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Water-soluble ruthenium complexes containing tris(*m*-sulfonatophenyl)phosphine (TPPTS). Preparation of a series of $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ complexes, $[Ru(H)_2(CO)(TPPTS)_3]$ and revisited procedures for previously described ruthenium-TPPTS compounds

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Abstract

The TPPTS ligand is the trihydrated form of the sodium salt of tris(*m*-sulfonatophenyl)phosphine. Complexes $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ **1** and $[Ru(H)(X)(TPPTS)_3]$, where X = Cl **2**, OAc **3**, have been prepared by a phosphine exchange from $[Ru(Cl)_2(PPh_3)_3]$ and $[Ru(H)(X)(PPh_3)_3]$ as previously described by Basset. Complex **1** presents in solution a solvolysis phenomenon which has been studied by ^{31}P NMR. Complex **1** is a useful starting material to easily prepare **2**, $[Ru(H)_2(TPPTS)_4]$ **4**, the new species $[Ru(H)_2(CO)(TPPTS)_3]$ **5**, and the series of the new water-soluble complexes $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ **6**, where arene = benzene, toluene, *p*-xylene, ethylbenzene, cumene, tetraline, cinnamic-, and dihydrocinnamic alcohols. All these compounds have been characterized by ^1H, ^{13}C, and ^{31}P NMR. Complexes **6** can also been obtained, but with an excess of TPPTS and sometimes OTPPTS, from $RuCl_3 \cdot 3H_2O$/n TPPTS, or from **2** and **3** as well.

1. Introduction

The use of water-soluble ruthenium complexes has attracted considerable attention in the last few years due to the easy separation of active hydrogenation catalysts from the organic products [1–9]. The synthesis and catalytic behaviour of these ruthenium compounds has recently been reviewed [10,11]. In most of the systems described in the literature, water-soluble phosphine ligands have been used to maintain the corresponding ruthenium complexes in the aqueous phase. A large use of tris(*m*-sulfonatophenyl)phosphine, most often its sodium salt, hereafter named TPPTS, has been done due to its high solubility in water (1100 g l^{-1}) [12]. The first reported TPPTS-ruthenium complexes were clusters of general formula $[Ru_3(CO)_{12-x}(TPPTS)_x]$, $x = 1$, 2 or 3 [13]. Herrmann et al. have prepared [14] the two complexes $[RuCl_2(TPPTS)_2]$ and $[Ru(NO)_2(TPPTS)_2]$ mainly by addition of TPPTS to the

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ruthenium salt $RuCl_3 \cdot 3H_2O$ followed by a gel permeation chromatography purification [11]. More recently Basset and his group have described the synthesis of $[RuCl_2(TPPTS)_2]_2$, $[Ru(H)(Cl)(TPPTS)_3]$, $[Ru(H)(OAc)(TPPTS)_3]$, and $[Ru(H)_2(TPPTS)_4]$ by an exchange method from the corresponding triphenylphosphine complexes [3,15]. By substitution of the appropriate ligands the complexes $[Ru(H)(I)(TPPTS)_3]$, $[Ru(Cl)_2(CO)_2(TPPTS)_2]$, and $[Ru(OAc)(CO)_2(TPPTS)]_2$ have also been obtained [15].

These complexes have been shown to be active precursors for the hydrogenation of propanal [3,4]. Significantly $[Ru(H)(Cl)(TPPTS)_3]$, generated in situ from $RuCl_3 \cdot 3H_2O$ in the presence of an excess of TPPTS, presents a high selectivity for the hydrogenation of α,β-unsaturated aldehydes into the corresponding allylic alcohols, as shown by Grosselin et al. [2].

We were interested in the hydrogenation of α,β-unsaturated carbonyl compounds and the relationship between the catalytic activity and the structure of the precursor. For this reason, a study of easy and reproducible procedures to prepare pure isolated complexes was undergone. Several known compounds were prepared on a large scale with satisfactory yields. In addition, new complexes have been obtained, particularly those with η^6-coordinated arene ligands. Special emphasis has been given to the characterization of the complexes of this study by ^1H, ^{13}C and ^{31}P NMR.

2. Results and discussion

2.1. Study of the complex $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ 1

The first synthesis of complex **1**, although a mononuclear structure was ascribed to it, has been reported by Herrmann et al. [14]. Addition of an excess of TPPTS to $RuCl_3 \cdot 3H_2O$ in water at 50°C for 1 day, followed by a purification procedure using gel permeation chromatography gave **1** in 61% yield. This complex was characterized by a singlet in ^{31}P NMR at 57.0 ppm (D_2O at 5°C).

Direct addition of TPPTS to the commercial salt $RuCl_3 \cdot 3H_2O$, or exchange of ligands between TPPTS and DMSO in $[Ru(Cl)_2(DMSO)_4]$ or cyclooctadiene in $[Ru(\mu\text{-}Cl)_2(\eta^4\text{-}C_8H_{12})]_n$, led respectively to too low yields, species containing still coordinated DMSO, and abundant quantities of free ligand and OTPPTS. The best procedure to obtain $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ with no free TPPTS is to start from $[Ru(Cl)_2(PPh_3)_3]$ dissolved in THF [15] and to add 1.8 equivalents of TPPTS in water; the exchange proceeds very fast and provides **1** with 95% yield with regard to TPPTS (Eq. (1)).

$$2[Ru(Cl)_2(PPh_3)_3] + 4TPPTS \rightarrow [Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2 + 6PPh_3 \quad (1)$$

At 25°C, a 0.2 M solution of **1** presents two singlets in ^{31}P NMR at 56.4 and 57.0 ppm in approximately a 1:2 ratio of intensities. The major compound will be named **1a**, the second one **1b**. No change of the spectrum is observed after one week, or when a mixture H_2O/D_2O is used instead of pure D_2O. However, temperature, concentration, and an excess of TPPTS or Cl^- ions are important parameters which affect the relative concentrations of compounds. The effect of the temperature is versible since after heating or cooling a given spectrum is restored for a given temperature. At 5°C, in addition to the signals of **1a** and **1b**, a third peak of weak intensity is detected at 57.4 ppm. At higher temperatures this species **1c** is no more detected. When the temperature is raised the relative intensity of **1b** decreases until it is no more observed near to 60°C.

In their analysis of the ^{31}P spectra of the pentacoordinated complex $[Ru(Cl)_2(PPh_3)_3]$, Armit et al. [16] have proposed an exchange phenomenon between this mononuclear complex and $[Ru(Cl)(\mu\text{-}Cl)(PPh)_3)_2]_2$ for which two isomeric square-planar or trigonal-bipyramidal

based pentacoordinated ruthenium centers have been retained. In our case, further experiments have shown that such an hypothesis is presumably not well-grounded. Indeed, when the 0.2 M solution is diluted to 0.05 M and 0.02 M, species **1c** growths whereas **1b** decreases significantly. Similarly, adding 10 equivalents of NaCl to the 0.05 M solution gives rise to two peaks due to **1a** and **1b** of almost the same intensities. Addition of 50 equivalents of NaCl per dinuclear complex affords the signal of **1a** to disappear and two signals at 48.7 and 51.2 ppm to be present beside **1b**. Moreover, an excess of one equivalent of TPPTS modifies the ^{31}P NMR spectra since the signal of **1b** broadens whereas **1a** is not perturbed, and simultaneously one broad signal at 43.5 ppm and the signal of free TPPTS at −5.9 ppm (unusually broad) also are observed.

