalyzed hydrogenation of conjugated aldehydes or ketones. The hydrosilylation reaction catalyzed mainly by rhodium complexes was forsaken [13]. We focused our work on water-soluble ruthenium complexes containing the TPPTS ligand [14] in order to evaluate their catalytic performances for the hydrogenation of interest and incidentally solve the problem of separating the catalyst from the reaction products. Great care was devoted to identifying the products which appeared during catalysis, particularly phosphonium salts, and to following the transformations of the various ruthenium precursors used.

2. Experimental section

2.1. General data

All organic products were of commercial origin and of high purity (> 99%), except for TPPTS and prenal which were kindly given by Rhône–Poulenc. All the aldehydes were distilled and stored under argon. Water was deionized and saturated with argon. The ruthenium–TPPTS complexes were prepared as previously described [14,15]. Hydrogenation studies were performed in a stainless steel autoclave of 100 ml equipped with a magnetic stirrer, a pressure gauge, and two valves. The autoclave was charged with the catalyst in the solid form, purged with argon by successive vacuum and flushing with argon operations. Water and then the reactants and the organic solvent were introduced with a syringe through a septum. The autoclave was purged several times with hydrogen. Two procedures were adopted for the catalytic runs: either introducing a given pressure of hydrogen at room temperature and then heating at the desired temperature or admitting hydrogen at a constant pressure during all of the run. After a given reaction time, the stirring was stopped and the autoclave cooled quickly until around 20°C. The autoclave was purged slowly of hydrogen; argon was introduced, and the two organic and aqueous phases were rapidly transferred with a cannula to a separatory funnel.

Gas chromatography analyses were done using a Carlo Erba GC 6000 Vega series 2 apparatus equipped with a CP WAX 58 B Chrompack column. ^{1}H, ^{13}C and ^{31}P NMR measurements were carried out on Bruker AC 200, WH 250 or AMX 400 spectrometers. Chemical shifts are given in ppm using TMS or H_3PO_4 85% as external standards.



Scheme 1.

2.2. Preparation and characterization of phosphonium salts 7, 10–13

2.2.1. Preparation of [{$PhCH_2CH_2CH(OH)$}$P(C_6H_4$-m-$SO_3Na.H_2O)_3$]Cl 7a

To 1 g of TPPTS (1.61 mmol), dissolved in 15 ml of water, are added 1.5 ml (8.25 mmol) of HCl in isopropanol, then 8.5 ml (64.55 mmol) of dihydrocinnamaldehyde. A vigorous stirring was maintained at 90°C for 4 h. After cooling two uncolored phases were obtained which were separated by decantation. The aqueous phase was washed with 20 ml of diethylether and evaporated to dryness. A white crystalline solid was collected, washed with 20 ml of diethylether, dried under vacuum for 3 h at 50°C and stored under argon at room temperature.

^{31}P {^{1}H} NMR (101.26 MHz, D_2O) showed that compound **7a** was obtained with ca. 59% yield: δ +20.8 (s), besides 30% of TPPTS, 3% of OTPPTS, and two unassigned signals at δ +25.7 and δ +22.3. Other ^{1}H and ^{13}C NMR data are as follows. ^{1}H NMR (200.13 MHz, D_2O): δ +7.85–6.47 (m, Ar–*H*); 5.13 (d, $^{2}J_{PH}$ = 9.7, C_1H); 2.23 (m) and 1.54 (m) belonging to the CH_2–CH_2 framework. ^{13}C NMR (62.90 MHz, D_2O): δ +148–118 (aromatic carbon atoms); 71.2 ($^{1}J_{PC}$ = 52.4, P–C_1); 35.7 (P–C–C–C_3); 33.2 ($^{2}J_{PC}$ = 14.3, P–C–C_2).

2.2.2. Preparation of [{$PhCH_2CHClCH(OH)$}$P(C_6H_4$-m-$SO_3Na \cdot H_2O)_3$]Cl 7b

By a similar procedure cinnamaldehyde was added to TPPTS in hydrochloric medium to produce **7b** as a pale yellow crystalline solid.

^{31}P {^{1}H} NMR (101.26 MHz, D_2O, 25°C) showed that this solid contained approximately 82% of **7b** (25.6 ppm), 3% of OTPPTS, 4 and 11% of two unknown species characterized by singlets at 26.9 and 26.5 ppm. The numbering is shown in Scheme 1.

^{1}H NMR (400.13 MHz, D_2O): δ +8.00 (d, $^3J_{HH}$ = 7.7, H_{11}, 1H); 7.65 (d, $^3J_{PH}$ = 11.9, H_{13}, 1H); 7.52 (m, $^3J_{HH}$ = 7.6, H_{10}, 1H); 7.46 (dd, $^3J_{HH}$ = $^3J_{PH}$ = 7.6, H_9, 1H); 7.05 (t, $^3J_{HH}$ = 7.5, H_7, 1H); 6.95 (t, $^3J_{HH}$ = 7.5, $H_{6,6'}$, 2H); 6.67 (d, $^3J_{HH}$ = 7.5, $H_{5,5'}$, 2H); 4.86 (d, $^2J_{PH}$ = 11.2, H_1, 1H); 4.50 (m, H_2, 1H); 2.22 (m, H_3, 2H). ^{13}C NMR (62.9 MHz, D_2O): δ +147.1 ($^3J_{PC}$ = 12.8, C_{12}); 139.7 (J_{PC} = 9.3, C_9 or C_{10} or C_{13}); 135.1 (C_{11}); 133.9 (J_{PC} = 12.7, C_9 or C_{10} or C_{13}); 133.6 (J_{PC} = 10.5, C_9 or C_{10} or C_{13}); 119.2 ($^1J_{PC}$ = 84.1, C_8); 132.7, 132.6, 132.1 ($C_{5,5'}$, $C_{6,6'}$ or C_7); 131.8 ($^4J_{PC}$ = 5.9, C_4); 90.4 ($^2J_{PC}$ = 18.2, C_2); 41.5 ($^1J_{PC}$ = 46.3, C_1); 40.2 (C_3).

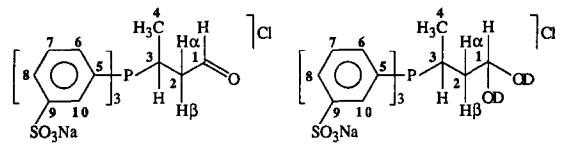
2.2.3. Preparation of [{$OHCCH_2CH(CH_3)$}$P(C_6H_4$-m-$SO_3Na.H_2O)_3$]Cl **10**

To a solution of 5 ml of water containing 1 g (1.61 mmol) of TPPTS were successively added under stirring 0.5 ml (2.50 mmol) of HCl in isopropanol and 0.3 ml (3.62 mmol) of butenal. The resulting colorless solution was maintained at 25°C for 10 min under vigorous stirring, then dried in vacuo. A white crystalline solid was collected after washing with diethylether (20 ml) and drying under vacuum at 50°C for 2 h (yield 90%, 1.06 g).

^{31}P {^{1}H} NMR (101.26 MHz, D_2O,) revealed the presence of a singlet at 31.5 ppm (**10**, ca. 21%), a singlet at 31.3 ppm due to the hydration by D_2O of this compound (**12**, ca. 78%). Around 1% of the oxide OTPPTS was detected.

