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The chemistry and catalytic properties of ruthenium and osmium compounds. Part 7. Regioselective hydrogenation of cinnamaldehyde (3-phenyl-2-propenal) catalyzed by Ru and Os triphenylphosphine complexes in homogeneous solution and by *meta*-sulfonatophenyl-diphenyldiphosphine (TPPMS) and tris-*meta*-sulfonato-phenylphosphine (TPPTS) derivatives in an aqueous biphasic system

Roberto A. Sánchez-Delgado *, Miriam Medina, Francisco López-Linares, Alberto Fuentes

Chemistry Center, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela

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Abstract

NMR data for two Ru–TPPMS complexes previously described as unsaturated monomeric species have led to their reformulation as the chloro-bridged dimers $[RuCl(TPPMS)_2(\mu\text{-}Cl)]_2$ (**1**) and $[RuH(TPPMS)_2(\mu\text{-}Cl)]_2$ (**2**); three new water-soluble complexes $OsH_4(TPPMS)_3$ (**3**), $OsHCl(CO)(TPPMS)_2$ (**4**), and $[OsCl(TPPMS)_2(\mu\text{-}Cl)]_2$ (**5**) have been synthesized and characterized. Complexes **1–5**, as well as mixtures of Ru and Os salts with TPPMS and TPPTS catalyze the hydrogenation of cinnamaldehyde under mild reaction conditions in aqueous biphasic systems; the activities and selectivities of these catalysts have been compared with those of homogeneous PPh_3 analogues. In general there is a clear advantage in using the aqueous biphasic mixtures over their analogous homogeneous solutions, since catalyst recovery and recycling are easy and because the regioselectivity towards the production of the α, β-unsaturated alcohol is considerably enhanced on going from the homogeneous PPh_3 to the biphasic TPPMS and TPPTS systems, particularly in the case of Ru.

1. Introduction

The selective reduction of α, β-unsaturated aldehydes (Scheme 1) is of considerable importance in the synthesis of fine chemicals [1].

* Corresponding author. Tel.: +58-2-5011320; fax: +58-2-5011350; e-mail: rsanchez@ivic.ivic.ve.

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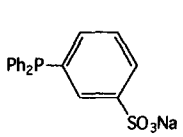
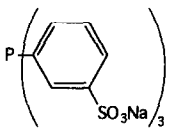
Boron and aluminum hydrides are commonly used in the stoichiometric regioselective reduction of carbonyl groups [2] but homogeneous *catalytic* hydrogenation can be a more efficient synthetic method, particularly when high selectivities are required or when the reaction needs to be carried out in a large scale; the homogeneous reduction of the C=C bond (path (a)) can be carried out with relative ease by use of a number of transition metal complexes [3] but selective hydrogenation of the C=O bond (path (b)) is more difficult to achieve [4].

Homogeneous catalysis suffers from the practical disadvantage of catalyst recovery and recycling as well as product separation which can be difficult and costly (see, e.g., [5]). Over the last few years, liquid biphasic catalysis has emerged as a very useful alternative technology to overcome these difficulties, as exemplified by the highly successful Rhone-Poulenc/Ruhr Chemie hydroformylation process [6]. In most of the biphasic systems studied [6,7] an organic layer contains the substrates and the products, while the catalyst is held in an aqueous phase by coordination to appropriate water-soluble ligands, most notably the sulfonated phosphines *meta*-sulfonatophenyldiphenyldiphosphine (TPPMS) and tris-*meta*-sulfonatophenylphosphine (TPPTS), commonly used as sodium salts.

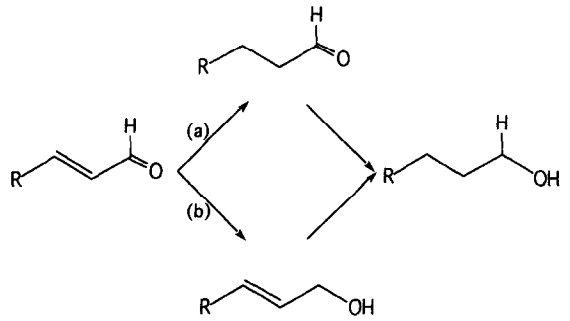


TPPMS



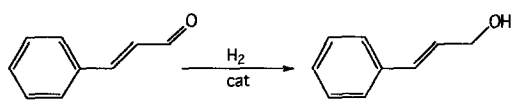
TPPTS

The two layers are brought into contact and the reaction takes place either in one of the two phases or at the interface. Although the concept has been elegantly extended to non-aqueous liquid biphasic systems [8] the field of water-soluble ligands and complexes and their use in catalysis continues to attract a great deal of attention, since water is abundant, inexpensive, and environmentally friendly.



Scheme 1. Possible products of the hydrogenation of α, β-unsaturated aldehydes.

Between 1979 and 1986 we carried out extensive studies on the homogeneous catalytic hydrogenation of aldehydes and ketones by Ru and Os compounds [9,10] including some early examples of moderately selective Os catalysts for the reduction of the C=O bond of α, β-unsaturated aldehydes [10]. More recently, the group of Basset disclosed examples of liquid biphasic hydrogenation of aldehydes using Ru–TPPTS complexes [11] while Joó and Bényei used the Ru–TPPMS/HCOONa combination to reduce the C=O bond of simple as well as α, β-unsaturated aldehydes [12]. In this paper we describe our efforts to develop highly efficient aqueous-biphasic catalysts for the regioselective reduction of cinnamaldehyde (3-phenyl-2-propenal) to cinnamyl alcohol (3-phenyl-2-propenol) (Eq. (1)), as well as a comparison with analogous homogeneous systems.