As displayed on Fig. 1, a double pentacoordinated geometry **1b** is assigned to complex **1**. This complex is in equilibrium with **1a** where a Cl^- ligand has been substituted with a water molecule. Further hydrolysis leads to **1c**. Diluting the solutions favours the equilibrium towards **1c**, whereas addition of sodium chloride shifts the equilibrium on the left side. Due to the presence of the sulfonate groups, the ionic strength of the medium is not dramatically changed by the addition of 10 equivalents of NaCl. In our opinion further addition of an excess of Cl^- ions should give rise to an anionic species like $[Ru_2(Cl)_2(\mu\text{-}Cl)_3(TPPTS)_4]^-$ which presents a signal at 48.7 or 51.2 ppm [17]. With regard to the temperature effect, the spectra are particularly well resolved at 5°C so that **1c** can be detected. Raising the temperature should shift the equilibria between species **1a**, **1b** and **1c**. At 60°C the signal of **1b** has completely disappeared. Due to the proximity of the signals of **1a** and **1c**, the peak observed at 60°C can be attributed to either **1a** or **1c**.

On the other hand, when one or two equivalent(s) of TPPTS is added in the medium, species **1b** should lead to a pentacoordinated 16 electron complex such as $[Ru(Cl)_2(TPPTS)_3]$ whose ^{31}P shift compares well to that of $[Ru(Cl)_2(PPh_3)_3]$ (43.5 and 41.3 ppm [16] respectively).

Complex **1** is a very useful starting material to prepare other complexes of interest.

2.2. Synthesis of $[Ru(H)(Cl)(TPPTS)_3]$ 2

In the presence of two TPPTS equivalents, heating at reflux aqueous solutions of **1** under hydrogen for 2 h leads to complex $[Ru(H)(Cl)(TPPTS)_3]$ **2** (Eq. (2)). The removal of one chloro ligand as hydrochloric acid is assisted by adding triethylamine, although triethylammonium chloride still remains in solution. The ^1H and ^{31}P NMR data, are consistent with this formula [15]. Alternatively, complex **2** can be directly generated under a H_2 pressure of 20–35 bar and at 40–85°C starting either from $RuCl_3 \cdot 3H_2O$ with five equivalents of

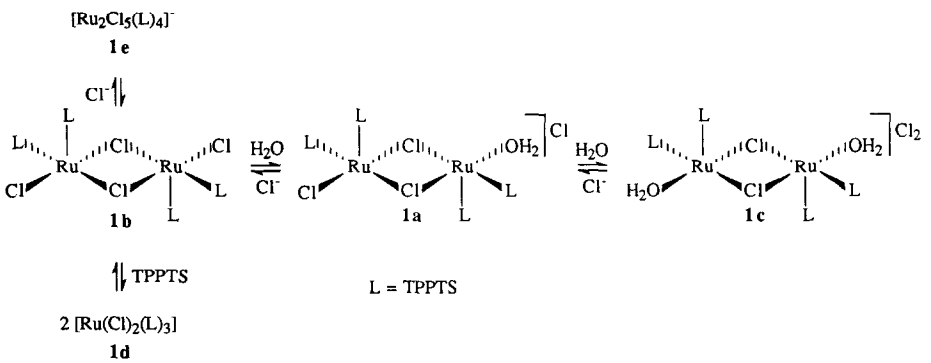


Fig. 1. Equilibrium between neutral **1b** and cationic **1c** and **1d** species; effect of addition of TPPTS or an excess of Cl ions.

TPPTS, or from **1** with one more TPPTS ligand per ruthenium atom. Removing most of hydrochloric acid under vacuum shows that complex **2** is actually present in ^{31}P NMR, whereas in ^{1}H NMR the hydride ligand is not observed anymore [2] due to an exchange phenomenon between $[Ru(H)(Cl)(TPPTS)_3]$ and D_2O catalyzed by a few HCl. When the formation of **2** is performed in the presence of triethylamine the hydride signal of **2** is unambiguously detected in ^{1}H NMR. In addition, a ^{2}D NMR experiment carried out on complex **2** obtained by reduction of $RuCl_3 \cdot 3H_2O$ with 5 TPPTS in the absence of NEt_3, revealed the presence of a large Ru–D signal at -17.6 ppm.

$$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2 + 2TPPTS + 2H_2 \rightarrow 2[Ru(H)(Cl)(TPPTS)_3] + 2HCl \quad (2)$$

2.3. Synthesis of $[Ru(H)_2(TPPTS)_4]$ 4

Instead of proceeding to the exchange reaction of PPh_3 with TPPTS in the complex $[Ru(H)_2(PPh_3)_4]$ [15], we obtained **4** as a pure compound by adding four equivalents of TPPTS and ca. eight equivalents of $NaBH_4$ to complex **1** (Eq. (3)). The reaction is completed at room temperature within 10–15 min, and the yield in isolated deep-yellow microcrystalline material is higher than 95%. In ^{1}H NMR a pseudo-quartet due to an overlap of signals was observed in the high field region at -10.6 ppm, and in ^{31}P NMR, two broad singlets were detected at 55.0 and 42.4 ppm.

$$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2 + 4TPPTS + 4NaBH_4 + 12H_2O \rightarrow 2[Ru(H)_2(TPPTS)_4] + 4NaCl + 4B(OH)_3 + 12H_2 \quad (3)$$

Two other methods to prepare **4** can be used. Addition at room temperature under one atmosphere of hydrogen of one equivalent of TPPTS and two equivalents of $NaBH_4$ to complex **2** affords **4** very quickly (10 min). Starting from $RuCl_3 \cdot 3H_2O$ under a hydrogen atmosphere leads to **4**, by adding 4.5TPPTS and $12NaBH_4$ then heating at 50°C for 10 min. Although a slight excess of TPPTS, OTPPTS, and traces of free $NaBH_4$ are present in the medium, this procedure is interesting because it gives a convenient access to **4**, starting directly from the commercial salt.

2.4. Synthesis of $[Ru(H)_2(CO)(TPPTS)_3]$ 5

Addition of two moles of TPPTS and 8 equivalents of $NaBH_4$ to complex **1** under a CO atmosphere affords **4** within 5 min at 80°C. Around 5% of a new species is concurrently formed whose spectroscopic characteristics ($\delta_P = 57.2$ (s), no hydride signal, $\nu_{CO} = 1893$ cm^{-1}) parallel those of $[Ru(CO)_3(PPh_3)_3]$ [18,19] so that its formula is presumably $[Ru(CO)_3(TPPTS)_2]$. The PPh_3/TPPTS exchange from $[Ru(H)_2(PPh_3)_4]$ under CO gives **5** but with low yields.