Infrared (KBr pellets) showed the presence of the aldehyde function for **10**: ν_{CO} = 1727 (s) cm^{-1}. The numbering is shown in Scheme 2.

^{1}H NMR (400.13 MHz, D_2O): Species **10**: δ +9.52 (s br., H_1, 1H); 8.17–7.36 (m, Ar*H*, 4H); 4.54 (s br., H_3, 1H); 3.10 and 2.60 (m, H_2 α or β, 2H); 1.10 (dd, $^3J_{HH}$ = 4.4; $^3J_{PH}$ = 18.1, H_4, 3H). Species **12**: δ +8.15 (d, $^3J_{PH}$ = 12.8, H_{10}, 1H); 8.11 (d, $^3J_{HH}$ = 7.8, H_8, 1H); 7.88 (dd, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 8.2, H_6, 1H); 7.68 (dt, $^3J_{HH}$ = 7.9, $^4J_{PH}$ = 3.1, H_7, 1H); 5.23 (dd, $^3J_{HH}$ = 5.1, $^3J_{HH}$ = 2.5, H_1, 1H); 4.05 (m, H_3, 1H); 1.99 (m, $^3J_{HH}$ = 7.7, H_2 α or β); 1.38 (m, H_2 α or β); 1.19 (dd, $^3J_{HH}$ = 6.7, $^3J_{PH}$ = 20.2, H_4, 3H).



10 12

Scheme 2.

^{13}C NMR (62.9 MHz, D_2O): Species **10**: δ +202.9 (C_1); 146.4–119.6 (aromatic carbons); 45.3 (C_2); 23.1 (C_3); 16.4 (C_4). Species **12**: δ +147.7 ($^3J_{PC}$ = 12.6, C_9); 139.1 (J_{PC} = 9.2, C_6 or C_7 or C_{10}); 135.0 (C_8); 134.2 (J_{PC} = 11.9, C_6 or C_7 or C_{10}); 133.0 (J_{PC} = 10.5, C_6 or C_7 or C_{10}); 119.9 ($^1J_{PC}$ = 83.8, C_5); 90.6 ($^3J_{PC}$ = 17.8, C_1); 40.0 (C_2); 25.4 ($^1J_{PC}$ = 48.9, C_3); 15.6 (C_4).

2.2.4. Preparation of [{$HOCH_2CH_2CH(CH_3)$}$P(C_6H_4$-m-$SO_3Na.H_2O)_3$]Cl **13**

Addition of 2-butenol on TPPTS under the same conditions produced a white crystalline solid which was shown by ^{31}P {^{1}H} NMR to contain only TPPTS.

From a catalytic test where **10–11** were hydrogenated, **13** was characterized by ^{1}H and ^{13}C NMR (see numbering scheme for **10**).

^{1}H NMR (400.13 MHz, D_2O): δ +8.64–7.16 (m, Ar*H*, 4H); 4.09 (m, H_3, 1H); 3.70 (m, H_1, 2H); 2.10 (m, H_2, 2H); 1.26 (dd, $^3J_{HH}$ = 6.7, $^3J_{PH}$ = 20.1, H_4, 3H). ^{13}C NMR (62.9 MHz, D_2O): δ +147.6 ($^3J_{PC}$ = 12.8, C_9); 139.2 (J_{PC} = 9.6, C_6 or C_7 or C_{10}); 135.0 (C_8); 134.2 (J_{PC} = 12.0, C_6 or C_7 or C_{10}); 133.0 (J_{PC} = 11.1, C_6 or C_7 or C_{10}); 120.1 ($^1J_{PC}$ = 84.5, C_5); 60.3 ($^3J_{PC}$ = 15.5, C_1); 34.8 (C_2); 25.2 ($^1J_{PC}$ = 47.8, C_3); 14.9 (C_4).

2.3. Preparation of [$Ru(H)(OCOCH_2CH_2C_6H_5)(PPh_3)_3$] **9**

A procedure similar to that previously described by Young and Wilkinson [16] for the preparation of [$Ru(H)(OAc)(PPh_3)_3$] was

adopted. An excess of the sodium salt of the carboxylic acid was reacted with $[Ru(Cl)_2(PPh_3)_3]$ in refluxing methanol under a hydrogen atmosphere.

In 50 ml of methanol saturated with hydrogen by constant bubbling along the synthesis, 0.6 g (0.63 mmol) of $[Ru(Cl)_2(PPh_3)_3]$ and 0.92 g (5.34 mmol) of $C_6H_5CH_2CH_2COONa$ were added. The medium was stirred and heated at reflux for 45 min. From the orange solution a yellow solid precipitated which, after cooling and elimination of the supernatant solution, was washed with diethylether (10 ml), water (5 ml), methanol (3 ml), then diethylether (5 ml). The yellow powder was dried under reduced pressure and stored under argon (0.29 g, yield 44%).

Elemental analysis, exp. (calc.%): C 71.51 (71.88); H 5.23 (5.26). IR (nujol mulls): ν_{Ru-H} = 2062 (m); $\nu_{as}(COO)$ = 1526 (s); $\nu_s(COO)$ = 1479 (s) cm^{-1}.

Admitting an octahedral geometry for the complex with two phosphine ligands in the axial positions (P_A) one PPh_3 (P_B), the hydride and the η^2-bonded carboxylate ligands are in the equatorial plane. NMR data are listed in Table 1.

3. Results and discussion

As catalyst precursors or as species identified after catalysis, the following complexes were used with the same numbering as in the previous paper [14]: $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ **1**, $[Ru(H)(Cl)(TPPTS)_3]$ **2**, $[Ru(H)(OAc)(TPPTS)_3]$ **3**, $[Ru(H)_2(TPPTS)_4]$ **4**, $[Ru(H)_2(CO)(TPPTS)_3]$ **5** and $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ **6**.

3.1. Catalytic hydrogenation of α,β-unsaturated aldehydes

Two main substrates have been examined, i.e. *trans*-cinnamaldehyde (3-phenyl-2-propenal) and *trans*-crotonaldehyde (2-butenal). In the former case, the carbon–carbon double bond is sterically crowded and its solubility in water is dramatically reduced with regard to crotonaldehyde. Prenal or 3-methyl-2-butenal has also been explored with the most active catalyst precursor.

3.1.1. Hydrogenation of cinnamaldehyde

All the reactions have been carried out at 40°C in a water/toluene (10 ml/10 ml) medium

Table 1
NMR data of $[Ru(H)(OCOCH_2CH_2Ph)(L)_3]$

	L = PPh_3 [a]	L = TPPTS [b]
$^{31}P\{^1H\}$ (101.26 MHz, 25°C)		
P_A	44.2 (d, $^2J_{PP}$ = 27 Hz)	45.2 (d, $^2J_{PP}$ = 28 Hz)
P_B	78.0 (t, $^2J_{PP}$ = 27 Hz)	78.7 (t, $^2J_{PP}$ = 28 Hz)
^1H (200.13 MHz, 21°C)		
Ar–*H*	7.74–6.62 (m)	—
C*H*$_2$	2.17 (t, $^3J_{HH}$ = 8 Hz)	2.25 (t, $^3J_{HH}$ = 7 Hz)
C*H*$_2$	1.76 (t, $^3J_{HH}$ = 8 Hz)	1.90 (t, $^3J_{HH}$ = 7 Hz)
Ru–*H*	−18.71 (qd, $^2J_{PH}$ = 27 Hz)	−18.75 (qd, $^2J_{PH}$ = 26 Hz)
^{13}C (62.9 MHz, 24°C)		
OCOR	183.6	185.4
Ar–*C*	139–123	—
*C*H$_2$	39.0	40.9
*C*H$_2$	30.5	32.4

L = PPh_3: isolated complex; L = TPPTS: solid recovered after catalysis.
[a] NMR analyses in $CDCl_3$.
[b] NMR analyses in D_2O.

under a hydrogen pressure of 20 bar. The substrate to ruthenium molar ratio was 200. The results are shown on Table 2.