(1)

For this purpose we have employed in situ prepared mixtures of M–PPh_3, M–TPPMS, and M–TPPTS (M = Ru, Os), as well a series of known M–PPh_3 complexes, some previously reported Ru–TPPMS derivatives which we have reformulated on the basis of new NMR evidence, and three new Os–TPPMS complexes

whose synthesis and characterization are also described herein. While this work was in progress, researchers from Rhone-Poulenc [13] reported the highly selective M–TPPTS aqueous biphasic catalytic hydrogenation of α, β-unsaturated aldehydes to the corresponding saturated aldehydes (Rh) or unsaturated alcohols (Ru), and Darensbourg et al. described similar high selectivities for Rh–PTA and Ru–PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) derivatives [14].

Although homogeneous catalysis by osmium complexes has developed considerably in recent times [15], to our knowledge there are no previous examples of water-soluble Os complexes with sulfonated phosphines or of their use in catalytic reactions in aqueous biphasic systems.

2. Experimental

2.1. General Procedure

All manipulations were routinely performed under a N_2 atmosphere by using standard Schlenk techniques unless otherwise stated. The solvents were purified by known procedures and purged with N_2 prior to use. Commercial cinnamaldehyde (Aldrich) was purified by distillation. TPPMS [16] and TPPTS [17], as well as $RuCl_2(PPh_3)_3$ [18], $RuHCl(PPh_3)_3$ [19], $RuHCl(CO)(PPh_3)_3$ [20], $OsCl_2(PPh_3)_3$ [21], $OsHCl(CO)(PPh_3)_3$ [22], $[RuCl_2(TPPMS)_2]_2$ (**1**) [23], and $[RuHCl(TPPMS)_2]_2$ (**2**) [23] were synthesized by known procedures. All other chemicals were commercial products and were used without further purification. Infrared spectra were recorded on a Nicolet 5 DCX FT-IR spectrophotometer using samples as KBr disks. Solutions for NMR were prepared in an argon-filled glove box. NMR spectra were obtained on a Bruker AM 300 spectrometer. GC analyses were performed on a Varian 3700 chromatograph equipped with a flame ionization detector and a 10 m S-150 Megabore column.

2.2. Synthesis of $OsH_4(TPPMS)_3$ (3)

To a boiling solution of TPPMS · $2H_2O$ (0.50 g, 1.25 mmol) in ethanol (15 ml) was added rapidly and successively $OsCl_3 \cdot 3H_2O$ (0.11 g, 0.31 mmol) in ethanol (5 ml) and $NaBH_4$ (0.04 g, 1.3 mmol) also in ethanol (5 ml); the mixture was refluxed for 5 min and then it was allowed to cool to room temperature. Complex **3** precipitated from the resulting amber solution as a sepia colored powder, which was collected by filtration and washed with ethanol (3 × 5 ml) and *n*-hexane (2 × 5 ml) and dried under vacuum; yield 74%.

2.3. Synthesis of $OsHCl(CO)(TPPMS)_2$ (4)

A mixture of TPPMS · $2H_2O$ (0.50 g, 1.25 mmol) and $OsCl_3 \cdot 3H_2O$ (0.11 g, 0.31 mmol) was dissolved in 2-methoxyethanol (15 ml) and heated under reflux for 24 h under N_2, during which time the color of the solution changed from dark brown to orange and finally light yellow. The solution was allowed to cool to room temperature and diethylether (50 ml) was added at −10°C with vigorous stirring; this caused immediate precipitation of complex **4** as a light yellow powder, which was collected by filtration and washed with cold diethylether (2 × 5 ml) and cold acetone (2 × 5 ml) and dried under vacuum; yield 45%.

2.4. Synthesis of $[OsCl_2(TPPMS)_2]_2$ (5)

To a solution of $OsCl_3 \cdot 3H_2O$ (0.08 g, 0.22 mmol) in H_2O (15 ml) was added TPPMS · $2H_2O$ (0.57 g, 1.42 mmol) in H_2O (15 ml); the mixture was refluxed for 22 h after which the solution was brownish green. After ca. 1/2 of the solvent was evaporated and the mixture was cooled to room temperature, complex **5** precipitated as a dark green powder which was filtered, washed with diethylether (2 × 3 ml) and dried under vacuum; yield 40%. When an analogous reaction was carried out in methanol as the solvent, the complex is recovered as a yellow–

brown solid (presumably a solvate) in 60% yield.

2.5. Catalytic hydrogenations

In a typical experiment an aqueous solution of the catalyst or the catalytic mixture (e.g., metal salt + TPPMS) (40 ml, 5.7×10^{-3} M in Os) and a toluene solution of the substrate (50 ml, 5.5×10^{-1} M) were introduced into a glass-lined stainless steel autoclave (600 ml, Parr) fitted with internal stirring and a sampling valve. Air was removed by flushing three times with hydrogen; the reactor was charged to the desired pressure and subsequently heated to the required temperature with stirring at 620 rpm. The moment when the temperature reached the desired value was taken as t_0. During the catalytic run, samples of the reaction mixture were periodically extracted via the sampling valve, and the total pressure of the system was continuously adjusted to a constant value by admitting hydrogen from a high pressure reservoir. The samples were cooled in ice and both phases were immediately analyzed by gas chromatography.