Complex **5** can be advantageously prepared by bubbling CO in an aqueous solution of **4**. The reaction (Eq. (4)) is complete at room temperature within 10–15 min as monitored by ^{31}P NMR.

$$[Ru(H)_2(TPPTS)_4] + CO\ (1\ atm) \rightarrow [Ru(H)_2(CO)(TPPTS)_3] + TPPTS \quad (4)$$

Complex **5** $[Ru(H)_2(CO)(TPPTS)_3]$ was fully characterized by ^{1}H ^{31}P NMR and infrared spectroscopy. For the hydride signals, the shifts as well as the various coupling constants are quite comparable to those of $[Ru(H)_2(CO)(PPh_3)_3]$ [20]. These data are consistent with an equatorial hydride ligand coupled with two *cis* and one *trans* TPPTS ligands and with an axial hydride ligand coupled with two *cis* equivalent and one *cis* TPPTS ligands, as shown on Fig. 2.

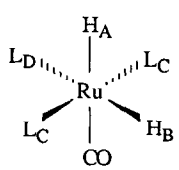


Fig. 2. Proposed geometry for complex $[Ru(H)_2(CO)(TPPTS)_3]$.

In ^{31}P NMR the two L_C phosphine ligands give a doublet at 58.1 ppm ($^2J_{PP}$ = 17.5 Hz) and L_D gives a triplet at 47.2 ppm ($^2J_{PP}$ = 17.5 Hz). For comparison: the ^{31}P shifts reported for $[Ru(H)_2(CO)(PPh_3)_3]$ are 61.8 and 47.5 with a $^2J_{PP}$ = 17.5 Hz coupling constant [21].

In infrared the ν_{CO} band is observed at 1941 cm^{-1}. Whereas $[Ru(H)_2(CO)(PPh_3)_3]$ presents two ν_{Ru-H} stretching frequencies at 1960 (m) and 1898 (m) cm^{-1} in addition to the ν_{CO} at 1940 cm^{-1}, we only detected a large peak of medium intensity at 1893 cm^{-1} with two shoulders at 1905 and 1850 cm^{-1}. In the present TPPTS-complex **5** which contains $[Ru(CO)_3(TPPTS)_2]$ as by-product with its ν_{CO} band at 1893 cm^{-1}, the ν_{Ru-H} bands are not detected (1960 and 1898 cm^{-1} expected). It has already been mentioned in the literature that the triphenylphosphine complex $[Ru(H)(OH)(PPh_3)_2(solvent)]$ leads to $[Ru(CO)_3(PPh_3)_2]$ under a CO atmosphere [22]. Similar irradiation of $[Ru(H)_2(CO)(PPh_3)_3]$ under CO affords $[Ru(CO)_3(PPh_3)_2]$ [19].

2.5. Synthesis of $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ complexes **6**

Studies on the hydrogenation of α,β-unsaturated aldehydes [23], when carried out in toluene, led us to observe that precursors **1**, **2** or $RuCl_3 \cdot 3H_2O$ with an excess of TPPTS, afforded the complex $[Ru(H)(\eta^6\text{-}C_6H_5CH_3)(TPPTS)_2]Cl$. The reaction of various aromatic ligands was thus investigated starting from **1** since only one species is obtained for a given ligand (Eq. (5)).

$$[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2 + 2\,\text{arene} + 2H_2 \rightarrow 2[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl + 2HCl \quad (5)$$

Complex $[Ru(H)(\eta^6\text{-}C_6H_5CH_3)(TPPTS)_2]Cl$ **6a** was prepared from water solutions of **1** and an excess of toluene under 35 bar of hydrogen at 60°C for 1 h 30. From this biphasic medium **6a** was obtained almost quantitatively in the acidic aqueous phase. The yield in isolated **6a** was greater than 90%. This complex presents in ^{31}P NMR a singlet at 56.1 ppm. In ^1H NMR, the hydride ligand is detected at −9.56 ppm as a 1:2:1 triplet due to the coupling with two equivalent phosphine ligands in *cis* position owing to the $^2J_{PH}$ value of 36 Hz. The η^6-bonded toluene ligand gives rise to a singlet at 2.24 (3H, methyl), a doublet at 4.79 ($^3J_{HH}$ = 6.1, 2H *ortho*) a triplet at 5.58 ($^3J_{HH}$ = 6.0, 2H *meta*), and a triplet at 6.26 ($^3J_{HH}$ = 5.9, 1H *para*). In addition, the signals of the two TPPTS ligands are found in the 7.3–7.8 region. These assignations were confirmed by ^{13}C NMR, especially by using the *J* modulated spin echo method.

As reported in Tables 1–3, all the signals have been assigned. Particularly informative are in ^{13}C the peak at 119.3 for the *ipso*-carbon of toluene, the three aromatic C–H signals at 95.5, 96.5 and 102.4 and the CH_3 signal at 22.9 ppm. Such arene complexes containing TPPTS ligands are unprecedented. The analogous $[Ru(H)(\eta^6\text{-arene})L_2]^+$ complexes [24–32] containing mainly PPh_3 as phosphine ligand were already reported in the literature. The complex $[Ru(H)(\eta^6\text{-}C_6H_5CH_3)(PPh_3)_2][BPh_4]$, whose X-ray structure was determined, presents a hydride signal at −9.53 ppm (t, $^2J_{PH}$ = 37.7 ppm) which compares to the shift and the $^2J_{PH}$ value

Table 1
$^{31}P\{^1H\}$ NMR data of complexes $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ **6a–6h** (101.26 MHz, D_2O, 25°C)

$[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$	Arene	δ (ppm) [a]
6a	toluene	56.1
6b	benzene	55.1
6c	*p*-xylene	55.8
6d	ethylbenzene	55.8
6e	cumene	55.5
6f	tetraline	57.3
6g	dihydrocinnamic alcohol	55.6
6h	*cis*-cinnamic alcohol	55.5

[a] Multiplicity: singlet.

found in **6a** [25]. Fig. 3 shows a representation of **6a** where toluene occupies three coordination positions of an octahedron.