The ruthenium salt $RuCl_3.3H_2O$ in the presence of 5 mol of TPPTS gave a 81% yield in hydrogenated products with a high selectivity in unsaturated alcohol (96%) as already described by Grosselin et al. [1]. Although it is necessary to be careful with the integration of the ^{31}P NMR signals, analysis of the reaction medium after catalysis showed that two main ruthenium species exist, i.e. $[Ru(H)(Cl)(TPPTS)_3]$ and $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ **6** in ca. the same quantities, (arene = toluene **6a**, *cis*-cinnamic alcohol **6h** and dihydrocinnamic alcohol **6g**). Nearly equivalent quantities of free TPPTS and OTPPTS were detected. Large amounts of a phosphonium salt were revealed by a singlet at 25.6 ppm. From the ^1H NMR spectra the phosphonium chloride could be $[(PhCH_2CHXCHOH)P(C_6H_4\text{-}m\text{-}SO_3Na)_3]Cl$, with X = H **7a** or Cl **7b**. The phosphonium salt **7b** has been independently prepared almost quantitatively by addition of cinnamaldehyde to TPPTS and requires the presence of a hydrochloric medium. The same procedure converts more slowly dihydrocinnamaldehyde into **7a**. ^{31}P chemical shifts allow to assign unambiguously to **7** a **7b** structure since **7a** presents a singlet at 20.8 and **7b** a singlet at 25.6. Direct synthesis of phosphonium compounds by addition of an aldehyde to $Ph_2P(C_6H_4\text{-}m\text{-}SO_3Na)$ in acidic medium has already been reported by Darensbourg et al. [17]:

$$RuCl_3 \cdot 3H_2O + 5TPPTS + \tfrac{1}{2}H_2 \rightarrow [Ru(H)(Cl)(TPPTS)_3] + 2HCl + \tfrac{1}{2}OTPPTS + \tfrac{3}{2}TPPTS + \tfrac{5}{2}H_2O; \quad (1)$$

$$[Ru(H)(Cl)(TPPTS)_3] + \text{arene} \rightarrow [Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl + TPPTS; \quad (2)$$

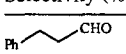
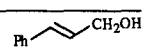
$$TPPTS + 2HCl + PhCH{=}CHCHO \rightarrow [\{PhCH_2CHClCH(OH)\} \times P(C_6H_4\text{-}m\text{-}SO_3Na)_3]Cl. \quad (3)$$

Eqs. (1)–(3) show the reduction of $RuCl_3 \cdot 3H_2O$ into the ruthenium (II) complex **2**, the secondary reaction of **2** with toluene, dihydrocinnamic alcohol and cinnamic alcohol to afford complexes **6** and finally the formation of the phosphonium salt **7b**, whose structure is displayed in the experimental section.

Complex **1** gave poor yields either in water/toluene (14%) or in water/ether (26%) medium, although the regioselectivity in unsaturated alcohol was ca. 90%. After catalysis, only complexes of type **6** were found in solution.

Complex $[Ru(H)(Cl)(TPPTS)_3]$ **2** gave a 73% conversion of the unsaturated aldehyde. This result seems to be quite unexpected since **2**

Table 2
Catalytic hydrogenation of cinnamaldehyde by ruthenium-TPPTS complexes [a]

Catalyst	Conversion (%)	Selectivity (%)		
				
$RuCl_3 \cdot 3H_2O$/5TPPTS	81	2	2	96
$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	14	9	0	91
$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	26	7	0	93
$[Ru(H)(Cl)(TPPTS)_3]$	73	1	3	96
$[Ru(H)_2(TPPTS)_4]$	97	2	3	95
$[Ru(H)(\eta^6\text{-}C_6H_5CH_3)(TPPTS)_2]Cl$ [b]	0	—	—	—
$[Ru(H)(OAc)(TPPTS)_3]$	92	traces	4	96

[a] Conditions: [Ru] = 0.2 mmol; [substrate]/[Ru] = 200; $H_2O/PhCH_3$ = 10 ml /10 ml; P_{H_2} (40°C) = 20 bar; T = 40°C; duration = 3 h.
[b] Organic solvent: Et_2O (10 ml).

generated in situ from the $RuCl_3 \cdot 3H_2O$/5TPPTS system led to a better activity taking into account the induction period necessary to its formation [1]. The selectivity in unsaturated alcohol was 96% as starting from $RuCl_3 \cdot 3H_2O$.

We observed that, at the end of catalytic runs, complexes **6** (mixture of **6a**, **6h**, and **6g**) were predominant with small amounts of **7b**, traces of OTPPTS and TPPTS being also present. However, species **6a** is inactive for the hydrogenation of cinnamaldehyde under our conditions. Since five equivalents of TPPTS were added to $RuCl_3 \cdot 3H_2O$ and complexes **1** and **2** contain only two and three equivalents of ligand per ruthenium atom respectively, we can deduce that the kinetics to produce **6** directly from **1** and **2** are faster than from $RuCl_3 \cdot 3H_2O$. The intermediate species $[Ru(H)(Cl)(TPPTS)_2(H_2O)]$, previously observed by Basset and his group [11], which should react with the arene ligands to produce **6**, is thus formed more quickly starting from **1** and **2**. Moreover, the presence of an excess of TPPTS plays a role on the equilibrium between **2** and $[Ru(H)(Cl)(TPPTS)_2(H_2O)]$ and should reduce the rate of the substitution of the Cl^- and H_2O ligands by arene in the latter complex.

Precursor $[Ru(H)_2(TPPTS)_4]$ **4** gave the most interesting results since a 97% conversion of cinnamaldehyde and a selectivity of 95% in cinnamic alcohol were obtained. Actually, complex **4** does not give rise to an arene complex of type **6** in the presence of toluene or a cinnamic group, at least under our experimental conditions. Investigation of the fate of **4** after a catalytic run was carried out by ^1H, ^{31}P and ^{13}C NMR spectroscopy. Complex **4** represents around 50% of the ruthenium species present in solution, besides $[Ru(H)_2(CO)(TPPTS)_3]$ **5** and the carboxylate complex $[Ru(H)(OCOCH_2CH_2Ph)(TPPTS)_3]$ **8**. This latter compound (Fig. 1) was identified by comparison with the ^{31}P NMR data of $[Ru(H)(OCOCH_2CH_2Ph)(PPh_3)_3]$ **9**, that we prepared according to a method similar to that of $[Ru(H)(OAc)(PPh_3)_3]$ [16].

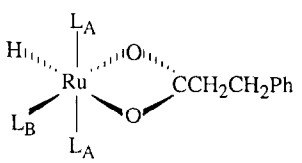


Fig. 1. Proposed structure for complexes **8** and **9**.