3. Results and discussion

3.1. Synthesis and characterization

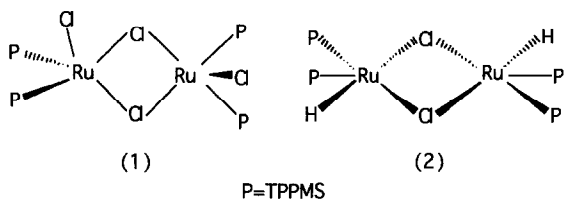
3.1.1. Ru complexes

The complex $[RuCl_2(TPPMS)_2]_2$ (**1**) has been previously synthesized by Joó and coworkers by direct reaction of TPPMS with $RuCl_3 \cdot 3H_2O$ in ethanol while $[RuHCl(TPPMS)_2]_2$ (**2**) could also be prepared by an adaptation of the direct method used for the synthesis of the PPh_3 analog using TPPMS as the ligand [23]. Alternatively, Wilkinson demonstrated that these compounds can be obtained by ligand exchange reactions of the analogous PPh_3 complexes with an excess of the sulfonated ligand [24]. Previous efforts to characterize these complexes were based mainly on microanalysis and IR spectra, and we have now complemented these data with NMR spectroscopy. Although both complexes were originally described as coordinatively unsaturated monomeric species, the most relevant NMR features collected in Table 1 and discussed below led us to reformulate both structures as the dimers depicted by **1** and **2**.

Table 1
Selected NMR data for Ru and Os TPPMS complexes [a]

Complex	^1H, δ(M–H) (ppm)	J_{H-P} (Hz)	$^{31}P\{^1H\}$, δ (ppm)
$[RuCl_2(TPPMS)_2]_2$	—		55.3 (s)
			54.4 (s)
$[RuHCl(TPPMS)_2]_2$	−8.7 (td)	38	
		9 [b]	52.4 (AB) [c]
$OsH_4(TPPMS)_3$	−8.2 (q)	8.5	24.4 (s)
$OsHCl(CO)(TPPMS)_2$	−10.0 (t)	21	10.0 (s)
$[OsCl_2(TPPMS)_2]_2$	—	—	22.0 (s)
			18.0 (s)

[a] In D_2O.
[b] J_{H-H}.
[c] AB quartet: δ(A), 52.4 ppm; δ(B), 51.7 ppm; J_{A-B}, 38 Hz.



(1) (2)

P=TPPMS

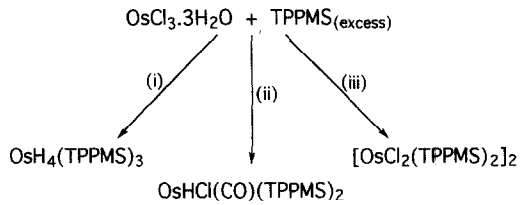
For complex **1** the $^{31}P\{^1H\}$ NMR spectrum consists of two equally intense singlets, which we assign to two magnetically inequivalent sets of phosphine ligands with a very small or no coupling between them, each one attached to a different Ru atom in a dimeric structure whose conformation provides the asymmetry in the structure. The closely related dimers $[RuCl_2(PPh_3)_2]_2$ [25] and $[RuCl_2(TPPTS)_2]_2$ [26] are known and their ^{31}P NMR spectra consist of singlets at 56.6 ppm and 56 ppm, respectively. For complex **2**, the spectra are more informative: in the ^1H NMR spectrum a high field triplet of doublets is observed with coupling constants of 38 Hz and 9 Hz, while the $^{31}P\{^1H\}$ spectrum displays a well resolved AB quartet centered at 52.11 ppm with J(A–B) =

38 Hz. The spectra are unchanged down to −40°C. These data are consistent with the dimeric structure **2** shown above in which each Ru is surrounded by a terminal hydride, two P atoms and two bridging chlorides. Each hydride is thus coupled to the phosphorus nuclei on the same metal atom and further coupled through the Cl bridges to the hydride located in a transoid position of the second Ru atom. In this case the molecule adopts a slightly different conformation of higher symmetry, probably due to the lower steric requirements of the hydride in comparison with a chloride, which makes the two AB pairs of phosphorus nuclei mutually equivalent. Further evidence for this formulation are the facts that (i) complex **1** reacts with H_2 in water to yield **2**, and (ii) both **1** and **2** undergo bridge-splitting reactions with strongly coordinating ligands (e.g., pyridine) to yield the corresponding monomeric derivatives $RuXCl(TPPMS)_2(py)_2$ (X = H, Cl), which display clear NMR patterns; this chemistry will be reported separately. Although monomeric complexes $RuHClP_3$ (P = TPPMS [24], TPPTS [26] have been observed in acidic solutions, we have found no evidence for the presence of a hydrido(tris)phosphine complex under our (unbuffered) reaction conditions.

3.1.2. Os complexes

The new osmium complexes were synthesized by adaptations of the methods used to prepare analogous PPh_3 derivatives, as summarized in Scheme 2. In contrast to previous reports concerning Ru chemistry [24], direct ligand exchange reactions between TPPMS and the corresponding PPh_3 complexes gave poor results in the case of Os, mainly because of the greater strength of the Os–P bond; in most cases the starting material was recovered unchanged or the product yields were very low after prolonged reaction times. Characterization of the new complexes was achieved by spectroscopic data, a selection of which is presented in the Experimental section and in Table 1.