Similarly, complex **3** [Ru(H)(OAc)(TPPTS)$_3$] reacts with toluene under hydrogen to afford [Ru(H)(η^6-$C_6H_5CH_3$)(TPPTS)$_2$](OAc) **6a'**, although the reaction is not complete (Eq. (6)). The ^{1}H and ^{31}P NMR spectra are similar to those of **6a** (−9.49 and 56.1 respectively for Ru–H and Ru–P) independently of the acetate counterion signal at 1.89 ppm (note that in **3** the OAc signal is at 1.33 ppm). The situation differs notably when we start from **1** or **3** to prepare the cationic entity [Ru(H)(η^6-$C_6H_5CH_3$)(TPPTS)$_2$]$^+$. Indeed, complex **1** has only two TPPTS ligands per ruthenium atom, whereas **3** has three TPPTS. In addition, the acetato ligand has a better coordinating ability

Table 2
^{1}H NMR data of the complexes [Ru(H)(η^6-arene)(TPPTS)$_2$]Cl **6a–6h** (200.13 MHz, D_2O, 21°C)

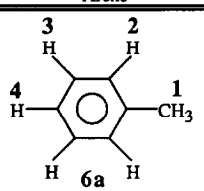
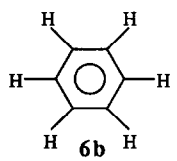
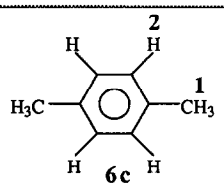
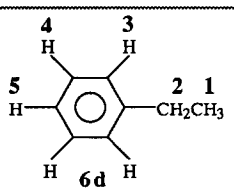
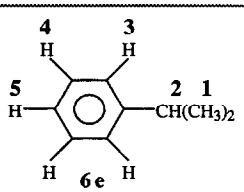
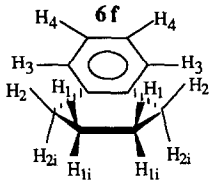
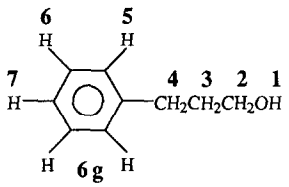
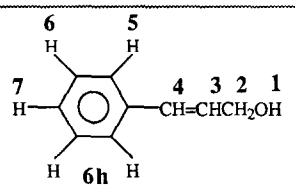
[Ru(H)(η^6-arene)(TPPTS)$_2$]Cl Arene	δ (ppm)	Assignment	Coupling constant (Hz)	
 **6a**	7.80-7.29 (m, 24 H)	Ar-H (TPPTS)	*nd*	
	6.26 (t, 1 H)	H_4 arene	5.9	$^3J(H\text{-}H)$
	5.58 (t, 2 H)	H_3 arene	6.0	$^3J(H\text{-}H)$
	4.79 (d, 2 H)	H_2 arene	6.1	$^3J(H\text{-}H)$
	2.24 (s, 3 H)	H_1 arene		
	- 9.56 (t)	Ru-H	36	$^2J(P\text{-}H)$
 **6b**	7.77-7.14 (m, 24 H)	Ar-H (TPPTS)	*nd*	
	5.63 (s, 6 H)	H arene		
	- 9.43 (t)	Ru-H	36	$^2J(P\text{-}H)$
 **6c**	7.82-7.05 (m, 24 H)	Ar-H (TPPTS)	*nd*	
	4.92 (s, 4 H)	H_2 arene		
	2.20 (s, 6 H)	H_1 arene		
	- 10.13 (t)	Ru-H	36.5	$^2J(P\text{-}H)$
 **6d**	7.81-7.15 (m, 24 H)	Ar-H (TPPTS)	*nd*	
	6.63 (t, 1 H)	H_5 arene	5.8	$^3J(H\text{-}H)$
	5.53 (t, 2 H)	H_4 arene	5.8	$^3J(H\text{-}H)$
	4.57 (d, 2 H)	H_3 arene	6.2	$^3J(H\text{-}H)$
	2.56 (q, 2 H)	H_2 arene	7.3	$^3J(H\text{-}H)$
	1.27 (t, 3 H)	H_1 arene	7.4	$^3J(H\text{-}H)$
	- 9.40 (t)	Ru-H	36	$^2J(P\text{-}H)$
 **6e**	7.82-7.32 (m, 24 H)	Ar-H (TPPTS)	*nd*	
	6.85 (t, 1 H)	H_5 arene	5.8	$^3J(H\text{-}H)$
	5.52 (t, 2 H)	H_4 arene	5.6	$^3J(H\text{-}H)$
	4.47 (d, 2 H)	H_3 arene	6.2	$^3J(H\text{-}H)$
	2.86 (m, 1 H)	H_2 arene	6.8	$^3J(H\text{-}H)$
	1.28 (d, 6 H)	H_1 arene	6.8	$^3J(H\text{-}H)$
	- 9.30 (t)	Ru-H	36.3	$^2J(P\text{-}H)$

Table 2 (continued)

[Ru(H)(η⁶-arene)(TPPTS)₂]Cl Arene	δ (ppm)	Assignment	Coupling constant (Hz)	
 **6f**	8.00-7.30 (m, 24 H)	Ar-H (TPPTS)	*nd*	
	6.23 (s, 2 H)	H_4 arene		
	4.38 (s, 2 H)	H_3 arene		
	2.03 (m, 2 H)	H_2 arene[1]	*nd*	
	1.68 (m, 4 H)	$H_1 + H_{2i}$ arene[1]	*nd*	
	1.49 (m, 2 H)	H_{1i} arene[1]	*nd*	
	- 9.94 (t)	Ru-H	36	$^2J(P\text{-}H)$
 **6g**	8.02-6.95 (m)	Ar-H (TPPTS, DCA)[2]	*nd*	
	6.55 (t, 1 H)	H_7 arene	5.8	$^3J(H\text{-}H)$
	5.55 (t, 2 H)	H_6 arene	5.7	$^3J(H\text{-}H)$
	4.63 (d, 2 H)	H_5 arene	6.1	$^3J(H\text{-}H)$
	3.61 (t, 2 H)	H_2 arene	6.3	$^3J(H\text{-}H)$
	2.57 (t, 2 H)	H_4 arene	7.7	$^3J(H\text{-}H)$
	1.84 (qt*, 2 H)	H_3 arene	7.6	$^3J(H\text{-}H)$
	- 9.43 (t)	Ru-H	36	$^2J(P\text{-}H)$
 **6h**	8.00-6.99 (m)	Ar-H (TPPTS, CA)[3]	*nd*	
	5.87 (s br, 2 H)	*cis*-H_{3+4} arene	*nd*	$^3J(H\text{-}H)$
	5.74 (t, 2 H)	H_6 arene	5.7	$^3J(H\text{-}H)$
	5.64 (t, 1 H)	H_7 arene	5.9	$^3J(H\text{-}H)$
	5.32 (d, 2 H)	H_5 arene	6.2	$^3J(H\text{-}H)$
	3.93 (s br, 2 H)	H_2 arene	*nd*	$^3J(H\text{-}H)$
	- 9.85 (t)	Ru-H	36	$^2J(P\text{-}H)$

[1]The assignations were made from 2-D ^1H {^{31}P}/^{13}C {^1H, ^{31}P} GE-HMQC ^1J {^{13}C, ^{31}P} NMR experiments.