In infrared, a ν_{Ru-H} stretching band was clearly noted at 2062 cm^{-1} for **9**, but for **8** it was not detected. Moreover, some sodium dihydrocinnamate was characterized in the aqueous phase by ^1H and ^{13}C NMR. We checked that the starting cinnamaldehyde did not contain any cinnamic acid. In the organic phase, besides the aldehydes and alcohols of interest, traces of ethylbenzene were detected by GC/MS. The formation of this product parallels that of the carbonyl complex **5**. Although it is difficult to assess whether styrene is the primary product or not, some decarbonylation of cinnamaldehyde or dihydrocinnamaldehyde occurs, involving presumably the classical CH oxidative addition and alkyl retro-*cis*-migration. The formation of complex **8** which contains a dihydrocinnamate ligand should require the addition of water to an intermediate species binding an acyl carbon atom arising from the oxidative addition of dihydrocinnamaldehyde. Some more data are required to present a complete mechanism of the reaction, but apparently the first stage of the decarbonylation of dihydrocinnamaldehyde would result either in the decarbonylation reaction to afford ethylbenzene and **5** as well, or in the attack of water to afford dihydrocinnamic acid and thus **8**. Wilkinson and his group [18] have already reported the formation of $[Ru(H)(RCOO)(PPh_3)_3]$ from $[Ru(H)_2(PPh_3)_4]$ in the presence of an aldehyde RCHO and suggested a mechanism in which an hydroxyruthenium intermediate species is involved.

In order to test the reactivity of the carboxylate complexes, the acetate complex **3** was examined. Table 2 shows that **3** is as active as $[Ru(H)_2(TPPTS)_4]$ since the conversion was 92% and the selectivity in unsaturated alcohol

96%. From the ^{1}H and ^{31}P NMR spectra it was clearly shown that complex **3** was still present after a catalytic run and that small amounts (ca. 10%) of a complex of type $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2](OAc)$, with arene = *cis*-cinnamic alcohol almost exclusively, was produced in the medium.

Thus, concerning the hydrogenation of cinnamaldehyde into cinnamic alcohol, this work shows that $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ and $[Ru(H)(Cl)(TPPTS)_3]$ lead to the formation of the arene complexes derived from cinnamic and dihydrocinnamic alcohols as well as from toluene. In contrast, two interesting catalyst precursors are $[Ru(H)_2(TPPTS)_4]$ and $[Ru(H)(OAc)(TPPTS)_3]$ which afford high conversions and selectivities in cinnamic alcohol. A slow decarbonylation of aldehyde was however noted with **4** leading to traces of $[Ru(H)_2(CO)(TPPTS)_3]$. Another side-reaction gives the carboxylate complex **8**, but careful analysis of the NMR spectra has shown that this compound does not give any arene complex of type **6**. Finally, complex **3** which has already be shown to give very slowly the toluene-complex $[Ru(H)(\eta^6\text{-}C_6H_5CH_3)(TPPTS)_2](OAc)$ [14], produces with low yields the species $[Ru(H)(\eta^6\text{-}cis\ C_6H_5CH{=}CHCH_2OH)(TPPTS)_2]$.

3.1.2. Hydrogenation of crotonaldehyde

Crotonaldehyde as well as its hydrogenated products present a good solubility in water so that the contact between the organic products and the ruthenium–TPPTS systems is greatly improved when compared to the previous one. We noted that when the autoclave, previously purged with argon, was charged with the reactants, heated at 40°C for 10 min, then pressurized at 20 bar of hydrogen, a 8% conversion of crotonaldehyde and a 79% selectivity in butenol were obtained (Table 3). An alternative procedure, after introduction of the reactants, was to pressurize immediately the autoclave at 19.5 bar and then to heat it at 40°C. The pressure was adjusted to 20 bar after 10 min. For the same 4 h reaction time a 100% conversion was obtained with, however, a 50/50 distribution in butenol and butanol. For shorter reaction times, thus for lower conversion rates, a higher selectivity in butenol was reached. For instance, as shown in Fig. 2, for 30 min durations (29% conversion) the selectivity was 99%. For 60 min a good compromise was obtained between the conversion (98%) and the selectivity in butenol (96%).

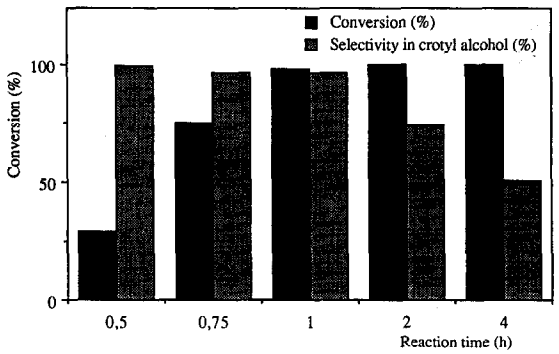


Fig. 2. Evolution of crotonaldehyde conversion and crotyl alcohol selectivity for different reaction times.

Concerning the first procedure, a green solution was collected which contains traces of TPPTS, a little TPPTS oxide, no ruthenium–TPPTS complexes, but abundant quantities of phosphonium salts. These products, which result from a 3-addition of TPPTS on the ethylenic

Table 3
Influence of the starting hydrogenation procedure on the catalytic activity of $RuCl_3 \cdot 3H_2O$/5TPPTS system with crotonaldehyde [a]

Procedure	Conversion (%)	CHO	CH_2OH	CH_2OH
Δ40°C, 10 min, then 20 bar H_2	8	16	5	79
Δ40°C with 19.5 bar H_2	100	traces	49	51

[a] Conditions: $[RuCl_3 \cdot 3H_2O] = 0.2$ mmol; [TPPTS]/[Ru] = 5; [substrate]/[Ru] = 200; $H_2O/PhCH_3$ = 10 ml/10 ml; P_{H_2} (40°C) = 20 bar; T = 40°C; duration = 4 h.

bond of crotonaldehyde (Eq. (4)), were fully characterized by ^{1}H, ^{31}P and ^{13}C NMR:

$$CH_3CH{=}CHCHO + P(C_6H_4\text{-}m\text{-}SO_3Na)_3 + HCl \rightarrow [(C_6H_4\text{-}m\text{-}SO_3Na)_3P\{CH(CH_3)CH_2CHO\}]Cl. \quad \textbf{(10)} \qquad (4)$$

Compound **10**, is characterized in the solid state by a strong ν_{CO} band at 1727 cm^{-1}. In D_2O solutions, the spectroscopic data are consistent with the phosphonium salt **10** and not its hydrated form **11** $[(C_6H_4\text{-}m\text{-}SO_3Na)_3P\{CH(CH_3)CH_2CH(OH)_2\}]Cl$ but mainly the deuterated compound **12** $[(C_6H_4\text{-}m\text{-}SO_3Na)_3P\{CH(CH_3)CH_2CH(OD)_2\}]Cl$. Small quantities of the hydrogenated compound **13** $[(C_6H_4\text{-}m\text{-}SO_3Na)_3P\{CH(CH_3)CH_2CH_2OH\}]Cl$ were also detected. The salt **10** was prepared independently by reacting TPPTS with crotonaldehyde in acidic medium. Its NMR data have been compared with those reported by Patin and coworkers on similar phosphonium salts prepared by reaction of TPPTS with activated alkenes [19]. Even addition of $RuCl_3 \cdot 3H_2O$ in water to TPPTS and crotonaldehyde led to **10** after 10 min at room temperature; simultaneously green solutions were obtained.