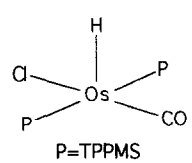
Thus, reaction of $OsCl_3 \cdot 3H_2O$ with excess



Scheme 2. Synthesis of new osmium complexes. (i) $NaBH_4$ /EtOH (reflux 5 min); (ii) 2-MeO–EtOH (reflux 24 h); (iii) H_2O (reflux 22 h).

TPPMS and $NaBH_4$ in EtOH rapidly yields $OsH_4(TPPMS)_3$ (**3**) as a sepia-colored solid which decomposes in air turning dark gray after about 10 min. At room temperature **3** dissolves well in water but the resulting solutions are very oxygen sensitive; it is also soluble in MeOH giving rise to somewhat more air-stable solutions. The ^1H NMR spectrum of **3** shows, besides the phenyl protons (7.1–7.8 ppm) a high field quartet with a small H–P coupling constant, while the $^{31}P\{^1H\}$ spectrum consists of only a singlet (see Table 1). These data are in agreement with the proposed formulation and indicate that the complex is highly fluxional; these features are very similar to the ones observed for the analogous $OsH_4(PPh_3)_3$ [19].

Prolonged reaction of $OsCl_3 \cdot 3H_2O$ with an excess of TPPMS in 2-methoxyethanol yields the hydrido-carbonyl derivative $OsHCl(CO)(TPPMS)_2$ (**4**) which is moderately air stable in the solid state and also in solution (H_2O, MeOH, dmso). A high field triplet with a $J(H–P) = 21$ Hz in the ^1H NMR spectrum, combined with a singlet in the $^{31}P\{^1H\}$ NMR spectrum indicate the presence of an Os–H *cis* to two mutually equivalent phosphine ligands. The IR spectrum also shows the metal hydride stretch and confirms the presence of a terminal carbonyl group (Table 1). The combined data point to the stereochemistry depicted for **4**:

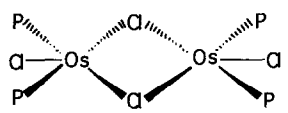


P=TPPMS

(4)

In this case the analogous PPh_3 complex contains three phosphine ligands [22]; it is not unusual for complexes of sulfonated phosphines to display a lower degree of coordination than their trialkyl or triaryl counterparts, due to steric effects and to charge accumulation around the metal caused by the sulfonato groups [7].

If $OsCl_3 \cdot 3H_2O$ is refluxed with an excess of TPPMS in water for 22 h a rather unstable dark green complex (**5**) is obtained, whose ^{31}P NMR spectrum consists of only a singlet at 21.8 ppm. If the reaction is carried out in methanol complex **5** is isolated as a more stable dark yellow solid whose ^{31}P NMR spectrum shows the same singlet around 22 ppm, plus a second signal of lower intensity at 18.0 ppm. The ^{1}H NMR spectra shown only the signals corresponding to the phenyl protons. Although these data are not conclusive, by analogy with complex **1** and related Ru literature precedents [25,26], we propose a dimeric chloro-bridged structure for **5**:



P=TPPMS

(5)

We believe that the second complex isolated from the methanol reaction is a closely related species, possibly a solvate.

As a final comment it is important to note that in our preparations the TPPMS ligand and its metal complexes were usually contaminated with varying amounts of the phosphine oxide which precluded accurate microanalytical results. Although an excellent chromatographic method has been described for the purification of this type of ligand and complexes [27], we found that recrystallization from MeOH produced samples of reasonable purity (ca. 95% by NMR). Moreover, we verified that the catalytic behavior described below was not affected by the presence of such small amounts of TPPMS or TPPTS oxides.

3.2. Hydrogenation catalysis

3.2.1. (A) Ru systems

The results of the hydrogenation of cinnamaldehyde with several homogeneous and biphasic Ru catalysts are collected in Table 2. The reduction can be carried out under moderate reaction conditions in a homogeneous toluene solution with a mixture of $RuCl_3 \cdot$

Table 2
Hydrogenation of cinnamaldehyde with homogeneous and biphasic Ru catalysts [a]

Entry	Catalyst	t (h)	Conv. (%)	Selectivity (%)		
				$PhCH{=}CHCH_2OH$	$PhCH_2CH_2CHO$	$PhCH_2CH_2CH_2OH$
Homogeneous systems [b]						
1	$RuCl_3 \cdot 3H_2O/PPh_3$	3	30	50	19	31
2	$RuCl_2(PPh_3)_3$	2	57	35	23	42
3	$RuHCl(PPh_3)_3$	2	83	31	3	65
4	$RuHCl(CO)(PPh_3)_3$	3	70	20	7	73
Biphasic systems [c]						
5	$RuCl_3 \cdot 3H_2O$/TPPMS	3	79	90	7	3
6	$RuCl_3 \cdot 3H_2O$/TPPTS	3	71	95	2	3
7	$[RuCl_2(TPPMS)_2]_2$	3	26	83	15	2
8	$[RuHCl(TPPMS)_2]_2$	3	68	54	19	27

[a] $[Ru] = 5.7 \times 10^{-3}$ M; $[subst] = 5.5 \times 10^{-1}$ M; [P]:[Ru] = 6; $T = 100°C$; $P(H_2) = 30$ atm.
[b] In toluene.
[c] In 1:1 toluene/water.