[2]The product is obtained with around 30% of dihydrocinnamic alcohol (DCA) whose shifts of the lateral chain are : 3.38 (t, $^3J_{H\text{-}H}$ = 6.6 Hz, 2 H), 2.35 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 2 H), 1.56 (qt, $^3J_{H\text{-}H}$ = 7.0 Hz, 2 H) ppm.

[3][Ru(H)(η⁶-*cis*-$C_6H_5CH{=}CHCH_2OH$)(TPPTS)₂]Cl is recovered with traces of **6g** and around 30% of *trans*-cinnamic alcohol (CA) whose shifts of the lateral chain are : 4.01 (d, $^3J_{H\text{-}H}$ = 5.6 Hz, 2 H), 6.08 (dt, $^3J_{H\text{-}H}$ = 5.7/16.1 Hz, 1 H), 6.32 (dt, $^3J_{H\text{-}H}$ = 16.2 Hz, 1 H) ppm.

than the chloro ligand, since starting from $[Ru(H)(Cl)(TPPTS)_3]$, complex **6a** is fully obtained with one mole of TPPTS in excess whereas from $[Ru(H)(OAc)(TPPTS)_3$ the yield in **6a′** is ca. 20%.

$$[Ru(H)(OAc)(TPPTS)_3] + PhCH_3 \rightarrow [Ru(H)(\eta^6\text{-}PhCH_3)(TPPTS)_2](OAc) + TPPTS \quad (6)$$

We have observed that several aromatic ligands have the same reactivity with regard to complex **1** giving rise to complexes **6** of general formula $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ containing benzene **6b**, *p*-xylene **6c**, ethylbenzene **6d**, cumene **6e**, tetraline (or 1,2,3,4-tetrahydronaphtalene) **6f**, dihydrocinnamic alcohol **6g**, and cinnamic alcohol **6h**. The same procedure as for **6a** gave compounds **6b–6h** in high isolated yields. These deep-yellow derivatives are highly soluble in water, and slightly air-sensitive in solution. Unexpectedly, in infrared, no ν_{Ru-H} band was detected. According to the NMR data (Tables 1–3), all the species have basically the same geometry. In complex **6h** the cinnamic alcohol ligand presents a *Z* conformation. However, for complexes **6g** and **6h**, the proton of the alcohol was not detected. For tetraline the satu-

rated cycle (see Fig. 4) gives rise to two signals for the CH_2 groups in α-positions with regard to the benzenic cycle and to two signals for the two others CH_2 groups. 2-D $^{13}C\{^1H, ^{31}P\}$–$^1H\{^{31}P\}$ NMR allowed us to assign the signals of tetraline coordinated to ruthenium (see Tables 2 and 3). The ^{13}C NMR signals are in the expected regions. The data are listed in Table 3.

Under the same experimental conditions, complex **4** $[Ru(H)_2(TPPTS)_4]$ does not react with toluene. Complex **4** is a stable 18 electron complex giving rise by dissociation of one TPPTS ligand to a formally 16 electron complex which should be in fact $[Ru(H)_2(TPPTS)_3(H_2O)]$ [3,4,15]. Presumably the main reason for the absence of reactivity of **4** with toluene is that it is difficult to generate a cationic species in this case.

Examination of the coordination of an aromatic group of various substrates has also been investigated. Attempts to coordinate styrene, benzaldehyde, benzyl- and benzylideneacetone, benzonitrile, benzoic acid gave a mixture of products; the phenyl ring is coordinated but in most of the cases the unsaturated substituent of the aromatic group has also been hydrogenated.

Table 3
^{13}C NMR data of the complexes $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ **6a–6h** (62.9 MHz, D_2O, 24°C)

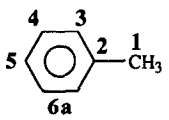
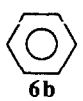
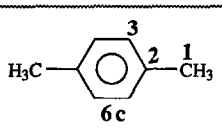
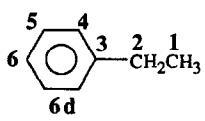
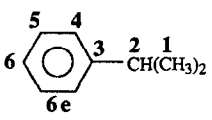
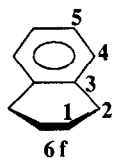
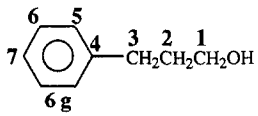
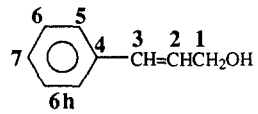
$[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ Arene	δ(ppm)	Assignment
 **6a**	145.2-130.2	Carbons of TPPTS ligands[1]
	119.3	C_2 η^6-toluene
	102.4	$C_{3 \text{ or } 4 \text{ or } 5}$
	96.5	$C_{3 \text{ or } 4 \text{ or } 5}$
	95.5	$C_{3 \text{ or } 4 \text{ or } 5}$
	22.9	C_1
 **6b**	145.3-130.4	Carbons of TPPTS ligands
	99.4	C-H η^6-benzene
 **6c**	145.3-130.3	Carbons of TPPTS ligands
	115.4	C_2 η^6-*p*-xylene
	99.3	C_3
	21.8	C_1
 **6d**	145.3-130.4	Carbons of TPPTS ligands
	126.6	C_3 η^6-ethylbenzene
	103.1	$C_{4 \text{ or } 5 \text{ or } 6}$
	97.9	$C_{4 \text{ or } 5 \text{ or } 6}$
	93.3	$C_{4 \text{ or } 5 \text{ or } 6}$
	29.8	C_2
	18.2	C_1
 **6e**	145.6-130.7	Carbons of TPPTS ligands
	131.9	C_3 η^6-cumene[2]
	103.4	C_5
	98.5	C_6
	91.3	C_4
	35.4	C_2
	26.4	C_1

Table 3 (continued)

[Ru(H)(η⁶-arene)(TPPTS)₂]Cl Arene	δ(ppm)	Assignment
 6f	145.4-130.5	Carbons of TPPTS ligands
	113.7	C_3 η⁶-tetraline[2]
	99.9	C_4
	99.5	C_5
	28.7	C_2
	24.3	C_1
 6g	145.4-130.8	Carbons of TPPTS ligands
	123.8	C_4 η⁶-DCA[3]
	102.9	$C_{5 \text{ or } 6 \text{ or } 7}$
	97.8	$C_{5 \text{ or } 6 \text{ or } 7}$
	94.2	$C_{5 \text{ or } 6 \text{ or } 7}$
	63.5	C_1
	36.9	$C_{2 \text{ or } 3}$
	33.2	$C_{2 \text{ or } 3}$
 6h	145.4-130.5	Carbons of TPPTS ligands
	129.0	$C_{2 \text{ or } 3}$ η⁶-CA[4]
	125.4	$C_{2 \text{ or } 3}$
	115.2	C_4
	99.6	$C_{5 \text{ or } 6 \text{ or } 7}$
	96.5	$C_{5 \text{ or } 6 \text{ or } 7}$
	95.4	$C_{5 \text{ or } 6 \text{ or } 7}$
	64.0	C_1

[1]The signals of the TPPTS aromatic carbons are : 130.2 (*p*-C-H, $^4J_{P\text{-}C} = 0$ Hz), 131.8 and 132.3 (*o*-C-H, $^2J_{P\text{-}C} \approx 5$ Hz), 136.4 (C-P, $^1J_{P\text{-}C} = 48.4$ Hz, $^3J_{P\text{-}C} = {}^3J_{C\text{-Hydride}} = 24.3$ Hz), 138.2 (*m*-C-H, $^3J_{P\text{-}C} \approx 5$ Hz), 145.2 (C-SO_3Na, $^3J_{P\text{-}C} \approx 5$ Hz) ppm.