Thus, by this procedure almost all the TPPTS ligand is transformed into the phosphonium salts that we identified. We noted that no black ruthenium precipitate was observed in the green solutions immediately after catalysis nor after one week. Due to the low conversion of butenal, no further attempt has been done to characterize the green ruthenium complex for which ^{1}H in the hydride region and ^{31}P NMR are silent. We rather focused our attention on the second procedure, where the heating is carried out under hydrogen pressure. The most significant ^{31}P NMR spectra were obtained after 2 h of reaction. In this case, three TPPTS-containing ruthenium species (around 20% of the phosphorus amount) were detected in roughly the same concentrations, namely $[Ru(H)(Cl)(TPPTS)_3]$, $[Ru(H)(\eta^6\text{-}C_6H_5CH_3))(TPPTS)_3]Cl$, and presumably $[Ru(H)(RCOO)(TPPTS)_3]$ **14**. Other species are present but as traces. Some free TPPTS ligand and significant quantities of OTPPTS were detected besides the most abundant species, i.e. **13**. This compound which was the minor phosphonium salt in the previous experiment results from the hydrogenation of **10**, since the direct reaction of TPPTS with butenol in acidic medium did not occur in our hands. Concerning complex **14**, two quadruplets have been detected in ^{1}H NMR at -18.7 and -18.9 ppm ($J_{PH} = 27$ Hz) at the same chemical shift as $[Ru(H)(OAc)(TPPTS)_3]$ [15]. We propose that R = $CH_3CH_2CH_2$ and $CH_3CH{=}CH$, but in ^{1}H NMR the signals of the two frameworks R have not been clearly assigned since they are obscured by the predominant phosphonium salt **13**.

After 30 min of reaction, ruthenium–TPPTS complexes only appeared in the background of the ^{31}P spectra, although the conversion of crotonaldehyde was already 29%. The two phosphonium salts **10** and **13** were the two main phosphorus-containing species; small quantities of free ligand and OTPPTS were also present in solution. However, after longer periods of reaction (4 h) the red-brown solutions contained the phosphonium salt **13**, the toluene complex **6a**, TPPTS oxide and traces of **14**.

Thus, even if this procedure produces more active species since a complete hydrogenation of crotonaldehyde into butenol was achieved in 1 h (Fig. 2), it is not possible to avoid the formation of the phosphonium salt **10**. In order to neutralize hydrochloric acid, an excess of triethylamine (10 equivalents) was added to the medium. The catalytic run was stopped after 30 min. The brown solution presents in ^{31}P NMR the two signals of TPPTS (ca. 80%) and OTPPTS (ca. 15%) and very weak unassignable signals. Around 3% hydrogenation of crotonaldehyde occurred. In ^{1}H NMR, besides the aryl signals of TPPTS and its oxide, the ethyl groups of $[HNEt_3]Cl$ were clearly detected. Integration of the signals showed that there are 3 equiva-

lents of ammonium salt with regard to the 5 equivalents of TPPTS initially introduced. Thus, the three chlorine atoms present in the $RuCl_3 \cdot 3H_2O$ salt were removed from ruthenium. Thus, the addition of triethylamine prevents the formation of the phosphonium salt but poisons the catalytic system. In this case also no metallic ruthenium was observed.

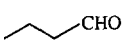
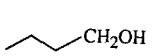
As no ruthenium compound was clearly identified to be responsible for the catalytic activity, we examined the behavior of all the characterized Ru–TPPTS complexes **1**, **2** and **4**.

Starting from $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ **1**, the hydrogenation reaction (second procedure), was characterized by low conversions and poor selectivities (Table 4). After 45 min either in toluene or in diethylether, roughly 5% of the crotonaldehyde was converted to butanal, butenol and butanol, the main product being butanal. ^{31}P NMR analysis after catalysis showed that around 50% of complex **1** has not been transformed, 7% of the phosphonium salt **10** (observed as previously as a mixture of **10–12**) and a lot of unidentified species are present. When using toluene for the organic phase, complex **6a** was slowly formed since ca. 5% were found after 45 min of catalysis.

However, complex $[Ru(H)(Cl)(TPPTS)_3]$, completely transformed crotonaldehyde in 35 min and afforded a selectivity of 93% in butenol; thus, 7% of butanol were formed, traces of butanal being detected. After catalysis, the orange aqueous phase was shown by ^{31}P NMR to contain various species. Around 5% TPPTS and 16% phosphonium salt were present besides traces of OTPPTS. Complex **2** has been largely transformed since about 10% only was found again. Around 5% of the complex $[Ru(H)(\eta^6\text{-}C_6H_5CH_3)(TPPTS)_2]Cl$ appeared. Two AX_2 systems were detected in ^{31}P NMR near 80 (triplet) and 50 (doublet) ppm; in ^1H NMR to pseudo-quartets at -18.8 and -19.6 ppm correspond to these systems and are consistent with a '$RuH(TPPTS)_3$' framework with phosphorus–hydride coupling constants of 26 Hz. The hydride ligand is in a axial position of an octahedron, the three phosphines being in the equatorial plane. In addition, small amounts of the complex $[Ru(H)(Cl)(CO)(TPPTS)_3]$ **15** were detected in ^1H NMR at -7.1 ppm, the signal being a double triplet (*cis*-$^2J_{PH} = 22$ Hz; *trans*-$^2J_{PH} = 102$ Hz). Tentatively, a weak ν_{CO} band at 1930 cm^{-1} can be assigned to **15**, which compares with the ν_{CO} band of $[Ru(H)(Cl)(CO)(PPh_3)_3]$ at 1922 cm^{-1} [20]. Moreover the NMR data of **15**, except for the ^{31}P signal which has not been detected with certainty, parallel those of the PPh_3 analog [21]. Seven remaining ^{31}P signals which account for 15% were not assigned.

Surprisingly, complex $[Ru(H)_2(TPPTS)_4]$ afforded lower conversions of crotonaldehyde than **2**, though it was the best precursor for cinnamaldehyde. Whereas a 93% selectivity in the

Table 4
Catalytic hydrogenation of crotonaldehyde by ruthenium-TPPTS complexes [a]

Catalyst	Time (min)	Conversion (%)	Selectivity (%)		
					
$RuCl_3 \cdot 3H_2O$/5TPPTS	30	29	traces	0	> 99
$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	45	5	63	5	32
$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ [b]	45	6	50	4	46
$[Ru(H)(Cl)(TPPTS)_3]$	35	100	traces	7	93
$[Ru(H)_2(TPPTS)_4]$	30	35	6	1	93

[a] Conditions: [Ru] = 0.2 mmol; [substrate]/[Ru] = 200; $H_2O/PhCH_3$ = 10 ml/10 ml; P_{H_2} (40°C) = 20 bar; T = 40°C.
[b] Organic solvent: Et_2O (10 ml).