$3H_2O/PPh_3$ or with well known $Ru-PPh_3$ complexes.

The order of activity was found to be $RuHCl(PPh_3)_3 > RuHCl(CO)(PPh_3)_3 > RuCl_2(PPh_3)_3 > RuCl_3 \cdot 3H_2O/PPh_3$. The selectivity for the unsaturated alcohol was low in all cases, reaching a maximum of 50% for $RuCl_3 \cdot 3H_2O/PPh_3$ (entry 1). Instead, a high selectivity for the reduction of the C=C bond was achieved with the two hydride complexes (entries 3 and 4).

From these results we conclude that some $Ru-PPh_3$ complexes may be practical homogeneous catalytic systems for the selective reduction of the C=C bond of cinnamaldehyde, but none of the catalysts tested is adequate for the selective hydrogenation of the C=O bond.

If *aqueous biphasic* Ru systems are used instead (Table 2, entries 5–8) we note that there is *a remarkable enhancement of the selectivity* towards the unsaturated alcohol with respect to the homogeneous solutions for all the catalysts tested; values increased e.g., from 50% for $RuCl_3 \cdot 3H_2O/PPh_3$ (entry 1) to 90% and 95% (entries 5 and 6) on switching to the analogous biphasic $RuCl_3 \cdot 3H_2O$/TPPMS and $RuCl_3 \cdot 3H_2O$/TPPTS systems, respectively.

We note further that the activities of complexes **1** and **2** (entries 7 and 8) are somewhat lower than those observed for the homogeneous analogues, whereas the selectivities in both cases are higher. Also, the activities and selectivities achieved with **1** and **2** are lower than those observed for the $RuCl_3 \cdot 3H_2O$/TPPMS or $RuCl_3 \cdot 3H_2O$/TPPTS mixtures. We believe that the same or very similar active species are operating in all cases, probably monomeric intermediates of the type $RuHClP_2L_2$ or $RuHClP_3L$ (P = TPPMS or TPPTS; L = substrate or solvent). Previous reports on the hydrogenation of aldehydes by Ru–TPPMS ascribed the catalytic activity to trisphosphine complexes [12]; the in situ preparations allow for both the bisphosphine and the trisphosphine complexes to be formed, whereas **1** and **2** can only operate through bisphosphine intermediates; this could explain the lower efficiency of the preformed complexes. Also, this lower activity may be related to the higher tendency of complexes **1** and **2**, as well as of their

Table 3
Hydrogenation of cinnamaldehyde with homogeneous and biphasic Os catalysts [a]

Entry	Catalyst	t (h)	Conv. (%)	Selectivity (%)		
				$PhCH=CHCH_2OH$	$PhCH_2CH_2CHO$	$PhCH_2CH_2CH_2OH$
Homogeneous systems [b]						
1	$H_2OsCl_6 \cdot 6H_2O/PPh_3$	3	4	50	30	20
2	$NaOsCl_6 \cdot 6H_2O/PPh_3$	6	88	56	33	11
3	$OsCl_3 \cdot 3H_2O/PPh_3$	3	90	84	3	13
4	$OsCl_2(PPh_3)_3$	3	100	0	47	53
5	$OsH_4(PPh_3)_3$	5	27	63	15	22
6	$OsHCl(CO)(PPh_3)_3$	3	44	43	9	48
Biphasic systems [c]						
7	$NaOsCl_6 \cdot 6H_2O$/TPPMS	6	47	71	12	17
8	$OsCl_3 \cdot 3H_2O$/TPPMS	3	42	85	10	5
10	$OsCl_3 \cdot 3H_2O$/TPPTS	3	63	89	6	5
11	$[OsCl_2(TPPMS)_2]_2$	14	6	100	0	0
12	$OsH_4(TPPMS)_3$	3	40	68	11	21
13	$OsHCl(CO)(TPPMS)_2$	6	58	60	18	22

[a] $[Os] = 5.7 \times 10^{-3}$ M; $[subst] = 5.5 \times 10^{-1}$ M; [P]:[Os] = 6; T = 100°C; $P(H_2)$ = 30 atm.
[b] In toluene.
[c] In 1:1 toluene/water.

monomeric derivatives, to decompose partially during the catalytic runs. Since for practical purposes the in situ preparations are the catalysts of choice, this point was not further investigated.

3.2.2. (B) Os systems

The results of hydrogenating cinnamaldehyde with several Os-derived catalysts are collected in Table 3.

In a homogeneous toluene solution the reduction can be carried out either with mixtures of Os salts with PPh_3 prepared in situ, or with known Os–PPh_3 complexes. For the in situ mixtures the order of activity was found to be $OsCl_3 \cdot 3H_2O \approx NaOsCl_6 \cdot 6H_2O \gg H_2OsCl_6 \cdot 6H_2O$, while a reasonable selectivity for the unsaturated alcohol was observed following the trend $OsCl_3 \cdot 3H_2O > NaOsCl_6 \cdot 6H_2O > H_2OsCl_6 \cdot 6H_2O$. In the case of the complexes, $OsCl_2(PPh_3)_3$ promoted a rapid hydrogenation reaction but the product contained only the saturated aldehyde and the saturated alcohol in a roughly 1:1 proportion; $OsH_4(PPh_3)_3$ and $OsHCl(CO)(PPh_3)_3$ were moderately active and selective for the unsaturated alcohol.