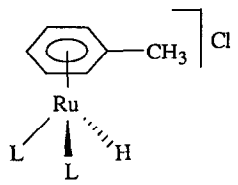
[2]The assignations were made from 2-D $^1H\{^{31}P\}/^{13}C\{^1H, ^{31}P\}$ GE-HMQC $^1J\{^{13}C, ^{31}P\}$ NMR experiments.

[3]DCA : dihydrocinnamic alcohol.

[4]CA : *cis*-cinnamic alcohol.

In addition, as Sanders, then Wilkinson et al. have reported the synthesis of $[Ru(H)(\eta^6\text{-}C_6H_5PPh_2)(PPh_3)_2]^+$ [30–32], we have added a large excess of triphenylphosphine to complex **1** in diethylether/water mixtures. In our standard conditions, two purple phases were simultaneously obtained, the acidic aqueous phase containing exclusively $[Ru(H)(Cl)(TPPTS)_3]$ and an excess of TPPTS but not the expected $[Ru(H)(\eta^6\text{-}C_6H_5PPh_2)(TPPTS)_2]^+$ complex.

Neat triphenylphosphite reacts with aqueous solutions of complex **1**. Presumably $[Ru(H)(\eta^6\text{-}C_6H_5OP(OPh)_2)(TPPTS)_2]^+$ is formed but rapid hydrolysis occurs leading to $[Ru(H)(\eta^6\text{-}C_6H_5OH)(TPPTS)_2]Cl$ or more presumably a η^6-phenoxo complex as previously described in the PPh_3 series of ruthenium complexes [32]. However, other side reactions should proceed since some free TPPTS was detected. In ^1H NMR, the hydride signal is at -10.31 (t, $^2J_{PH} = 34.5$ Hz), the aromatic hydrogen atoms are found at 4.34 (t, $^3J_{HH} = 5.6$ Hz, *p*-H), 4.81 (d,

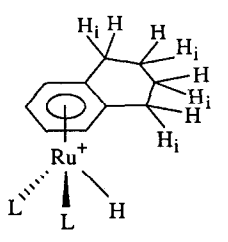


L = TPPTS

Fig. 3. Proposed geometry for complex $[Ru(H)(\eta^6\text{-}C_6H_5CH_3)(TPPTS)_2]Cl$.

$^3J_{HH} = 6.1$, 2 *o*-H) and 5.47 ppm (t, $^3J_{HH} = 6.0$ Hz, 2 *m*-H). In ^{31}P NMR, the signal of this complex was observed at 56.9 ppm, besides a broad peak at 5.5 ppm.

Finally, two reactions were carried out in order to attempt to displace the coordinated benzene ligand in complex **6b**. At room temperature carbon monoxide does not react. However, bubbling CO at 90°C for 1 h transforms around 80% of **6b** as estimated from ^{31}P NMR. In ^1H NMR, besides the triplet of **6b** at −9.38 ppm, four triplets of unequal intensities were measured at −14.25, −6.34, −4.80 and −4.22 ppm, the $^2J_{PH}$ values being in the 15–19 Hz range. ^{31}P NMR shows six species in addition to **6b**, *i.e.* two species which do not contain hydride ligands. We believe that the complex $[Ru(H)(Cl)(CO)_2(TPPTS)_2]$, in presumably several isomeric forms, has been produced. Indeed, three strong ν_{CO} bands, although having several shoulders, have been observed in infrared at 2066, 1996 and 1890 cm^{-1}. Thus it appears that the benzene ligand can be displaced by carbon monoxide, but the reaction produces several complexes in solution containing the framework



L = TPPTS

Fig. 4. Proposed geometry for complex $[Ru(H)(\eta^6\text{-tetraline})(TPPTS)_2]^+$.

$[Ru(H)(Cl)(CO)_x(TPPTS)_2]$. The same complex mixture has also been obtained by carbonylation of $[Ru(H)(Cl)(TPPTS)_3]$.

Addition at room temperature of two equivalents of $NaBH_4$ to **6b** with two moles of TPPTS in excess led slowly to $[Ru(H)_2(TPPTS)_4]$. This complex was unambiguously evidenced by ^1H and ^{31}P NMR. A few oxide of TPPTS was formed during this reaction. Here also the benzene ligand can be displaced by TPPTS provided the chloro ligand be substituted due to the introduction of BH_4^-, since the sole addition of TPPTS to **6b** does not transform it.

3. Conclusion

The complex $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ which was shown to exist in solution as a mixture of this neutral species and ionic water-containing species, is an useful starting material to prepare a number of TPPTS containing ruthenium(II) complexes. $[Ru(H)(Cl)(TPPTS)_3]$, $[Ru(H)_2(TPPTS)_4]$ can be obtained in high yields in the absence of extra TPPTS. The new complexes $[Ru(H)_2(CO)(TPPTS)_3]$ and $[Ru(H)(\eta^6\text{-arene})(TPPTS)_2]Cl$ have been prepared and fully characterized by ^1H, ^{31}P and also by ^{13}C for the arene complexes, NMR spectroscopy. In the following paper the catalytic activity of these precursors will be examined for the hydrogenation reaction of α,β-unsaturated aldehydes and more generally carbonyl compounds.

4. Experimental section

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. All chemicals, including $RuCl_3 \cdot 3H_2O$, were purchased from Aldrich, Janssen, SDS, and for gases from Prodair. All solvents were saturated with argon prior to use.

The ligand tris(*m*-sulfonatophenyl)phosphine (TPPTS) as a solution in water was generously

provided by Rhône–Poulenc. TPPTS was purified by precipitation from the aqueous solution by slow addition of ethanol. The resulting white solid was successively washed with ethanol and ether, dried under reduced pressure and stored under argon. According to the elemental analysis, the ligand is trihydrated so that a molecular weight of 622.47 g mol^{-1} was considered for the syntheses.

NMR spectra were recorded on a Brücker AC 200 for ^{1}H (200.13 MHz, 21°C, external reference TMS), or a Brücker WM 250 for ^{13}C (62.90 MHz, 24°C, external reference TMS) and ^{31}P (101.26 MHz, 25°C, external reference H_3PO_4 85% in D_2O); s: singlet, d: doublet, t: triplet, q: quartet, qt: quintet, sp: septuplet, m: multiplet, br: broad, asterisk: pseudo. All the samples were dissolved under argon in D_2O from SDS (D% > 99.8).