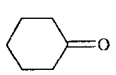
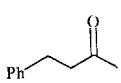
expected unsaturated alcohol has been found, now only 1% of butanol and 6% of butanal were obtained. The presence of butanal in the reaction medium can be related to the significant formation of CO-containing ruthenium complexes. Indeed, complex $[Ru(H)_2(CO)(TPPTS)_3]$ was observed, but as a minor product together with an unknown complex which presents a ν_{CO} band at 1918 cm^{-1} and a double doublet in ^{31}P NMR with a small J_{PP} coupling constant of around 9 Hz. In the absence of a hydride signal in ^1H NMR, we can only conclude that this species contains the fragment 'Ru(CO)$(TPPTS)_2$'. ^{31}P analysis of the aqueous phase after catalysis showed ca. 40% of free TPPTS, 40% of the unknown carbonyl complex, and 10% of $[Ru(H)_2(CO)(TPPTS)_3]$. The remaining 10% are shared between signals of weak intensity including that one of OTPPTS. In ^1H NMR, besides the signals of **5**, weak hydride quartets are detected at -17.3 ($^2J_{PH}$ = 25 Hz) and -18.7 ppm ($^2J_{PH}$ = 26 Hz). This latter signal certainly belongs to complex **14** (vide supra).

Thus, not only $RuCl_3.3H_2O$, but also $[Ru(H)(Cl)(TPPTS)_3]$ and $[Ru(H)_2(TPPTS)_4]$ catalyze the hydrogenation of crotonaldehyde into butenol with selectivities higher than 90%. Complex **2** is particularly active, but in order to reach the most satisfactory selectivities in butenol it is recommended to use short catalytic runs, i.e. to work at incomplete conversions. Instead of generating it in situ due to the presence of acidic medium which transforms TPPTS into phosphonium salts, we directly introduced **2**. This complex gives rise to numerous species during catalysis. Among those, $[Ru(H)(RCOO)(TPPTS)_3]$ **14** should be active since $[Ru(H)(OAc)(TPPTS)_3]$ has been shown to be a good catalyst for aldehyde hydrogenation (vide supra). Similarly, as $[Ru(H)(Cl)(CO)(PPh_3)_3]$ is also a good precursor for the reduction of aldehydes [22], the formation of $[Ru(H)(Cl)(CO)(TPPTS)_3]$ in the medium is not a drawback for the expected reaction.

3.1.3. Hydrogenation of prenal

Prenal, or 3-methyl-2-butenal, is interesting because the corresponding unsaturated alcohol is an important intermediate in the synthesis of fine chemicals. Its hydrogenation, extensively studied in the paper of Grosselin et al. [1], has been achieved with selectivities as high as 99% in prenol starting from the $RuCl_3 \cdot 3H_2O$/5TPPTS system. The prereduction procedure adopted by the authors generates complex **2**. As prenal presents more structural anal-

Table 5
Catalytic hydrogenation of 2-butanone, cyclohexanone and benzylacetone by ruthenium–TPPTS complexes [a]

Substrate	Catalyst	Conversion [b] (%)
	$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	33
	$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$/2TPPTS	20
	$[Ru(H)(Cl)(TPPTS)_3]$	19
	$[Ru(H)_2(TPPTS)_4]$	50
	$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	93
	$[Ru(H)(Cl)(TPPTS)_3]$	73
	$[Ru(H)_2(TPPTS)_4]$	> 99
	$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	5
	$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ [c]	5
	$[Ru(H)_2(TPPTS)_4]$	6

[a] Conditions: [Ru] = 0.35 mmol; [substrate]/[Ru] = 160; H_2O: 25 ml; P_{H_2} (25°C) = 35 bar; T = 80°C; duration = 16 h; no organic solvent.
[b] Selectivity in saturated alcohol = 100%.
[c] Mixture of water/isopropanol: 15 ml/10 ml.

ogy with crotonaldehyde than with cinnamaldehyde, we examined directly the catalytic activity of precursor **2**.

As expected, this complex affords very high reaction rates and good selectivities. Even for short reaction times such as 30 min, the hydrogenation proceeds further. Indeed, the substrate was fully converted and 27% of prenol was already hydrogenated in 3-methylbutanol (23%) or isomerized into 3-methyl-3-butenol (4%), as identified by GC/MS analyses. This product was also observed in the previous work by Grosselin et al. [1]. Thus, in order to prevent the second step of hydrogenation, it appears necessary to reduce the reaction time and to maintain an incomplete conversion.

3.2. Catalytic hydrogenation of ketones

3.2.1. Hydrogenation of saturated ketones

The ketone function is more difficult to hydrogenate than the aldehyde one. Before evaluating the catalytic performances of ruthenium water-soluble complexes in the hydrogenation reaction of α,β-unsaturated ketones, we examined the reactivity of 2-butanone, cyclohexanone, and benzylacetone (Table 5).

With neat benzylacetone as a representative aryl-containing substrate, the reaction with **1** proceeds slowly since 5% conversion was obtained in 16 h at 80°C and 35 bar of H_2 (measured at 20°C). At the end of the catalytic test all the precursor **1** was transformed into the inactive species [Ru(H)(η^6-arene)(TPPTS)$_2$]Cl, arene being mainly 4-phenyl-2-butanone or 4-phenyl-2-butanol. Similarly, [Ru(H_2)(TPPTS)$_4$] gave rise to 6% of the alcohol under the same experimental conditions. After the catalytic run this complex was recovered almost completely as shown by ^{31}P and ^{1}H NMR. In our opinion such a low activity is presumably due to the low solubility of the substrate in water.

Preliminary experiments with neat 2-butanone or cyclohexanone have shown that the hydrogenation occurred although it was slow even at 80°C. At the end of the reaction, a single phase was recovered containing 2-butanol/2-butanone mixtures. Then, the catalytic runs were conducted at 80°C in batch with a starting 35 bar hydrogen pressure and for 16 h. Complex **1** gave 33% of conversion into 2-butanol and no by-products were detected. After catalysis, around 30% of the precursor **1** was found in ^{31}P NMR as its mixture of two isomers [14]. In addition, besides two species present in small amounts (roughly 5%), 65% of a new complex was detected; a singlet at 82.4 ppm is consistent with the [Ru(H)(Cl)(TPPTS)$_2$(H_2O)] complex **16** previously reported [11]. In ^{1}H NMR, the hydride signal was not detected due to, probably, an H/D exchange between this ligand and D_2O [14]. Eq. (5) shows the formation of this complex from precursor **1**:

$$[Ru_2(Cl)_2(\mu-Cl)_2(TPPTS)_4] + 2H_2 + 2H_2O \rightarrow 2[Ru(H)(Cl)(TPPTS)_2(H_2O)] + 2HCl. \quad (5)$$

Presumably the active species is very similar to **16**. Thus, at 60°C and for 16 h, we only obtained 43% of this aquo species and the conversion was reduced to 18%. Moreover, addition of 2 equivalents of TPPTS to **1**, or direct introduction of [Ru(H)(Cl)(TPPTS)$_3$] afforded 20% and 19% of conversions, respectively. Complex **2** was fully recovered in this latter test. The presence of three equivalents of TPPTS per ruthenium atom leads to a competition between the ketone and TPPTS to coordinate to the metal center, whereas in **16** the water ligand is easily displaced.