Interestingly, a marked improvement in the regioselectivity for the production of the unsaturated alcohol under homogeneous conditions was achieved in a very simple way by adjusting the relative concentrations of the substrate and the catalyst. For instance, in the case of $OsHCl(CO)(PPh_3)_3$ (Fig. 1), if a [substrate]:[Os] ratio ≤ 50 is used, hydrogenation of the C=C bond takes place preferentially, but as this ratio is increased the selectivity switches over reaching a maximum value of 80% for the reduction of the C=O bond. This has interesting mechanistic implications which are discussed below.

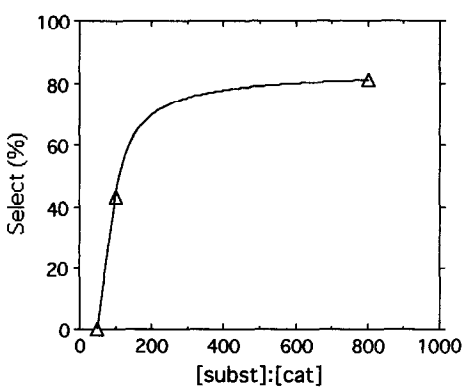


Fig. 1. Effect of the [substrate]:[cat] ratio on the selectivity for cinnamyl alcohol using $OsHCl(CO)(PPh_3)_3$ as the catalyst. Other reaction conditions as in Table 3.

From these results we can conclude that the combination of the readily available $OsCl_3 \cdot 3H_2O$ with 6 eq PPh_3 is the most practical *homogeneous* catalytic system in our series for the regioselective reduction of the C=O bond of cinnamaldehyde.

On turning to the aqueous biphasic systems we note that there is *a clear enhancement of the selectivity* towards the unsaturated alcohol with respect to the homogeneous solutions tested, although the effect is less spectacular than the one observed for the Ru systems on switching from homogeneous to biphasic conditions; for the Os catalytic mixtures prepared in situ the activities are somewhat reduced with respect to the PPh_3 analogs, whereas for the complexes the opposite trend was observed. In this series of experiments the activities followed the order $OsCl_3 \cdot 3H_2O$/ TPPTS > $NaOsCl_6 \cdot 6H_2O$/ TPPMS > $OsCl_3 \cdot 3H_2O$/TPPMS, and the selectivity trend for cinnamyl alcohol was $OsCl_3 \cdot 3H_2O$/TPPTS ≈ $OsCl_3 \cdot 3H_2O$/TPPMS > $NaOsCl_6 \cdot 6H_2O$/ TPPMS. The complex $[OsCl_2(TPPMS)_2]_2$ was found to be a poor catalyst (6 turnovers in 14 h) although at this low conversion the unsaturated aldehyde was formed exclusively. $OsH_4(TPPMS)_3$ was slightly less active but more selective than $OsHCl(CO)(TPPMS)_2$; both complexes perform better in activity and selectivity than their homogeneous counterparts. We can conclude that the most convenient aqueous biphasic systems in our Os series are those derived from mixtures of $OsCl_3 \cdot 3H_2O$ with TPPMS or better still TPPTS in view of their ease of preparation combined with good activities and high selectivities.

3.2.3. Catalyst recycling

Since the main advantage of using a biphasic catalyst may be the easy recovery and recycling of the catalyst, we have tested the durability of the best osmium system, namely $OsCl_3 \cdot 3H_2O$/TPPTS, by carrying out three consecutive cycles with the same catalyst aqueous solution, carefully separated from the organic phase under an inert atmosphere at the end of each run. As shown by the data contained in Table 4 no appreciable loss of activity or selectivity was apparent after the third cycle, demonstrating a good stability of the catalyst.

Table 4
Catalyst recycling [a]

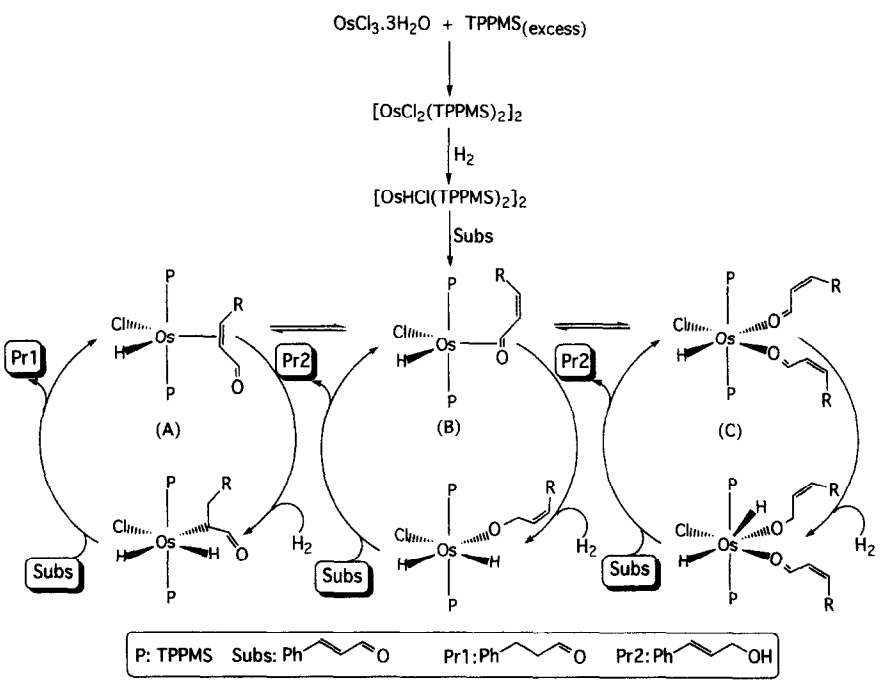
Run	t (h)	Conv. (%)	Select. (%) [b]
1	3	42	85
2	2	43	82
3	2	42	83

[a] Catalyst: $OsCl_3 \cdot 3H_2O$; reaction conditions as in Table 3.
[b] Selectivity for cinnamyl alcohol.