IR spectra were collected on a Perkin-Elmer 1710 FTIR spectrometer; w: weak, m: medium, s: strong, vs: very strong, br: broad. Solids were analyzed in nujol mulls or KBr pellets.

Elemental analyses were performed in the Service de Microanalyse de l'Ecole Nationale Supérieure de Chimie de Toulouse.

The complexes $[Ru(Cl)_2(PPh_3)_3]$ [33], $[Ru(H)(Cl)(PPh_3)_3] \cdot PhCH_3$ [34], $[Ru(H)(OAc)(PPh_3)_3]$ [35], $[Ru(H)_2(PPh_3)_4]$ [36], $[Ru(H)_2(CO)(PPh_3)_3]$ [20] and $[Ru(\mu\text{-}Cl)_2(\eta^4\text{-}C_8H_{12})]_n$ [37] have been prepared according to the reported procedures. The synthesis of $[Ru(Cl)_2(DMSO)_4]$ was adapted from a method described in the literature [38] and give a yellow powder in ca. 85% isolated yields.

4.1. Preparation of $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ 1

1 was prepared by a method slightly adapted from Basset's procedure [15]. $[Ru(Cl)_2(PPh_3)_3]$ (5.8 g; 6 mmol) was dissolved in 150 ml of THF and heated to 60°C. A 30 ml water-solution of TPPTS (6.3 g; 10.1 mmol) was added dropwise under vigorous stirring. The biphasic medium was stirred further for 30 min at 60°C. After cooling to room temperature, 140 ml of the orange organic layer was removed. The resulting solution was filtered out, then the deep-red aqueous phase was evaporated to dryness and dried in vacuo (1 h, 50°C). Further addition of 30 ml of water, filtration, evaporation and drying under vacuum (3 h, 50°C) led to a crystalline bright red–chestnut product. Calculated on TPPTS introduced, the yield was 6.9 g (96%). $^{31}P\{^{1}H\}$ NMR: $\delta + 57.0$ (s) isomer **1a** (ca. 65%), $\delta + 56.4$ (s) isomer **1b** (ca. 35%); ^{1}H NMR: $\delta + 7.1–8.1$ (m) Ar–H.

4.2. Preparation of $[Ru(H)(Cl)(TPPTS)_3]$ 2

4.2.1. Exchange method

An exchange procedure similar to that described for **1** was adopted to prepare complex **2** from $[Ru(H)(Cl)(PPh_3)_3] \cdot PhCH_3$. $[Ru(H)(Cl)(PPh_3)_3] \cdot PhCH_3$: 3 g (3.3 mmol); THF: 120 ml; TPPTS: 5 g (8 mmol); H_2O: 30 ml. A bright crystalline purple solid was recovered in 93% yield (ca. 5 g) compared with the TPPTS used. $^{31}P\{^{1}H\}$ NMR: $\delta + 58.8$ (s br); ^{1}H NMR: $\delta - 18.6$ (q, $^{2}J_{PH} = 25$ Hz) Ru–H, $\delta +$ 7.2–7.8 (m) Ar–H.

4.2.2. $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ / 2TPPTS / 20NEt_3

1.0 g of **1** (0.35 mmol) and 0.45 g (0.7 mmol) of TPPTS were dissolved in 15 ml of water; 1 ml (7.2 mmol) of NEt_3 were added under stirring and the reaction medium was heated at reflux for 2 h, while hydrogen was bubbled. The orange–red solution became purple. The solution was cooled and evaporated to dryness to give a raspberry–red solid which was washed with 15 ml of ethanol, dried in vacuo (2 h at 50°C). Around 1.6 g of product were obtained which contained ($^{31}P\{^{1}H\}$ NMR) ca. 78% of **2**, 3% of OTPPTS, 7% of TPPTS; two signals at $\delta + 78.9$ (t) 4% and 45.1 (d) 8% have not been assigned.

When the previous preparation was conducted without triethylamine a raspberry–red solid was similarly obtained from a very acidic aqueous solution. $^{31}P\{^{1}H\}$ NMR analysis showed

that **2** was mainly present beside **1**, TPPTS and traces of OTPPTS.

4.3. Preparation of [Ru(H)(OAc)(TPPTS)$_3$] 3

We have followed the exchange procedure starting from [Ru(H)(OAc)(PPh_3)$_3$] (1 g; 1.1 mmol), THF (80 ml), TPPTS (1.9 g; 3 mmol) and H_2O (15 ml). A deep-yellow crystalline product was isolated in ca. 90% yield (ca. 1.8 g). IR (KBr): ν_{as}(OCO) = 1527 (m) cm^{-1}, ν_s(OCO): non-observed; $^{31}P\{^1H\}$ NMR: δ + 79.4 (t, $^2J_{PP}$ = 29 Hz), δ + 45.9 (d, $^2J_{PP}$ = 29 Hz), A_2X system; ^1H NMR: δ − 18.7 (q, $^2J_{PH}$ = 26 Hz) Ru–H, δ + 1.3 (s) $OCOCH_3$, δ + 7.1–7.8 (m) Ar–H.

4.4. Preparation of [Ru(H)$_2$(TPPTS)$_4$] 4

Complex **4** can be prepared starting from either a ($RuCl_3 \cdot 3H_2O$/TPPTS) system, [Ru(Cl)(μ-Cl)(TPPTS)$_2$]$_2$ or [Ru(H)(Cl)(TPPTS)$_3$] in the presence of $NaBH_4$. Characterization by ^1H and $^{31}P\{^1H\}$ NMR of all these different samples are listed on Table 4.

4.4.1. $RuCl_3 \cdot 3H_2O$ / TPPTS / $NaBH_4$

0.1 g (0.38 mmol) of $RuCl_3 \cdot 3H_2O$ and 1.07 g of TPPTS (1.72 mmol) were dissolved in 10 ml of water. The deep-brown solution was stirred at room temperature while a slow stream of H_2 was passed through the mixture. After 10 min of bubbling, 0.17 g (ca. 4.5 mmol) of $NaBH_4 \cdot xH_2O$ were added: the solution became instantaneously brown–yellow whereas a strong release of gas was observed (H_2). Then, the mixture was heated for 10 min at 50°C. After cooling, evaporation to dryness and drying under vacuum (2 h, 50°C) a crystalline brown–yellow solid was obtained. Typical yield is 1.3 g.