Complex [Ru(H_2)(TPPTS)$_4$] has been used in the reduction of 2-butanone. Conversion was slightly improved with regard to the previous ones, since 50% was reached in 16 h. The hydrogenation was also fully selective in 2-butanol. NMR analysis after one run revealed the main presence of the starting material **4**, (ca. 62%), small amounts of [Ru(H_2)(TPPTS)$_3$(H_2O)] [15], and three unknown species showing in the hydride region

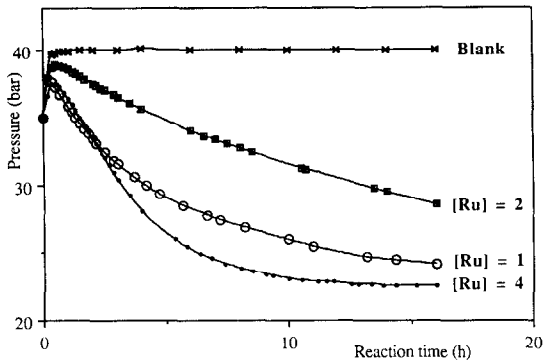


Fig. 3. Pressure drop during hydrogenation of cyclohexanone with catalysts **1**, **2**, and **4**.

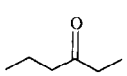
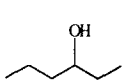
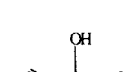
pseudo-quartets at −18.8 (4%) and −20.6 (12%) and a poorly-resolved triplet at −21.7 ppm (22%). In the absence of signals in the 0–10 ppm region, we can only conclude that these species present the two '$Ru(H)(TPPTS)_3$' and '$Ru(H)(TPPTS)_2$' frameworks.

Cyclohexanone was also examined in the hydrogenation reaction with complexes **1**, **2** and **4**. The results are displayed in Table 5. The conversions were significantly higher than with 2-butanone. For instance, a 99% yield was achieved with precursor **4**. Catalysis in this case is biphasic since cyclohexanone and cyclohexanol have a limited solubility in water. The organic and aqueous phases separate immediately. It is interesting to consider the curves of Fig. 3, where the pressure drop in the autoclave has been plotted versus time. Almost no induction period was present for **4**, the pressure increase being due to the rise in the temperature of the reactants as shown in the blank curve. An induction period of around 40 min was observed for complex $[Ru(H)(Cl)(TPPTS)_3]$. Here also complex **1** was more active than **2** due to the excess of TPPTS in the case of **2** which retards the coordination of cyclohexanone. By ^{31}P NMR we observed that **1** gave around 70% of species **16** in addition to **1**, **2** was recovered unchanged, and the dihydrido species **4** gave two unknown species ($\delta = 48.3$ and 62.4 ppm) besides the starting complex (ca. 90%).

3.2.2. *Hydrogenation of α,β-unsaturated ketones*

The hydrogenation of ketones having an unsaturation in α,β positions has also been examined with the precursors **1** and **4** which gave interesting results for the hydrogenation of ketones. The literature is rather scarce concerning active water-soluble systems using hydrogen. Indeed, $[Ru_2(OAc)(CO)_4(bipy)][BPh_4]$ or its analogues bearing various bidentate nitrogen-containing ligands and having several other counteranions [9] transformed selectively the carbon–carbon double bond of benzylideneacetone into benzylacetone. Further hydrogenation occurred starting from cyclohexenone since 56% of cyclohexanone and 44% of cyclohexanol were reported [9]. Similarly, *cis*-$[Ru(6,6'\text{-}Cl_2bipy)_2(OH_2)_2][CF_3SO_3]_2$ was active for the hydrogenation of several unsaturated ketones

Table 6
Catalytic hydrogenation of 4-hexen-3-one by ruthenium–TPPTS complexes [a]

Catalyst	Conversion (%)	Selectivity (%)		
				
$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	100	98	2	0
1 + 10$SnCl_2$	100	> 99	traces	0
1 + 10LiOH	100	24	76	0
1 + 10KOH	100	34	66	0
$[Ru(H)_2(TPPTS)_4]$	100	93	7	0

[a] Conditions: [Ru] = 0.35 mmol; [substrate]/[Ru] = 160; H_2O: 25 ml; P_{H_2} (25°C) = 35 bar; T = 80°C; duration = 16 h; no organic solvent.

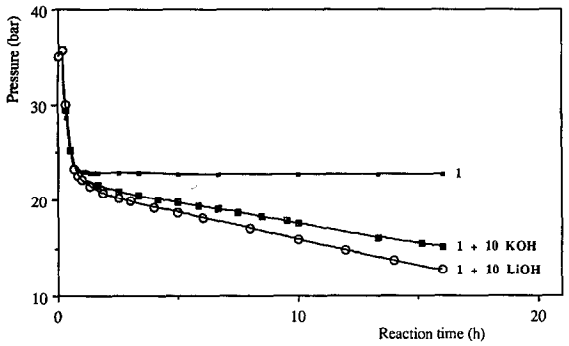


Fig. 4. Pressure drop during hydrogenation of 4-hexen-3-one with catalysts **1**, **1**/10LiOH, and **1**/10KOH.

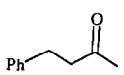
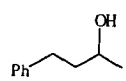
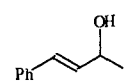
(benzylideneacetone, chalcone, cyclohexenone, mesityl oxide) into the corresponding saturated ketones at 130°C and 40 bar [3]. Some hydrogenation into the saturated alcohol was observed in some cases. Finally, Chan et al. reported that 1% of unsaturated alcohol was detected when the hydrogenation of benzylideneacetone or cyclohexenone was carried out in the presence of $[Ru(H)(\eta^6\text{-}C_6H_6)(CH_3CN)_3][BF_4]_2$ [8].

Table 6 shows our results on the hydrogenation of *trans*-4-hexen-3-one. The expected unsaturated alcohol was not observed at all. Complex $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ gave in 16 h a complete conversion of the C=C bond of the substrate and 1.5% of 3-hexanol was obtained. Whereas addition of a tin salt did not change this result, LiOH or KOH acted as promotors to convert further 3-hexanone into 3-hexanol. The nature of the cation influenced the capability of the catalyst to hydrogenate the ketone since LiOH provided 76% of 3-hexanol in 16 h. Batch experiments provide a good insight into this reaction. Indeed, Fig. 4 shows the pressure drop in the autoclave as a function of time at 80°C. Complex **1** alone transformed in 30 min the substrate into 3-hexanone and at 23 bar the reaction proceeded further very slowly, the curve showing almost no more evolution. Addition of LiOH or KOH, inducing enolisation, allowed the saturated ketone to be hydrogenated at lower pressures.

NMR data after catalysis showed that a lot of new species have been produced. In ^{31}P NMR, a signal at 82.4 ppm was assigned to $[Ru(H)(Cl)(TPPTS)_2(H_2O)]$. Four signals at ca. 59–60 ppm, besides those of **1**, are consistent with corresponding triplets observed in ^1H NMR in the -10 ppm region ($^2J_{PH} = 36$ Hz all) and were assigned to '$Ru(H)(TPPTS)_2$' fragments of species which presumably contain an alkyl group derived from the substrate since many signals were present in the 0–5 ppm region in ^1H NMR. In addition, a phosphonium signal was detected at 31.5 ppm. As no ketonic band was observed by infrared, the data are consistent with a $[(C_6H_4\text{-}m\text{-}SO_3Na)_3P\{CH(CH_3)CH_2CH(OH)CH_2CH_3\}]Cl$ formula.