3.2.4. The reaction mechanism

Although we have not yet carried out extensive mechanistic studies on this biphasic reaction, our results, together with the accumulated knowledge on related homogeneous systems, allow us to provide the mechanistic proposal depicted in Scheme 3. This includes a reasonable set of reactions for the general case of our in situ prepared catalysts leading to the active species actually entering the cycle; the extension of this proposal to the related homogeneous systems is obvious.

$MCl_3 \cdot 3H_2O$ (M = Ru, Os) first reacts with TPPMS to yield the dimer $[MCl_2(TPPMS)_2]_2$, which is subsequently transformed into $[MHCl(TPPMS)_2]_2$ by reaction with H_2; a bridge-splitting reaction with a substrate molecule (Subs) generates the monomeric intermediates $MHCl(TPPMS)_2(Subs)$, in which the unsaturated aldehyde may be coordinated through the C=C bond or through the C=O bond. This gives adequate entries into two catalytic cycles (**A** and **B**) leading to the saturated aldehyde (Pr1) and the unsaturated alcohol (Pr2), respectively, most likely by a standard series of



Scheme 3. Proposed mechanism for the hydrogenation of cinnamaldehyde.

elementary steps (oxidative addition of H_2, stepwise transfer of hydrides to the unsaturated bond and reductive elimination of the products); the selectivity of each catalyst will depend on the relative concentrations of **A** and **B** in the mixture. If the substrate concentration is high, two molecules may bind to the metal atom, as in **C**; in this case for steric reasons, end-on coordination through the C=O bond must be favored over side-on C=O or C=C coordination, leading to higher selectivities for the unsaturated alcohol through the third cycle on the right.

The large selectivity effects observed on switching from the homogeneous to the biphasic catalysts could be related to the fact that the more hydrophilic C=O bond must be pointing towards the aqueous phase where the metal center is located, whereas the hydrophobic C=C bond will tend to point away from the water and into the organic layer, thus favoring the formation of species **B** and **C** over **A**. A further point of interest which might be related to these selectivity effects is the recent report [28] on the very fast reaction of aldehydes with TPPMS, which could aid the selective formation of adequate intermediates for the production of the unsaturated alcohol; however, we do not have at this point any evidence for the direct intervention of such phosphonium salts in the catalysis. Clearly, further studies are needed in order to unravel enough mechanistic details for a full explanation of the interesting selectivity effects reported here, as well as to explore the scope of this reaction as a general synthetic method.

4. Conclusion

We have performed NMR studies which led to a reformulation of two Ru–TPPMS complexes as chloro-bridged dimers instead of the previously reported monomeric structures; also we have synthesized and characterized the first three Os–TPPMS water-soluble complexes.

The hydrogenation of cinnamaldehyde has been studied using as catalysts mixtures of Ru or Os salts with PPh_3 or its sulfonated analogues, as well as presynthesized complexes of such ligands. We have found that there is a clear advantage in using the aqueous biphasic Ru or Os/TPPMS or TPPTS systems over their homogeneous PPh_3 analogues since product separation and catalyst recycling are easy, and also very important because the regioselectivity towards the unsaturated alcohol is considerably enhanced on going from the homogeneous to the biphasic systems, more impressively for the Ru systems.

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References

[1] K. Bauer and D. Garbe, Ullman Encyclopaedia, 3rd Ed., Vol. A11 (VCH, New York, 1988).
[2] A.L. Gemal and J.L. Luche, J. Am. Chem. Soc. 103 (1981) 5454; S.I. Fukuzawa, T. Fujinami, S. Yamauchi and S Sakai, J. Chem. Soc. Perkin Trans. (1986) 1929.
[3] B.R. James, Homogeneous Hydrogenation (Wiley, New York, 1973); P.N. Rylander, Catalytic Hydrogenation in Organic Synthesis (Academic Press, New York, 1979); B.R. James, in: Comprehensive Organometallic Chemistry, ed. G. Wilkinson, F.G.A. Stone and E.A. Abel, Vol. 6 (Pergamon Press, Oxford, 1982).
[4] K. Hotta, J. Mol. Catal. 29 (1985) 105; E. Farnetti, J. Kaspar, R. Spogliarich, M. Graziani and M. Pesce, J. Chem., Soc. Chem. Commun. (1986) 746.
[5] G.W. Parshall and S.D. Ittel, Homogeneous Catalysis (Wiley Interscience, New York, 1992).
[6] B. Cornils and E. Wiebus, Chemtech Jan. (1995) 33.
[7] P.A. Chaloner, M.A. Esteruelas, F. Joó and L.A. Oro, Homogeneous Hydrogenation (Kluwer Academic Publishers, Dordrecht, Netherlands, 1993) ch. 5; W.A. Herrmann and C.W.