4.4.2. [Ru(Cl)(μ-Cl)(TPPTS)$_2$]$_2$ / TPPTS / $NaBH_4$

The same procedure was carried out but without heating after addition of sodium tetrahydroborate. **1**: 1.5 g (0.53 mmol), TPPTS: 1.32 g (2.12 mmol), H_2O: 15 ml, $NaBH_4 \cdot xH_2O$: 0.16 g (ca. 4.23 mmol). The initial orange solution became instantaneously deep-yellow after addition of $NaBH_4$. The release of gas was observed. A deep-yellow crystalline solid was

Table 4
NMR data of the complex [Ru(H)$_2$(TPPTS)$_4$] **4**

$^{31}P\{^1H\}$ (101.26 MHz, D_2O)

Signal			precursors		
δ (ppm)	multiplicity	assignation	$RuCl_3 \cdot 3H_2O$	**1**	**2**
55.0	s br	**4**	ca. 80%	ca. 100%	ca. 100%
42.4	s br	**4**			
34.6	s	OTPPTS	ca. 10%	trace	trace
21.3	s br	?	trace	—	trace
−5.7	s	free TPPTS	ca. 10%	trace	trace

^1H (200.13 MHz, D_2O)

δ (ppm)	multiplicity	assignation
8.1–6.6	m	Ar–H
−0.2	sp, $^2J_{B-H}$ = 27 Hz	^{10}B–H Free $NaBH_4$ [a]
−0.2	q, $^2J_{B-H}$ = 82 Hz	^{11}B–H Free $NaBH_4$ [a]
−10.6	q *, $^2J_{P-H}$ * = 33 Hz	Ru–H **4**

[a] This species is detected when $RuCl_3 \cdot 3H_2O$ is the precursor, rarely with **2**.

recovered in quantitative yield (ca. 2 g) calculated with the formula $[Ru(H)_2(TPPTS)_4] \cdot 2NaCl$.

4.4.3. *[Ru(H)(Cl)(TPPTS)$_3$] / TPPTS / NaBH$_4$*

The same method as described in Section 4.4.2 was adopted. The following quantities were used: **2**: 0.2 g (0.1 mmol), TPPTS: 0.0622 g (0.1 mmol), H_2O: 10 ml and $NaBH_4 \cdot xH_2O$: 0.0076 g (ca. 0.2 mmol). A deep-yellow crystalline solid $[Ru(H)_2(TPPTS)_4] \cdot NaCl$ was obtained in quantitative yield (ca. 0.27 g).

4.5. *Preparation of [Ru(H)$_2$(CO)(TPPTS)$_3$] 5*

4.5.1. *Exchange method*

$[Ru(H)_2(PPh_3)_4]$ (0.5 g; 0.4 mmol) was dissolved in 60 ml of THF and heated to 60°C. A solution of 0.67 g of TPPTS (1.1 mmol) dissolved in 10 ml of water was added dropwise under vigorous stirring, carbon monoxide being bubbled for 30 min. After cooling to room temperature, elimination of most of the organic phase, the solution was introduced in a separation funnel and the aqueous phase separated by decantation. Evaporation of water under reduced pressure led to a yellow crystalline solid (0.63 g, ^{31}P spectroscopic yield 14%) which was dried in vacuo for 3 h at 50°C. IR (nujol): $\nu_{CO} = 1941$ (vs br), 1905 (sh), 1893 (s), 1850 (sh) cm^{-1}; $^{31}P\{^1H\}$ NMR: $\delta - 5.7$ (s) free TPPTS, 57.2 (s)?, 47.2 (t, $^2J_{PP} = 17.5$ Hz) and 58.1 (d, $^2J_{PP} = 17.5$ Hz) ^1H NMR: $\delta - 8.8$ (tdd, $J = 29$, 73 and 6 Hz) H_B, -6.8 (tdd, $J = 28$, 18 and 6 Hz) H_A, 6.9–8.1 (m) Ar–H.

4.5.2. *From [Ru(Cl)(μ-Cl)(TPPTS)$_2$]$_2$*

A solution containing 0.3 g of **1** (0.105 mmol) and 0.13 g of TPPTS (0.21 mmol) was prepared and heated at 80°C. Carbon monoxide was bubbled into the solution and 0.032 g of $NaBH_4 \cdot xH_2O$ (ca. 0.85 mmol) was introduced. The orange solution became yellow as soon as a slight excess of $NaBH_4$ was introduced. The CO bubbling was maintained for 5 min. The solution was evaporated to dryness. After drying in vacuo (50°C, 1 h) an orange–yellow solid was collected (0.43 g). IR spectrum is similar to that of Section 4.5.1; from $^{31}P\{^1H\}$ NMR **5** was obtained with 85% abundance, 5% TPPTS and 5% OTPPTS were present besides traces ($\delta =$ 21.3 ppm, s) and 5% ($\delta = 57.2$ ppm, s) of two unknown products.

4.6. *Preparation of complexes [Ru(H)(η^6-arene)(TPPTS)$_2$]Cl 6*

The general procedure to prepare these complexes was derived from catalytic hydrogenations of benzylideneacetone in a biphasic system [23]. A 100 ml stainless steel autoclave was charged with $[Ru(Cl)(\mu\text{-}Cl)(TPPTS)_2]_2$ (1.0 g: 0.350 mmol) dissolved in 15 ml of water and 10 ml of the aromatic substrates (benzene, toluene, etc.). The autoclave was pressurized at 35 bar at room temperature, then heated to 60°C for 90 min. After cooling to the ambient conditions, the autoclave was depressurized, the reaction mixture collected and transferred in a separation funnel. The yellow aqueous phases were dried under reduced pressure to afford yellow solids with the following yields:

6a: toluene 0.45 g collected, yield 87%; elemental analysis exp. (calc. %) C 33.34 (35.02), H 3.02 (3.08).

6b: benzene 0.47 g (92%); C 33.44 (34.53), H 3.00 (2.97).

6c: *p*-xylene 0.46 g (88%); C 34.06 (35.50), H 3.11 (3.18)

6d: ethylbenzene 0.47 g (90%); C 35.17 (35.50), H 3.12 (3.18)

6e: cumene 0.47 g (89%); C 35.73 (35.97), H 3.34 (3.29)

6f: tetraline 0.47 g (89%); C 32.64 (36.48), H 3.37 (3.26)

NMR data of complexes **6** are collected in Tables 1–3.

4.7. *Carbonylation of [Ru(H)(η^6-C$_6$H$_6$)(TPPTS)$_2$]Cl*

Complex **6b** was carbonylated under one atmosphere of CO at 90°C for 1 h. $^{31}P\{^1H\}$ NMR

spectra showed that 22% of **6b** was still present. Infrared: 2066 (s), 2046 (sh), 1996 (s, br), 1970 (sh), 1943 (sh), 1895 (sh), 1890 (m, br) cm^{-1}.

4.8. Reaction of $NaBH_4$ with 6b

A 7 ml water solution containing 0.2 g (0.137 mmol) of **6b** and 0.17 g (0.28 mmol) of TPPTS was saturated with hydrogen and 0.01 g (0.26 mmol) of $NaBH_4$ was added at room temperature. Immediate liberation of H_2 occurred and the solution turned gold–yellow. Workup as previously described gave 0.36 g of a gold–yellow solid. From $^{31}P\{^1H\}$ NMR ca. 70% of **6b** were converted into $[Ru(H)_2(TPPTS)_4]$.

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