Reactions starting with $[Ru(H)_2(TPPTS)_4]$ gave complete conversion in 16 h of hexenone into 3-hexanone (93%) and 3-hexanol (7%). Although precursor **4** was mainly recovered, the exploration of this hydrogenation was stopped

Table 7
Catalytic hydrogenation of benzylideneacetone by ruthenium-TPPTS complexes [a]

Catalyst	Organic solvent	Conversion (%)	Selectivity (%)		
					
$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	$PhCH_3$	31	98	1	1
$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$	CH_2Cl_2	47	95	4	1
$[Ru(H)_2(TPPTS)_4]$	$PhCH_3$	88	78	18	4
$[Ru(H)_2(TPPTS)_4]$	THF	70	63	32	5

[a] Conditions: [Ru] = 0.35 mmol; [substrate]/[Ru] = 160; H_2O/organic solvent = 25 ml/10 ml; P_{H_2} (25°C) = 35 bar; T = 80°C; duration = 16 h.

since the first step was invariably the reduction of the carbon–carbon double bond. An attempt was carried out with benzylideneacetone since, independently of the +M effect of the phenyl substituent, this C=C double bond is more sterically crowded. The results are displayed in Table 7. As the substrate is a solid, an organic solvent was used. At 80°C in toluene or in dichloromethane, conversions of 31 and 47% were respectively obtained. Some unsaturated alcohol was observed for the first time but the selectivity remained at a very low level (ca. 1%). It is important to note that low amounts of 4-phenyl-2-butenol were produced (around 1% also). Some ruthenium black was present after catalysis, whatever the two solvents used. However this solid did not catalyze the hydrogenation of benzylacetone. In separate experiments, we checked that neat benzylacetone was hydrogenated by **1** in the saturated alcohol but the conversion was 5% in 16 h under the same conditions of temperature and pressure (see Table 5). After catalysis, complex **1** was fully transformed into the arene complex containing benzylacetone (IR and NMR).

Complex $[Ru(H)_2(TPPTS)_4]$ gave higher conversion rates, i.e. 88% in toluene or 70% in THF and the hydrogenation until 4-phenyl-2-butanol reached 18 and 32%, respectively. Around 5% of the expected benzylidene alcohol was, however, obtained. Any attempt to increase the selectivity in unsaturated alcohol was unsuccessful till now. Particularly, using isopropanol to dissolve the substrate and improve the transfer between the organic and aqueous phases led to an homogeneous single phase. Complex **4** was generated in situ by the simple addition of 4 equivalents of TPPTS to $[Ru(\eta^4\text{-}1,5\text{-}C_8H_{12})(\eta^6\text{-}1,3,5\text{-}C_8H_{10})]$ [23]. The reaction was significantly faster than previously noted. In 1 h, 41% of the substrate was consumed. However, the sole product obtained was benzylacetone, i.e. the saturated ketone. Thus, the two parallel reaction pathways to afford either benzylacetone or benzylidene alcohol in this case cannot be shifted towards the right direction.

From the THF/H_2O biphasic system the two species $[Ru(H)_2(TPPTS)_4]$ and $[Ru(H_2)(TPPTS)_3(H_2O)]$ were found by NMR in the water phase, with in addition traces of a complex which contains the '$Ru(H)(TPPTS)_3$' fragment.

4. Concluding remarks

This work has shown that the two complexes $[Ru(H)(Cl)(TPPTS)_3]$ and $[Ru(H)_2(TPPTS)_4]$ are good starting materials for the selective hydrogenation of α,β-unsaturated aldehydes into the corresponding unsaturated alcohols. This selectivity cannot be extended to the unsaturated ketones since the C=C bond is preferentially reduced.

Moreover, most of the precursors are transformed after the first catalytic run. In addition, either with the TPPTS ligand or with the complexes, reactions of the organic products were evidenced, giving respectively phosphonium salts and arene or carboxylate ruthenium species.

Even if some catalytic runs are satisfactory, the analysis of the aqueous phases shows that the recycling would be difficult in many cases.

Acknowledgements

This work was supported by FIRMENICH SA, which is gratefully acknowledged.

References

[1] J.-M. Grosselin, C. Mercier, G. Allmang and F. Grass, Organometallics 10 (1991) 2126.
[2] G. Allmang, F. Grass, J.-M. Grosselin and C. Mercier, J. Mol. Catal. 66 (1991) L27.
[3] C.-P. Lau and L. Cheng, J. Mol. Catal. 84 (1993) 39.
[4] F. Joó and A. Bényei, J. Organomet. Chem. 363 (1989) C19.
[5] A. Bényei and F. Joó, J. Mol. Catal. 58 (1990) 151.
[6] D.J. Darensbourg, F. Joó, M. Kannisto, A. Kathó and J.H. Reibenspies, Organometallics 11 (1992) 1990; D.J. Darensbourg, F. Joó, M. Kannisto, A. Kathó, J.H. Reibenspies and D.J. Daigle, Inorg. Chem. 33 (1994) 200.

[7] E. Fache, C. Mercier, N. Pagnier, B. Despeyroux and P. Panster, J. Mol. Catal. 79 (1993) 117.
[8] W.-C. Chan, C.-P. Lau, L. Cheng and Y.-S. Leung, J. Organomet. Chem. 464 (1994) 103.
[9] P. Frediani, M. Bianchi, A. Salvini, R. Guarducci, L.C. Carluccio and F. Piacenti, J. Organomet. Chem. 498 (1995) 187.
[10] F. Joó, Z. Tóth and M.T. Beck, Inorg. Chim. Acta 25 (1977) L61; F. Joó and Z. Tóth, J. Mol. Catal. 8 (1980) 369; Z. Tóth, F. Joó and M.T. Beck, Inorg. Chim. Acta 42 (1980) 153.
[11] E. Fache, C. Santini, F. Senocq and J.-M. Basset, J. Mol. Catal. 72 (1992) 337.
[12] E. Fache, F. Senocq, C. Santini and J.-M. Basset, J. Chem. Soc. Chem. Commun. (1990) 1776.
[13] G.Z. Zheng and T.H. Chan, Organometallics 14 (1995) 70, and references therein.
[14] M. Hernandez and Ph. Kalck, J. Mol. Catal., previous paper.
[15] E. Fache, C. Santini, F. Senocq and J.-M. Basset, J. Mol. Catal. 72 (1992) 331.
[16] R.J. Young and G. Wilkinson, Inorg. Synth. 12 (1977) 79.
[17] D.J. Darensbourg, F. Joó, A. Kathó, J.N. White Stafford, A. Bényei and J.H. Reibenspies, Inorg. Chem. 33 (1994) 175, and references therein.
[18] D.J. Cole-Hamilton and G. Wilkinson, Nouv. J. Chim. 1 (1977) 141.
[19] C. Larpent and H. Patin, Tetrahedron 44 (1988) 6107.
[20] N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorg. Synth. 15 (1974) 45.
[21] M.C. Barral, R. Jiménez-Aparicio, M.J. Larrubia, E.C. Royer and F.A. Urbanos, Inorg. Chim. Acta 186 (1991) 239.
[22] R.A. Sanchez-Delgado and O.L. De Ochoa, J. Mol. Catal. 6 (1979) 303; R.A. Sanchez-Delgado, A. Andriollo, O.L. De Ochoa, T. Suarez and N. Valencia, J. Organomet. Chem. 209 (1981) 77; R.A. Sanchez-Delgado, A. Andriollo and N. Valencia, J. Mol. Catal. 24 (1984) 217; Z. Brouckova, M. Czakova and M. Capka, J. Mol. Catal. 30 (1985) 241.
[23] P. Pertici, G. Vitulli, M. Paci and L. Porri, J. Chem. Soc. Dalton Trans. (1980) 1961.