Kohlpaintner, Angew. Chem. Int. Ed. Engl. 32 (1993) 1524; F. Joó and Z. Tóth, J. Mol. Catal. 8 (1980) 369.
[8] I.T. Horváth and J. Rábai, Science 266 (1994) 72.
[9] R.A. Sánchez-Delgado and O.L. de Ochoa, J. Mol. Catal. 6 (1979) 303; J. Organomet. Chem. 202 (1980) 427; R.A. Sánchez-Delgado, A. Andriollo, O.L. de Ochoa, T. Suárez and N. Valencia, J. Organomet. Chem. 209 (1981) 77; R.A. Sánchez-Delgado, A. Andriollo, K. Döppert, C. Ramírez and N, Valencia, Acta Cient. Venez. 33 (1982) 23; R.A. Sánchez-Delgado, A. Andriollo, and N. Valencia, J. Chem. Soc., Chem. Commun. (1983) 444; R.A. Sánchez-Delgado, U. Thewalt, N. Valencia, R.L. Márquez-Silva, A. Andriollo, J. Puga, H. Schöllhorn, H.-P. Klein and B. Fontal, Inorg. Chem. 24 (1986) 1097; R.A. Sánchez-Delgado, N. Valencia, R.L. Márquez-Silva, A. Andriollo, and M. Medina, Inorg. Chem. 24 (1986) 1106; R.A. Sánchez-Delgado and B.A. Oramas, J. Mol. Catal. 36 (1986) 283; R.A. Sánchez-Delgado and E. González, Polyhedron 8 (1989) 1431; R.A. Sánchez-Delgado, W.Y. Lee, S.R. Choi and M.J. Jun, Trans. Met. Chem. 16 (1991) 241; R.A. Sánchez-Delgado, M. Rosales and A. Andriollo, Inorg. Chem. 30 (1991) 1170.
[10] R.A. Sánchez-Delgado, A. Andriollo and N. Valencia, J. Mol. Catal. 24 (1984) 217; R.A. Sánchez-Delgado, A. Andriollo, E. González, N. Valencia, V. León and J. Espidel, J. Chem. Soc. Dalton Trans. (1985) 1859.
[11] E. Fache, C. Santini, F. Senocq and J.-M. Basset, J. Mol. Catal. 72 (1992) 337; E. Fache, C. Santini, F. Senocq and J.-M. Basset, J. Chem. Soc., Chem. Commun. (1990) 1776.
[12] F. Joó and A. Bényei, J. Organomet. Chem. 363 (1989) C-19; A. Bényei and F. Joó, J. Mol. Catal. 58 (1990) 151.
[13] Eur. Pats. 319 409, 320 339 (1989). G. Allmang, F. Grass, J.M. Grosselin and C. Mercier, J. Mol. Catal. 66 (1991) L27; J.M. Grosselin, C. Mercier, G. Allmang and F. Grass, Organometallics, 10 (1991) 2126; E. Fache, C. Mercier, N. Pagnier, B. Despeyroux and P. Panster, J. Mol. Catal. 79 (1993) 117.
[14] D.J. Darensbourg, N.W. Stafford, F. Joó, and J.H. Reibenspies, J. Organomet. Chem. 488 (1995) 99. D.J. Darensbourg, F. Joó, M. Kannisto, A. Kathó, J.H. Reibenspies and D.J. Daigle, Inorg. Chem. 33 (1994) 200.
[15] R.A. Sánchez-Delgado, M. Rosales, M.A. Esteruelas and L.A. Oro, J. Mol. Catal. 96 (1995) 231.
[16] S. Ahrland, J. Chatt, N.R. Davies and A.A. Williams, J. Chem. Soc. (1958) 276.
[17] Fr. Pat. 2 314 910 (1975); Eur. Pat. 133 410 (1983).
[18] T.A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 945.
[19] J.J. Levison and S.D. Robinson, J. Chem. Soc. (A) (1970) 2947.
[20] N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, Inorg. Synth. 15 (1974) 48.
[21] A. Oudeman, F. van Rantwijk and H. van Bekkum, J. Coord. Chem. 4 (1974/5) 1; P.R. Hoffman and K.G. Caulton, J. Am. Chem. Soc. 97 (1975) 4221; V.T. Coombe, G.A. Heath, T.A. Stephenson, J.D. Whitelock and L.J. Yellowlees, J. Chem. Soc. Dalton Trans. (1985) 947.
[22] L. Vaska, J. Am. Chem. Soc. 86 (1964) 1943; 88 (1966) 4100.
[23] Z. Tóth, F. Joó and M. Beck, Inorg. Chim. Acta 42 (1980) 153.
[24] A.F. Borowski, D.J. Cole-Hamilton and G. Wilkinson, Nouv. J. Chim. 2 (1978) 137.
[25] P.M. Armitt, A.S.F. Boyd and T.A. Stephenson, J. Chem. Soc. Dalton Trans. (1975) 1963.
[26] E. Fache, C. Santini, F. Senocq and J.-M. Basset, J. Mol. Catal. 72 (1992) 331.
[27] W.A. Herrmann, J.A. Kulpe, J. Kellner, H. Riepl, H. Bahrmann and W. Konkol, Angew. Chem. Int. Ed. Engl. 29 (1990) 391.
[28] D.J. Darensbourg, F. Joó, A. Kathó, J.N. White Stafford, A. Bényei and J.H. Reibenspies, Inorg. Chem. 33 (1994) 175.