Water-soluble ruthenium(II) catalysts [RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}] for isomerization of allylic alcohols and alkyne hydration†

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The novel water-soluble ruthenium(II) complexes [RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}] **2a–c** and [RuCl(η^6-arene){P(CH$_2$OH)$_3$}$_2$][Cl] **3a–c** have been prepared in high yields by reaction of dimers [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] (arene = C$_6$H$_6$ **1a**, *p*-cymene **1b**, C$_6$Me$_6$ **1c**) with two or four equivalents of P(CH$_2$OH)$_3$, respectively. Complexes **2/3a–c** are active catalysts in the redox isomerization of several allylic alcohols into the corresponding saturated carbonyl compounds under water/*n*-heptane biphasic conditions. Among them, the neutral derivatives [RuCl$_2$(η^6-C$_6$H$_6$){P(CH$_2$OH)$_3$}] **2a** and [RuCl$_2$(η^6-*p*-cymene){P(CH$_2$OH)$_3$}] **2b** show the highest activities (TOF values up to 600 h^{-1}; TON values up to 782). Complexes **2/3a–c** also catalyze the hydration of terminal alkynes.

Introduction

The development of metal-mediated catalytic transformations in aqueous media is an important issue in modern organometallic chemistry both from an academic and industrial point of view.[1,2] In addition to environmental considerations, the major advantages of water-soluble catalysts are those associated with the separation from the products and reuse of the catalytic species which can be easily achieved using a two-phase (water/organic solvent) system.[1,2] Thus, once the reaction is finished, separation of the two phases by simple decantation allows the isolation of the organic products (organic phase) and the quantitative recovery of the catalyst (aqueous phase).

The conversion of allylic alcohols into the corresponding saturated aldehydes or ketones is a useful synthetic process which usually requires a two-step sequence of oxidation and reduction reactions (path A or B in Scheme 1). Nevertheless, the ability of transition metals to migrate double bonds allows the development of an attractive alternative *i.e.* the *one-pot* internal redox process catalyzed by a transition-metal complex (path C in Scheme 1).[3] This catalytic process, which proceeds with a total atom economy, avoids: (*i*) the use of costly and toxic oxidizing reagents and (*ii*) the protection–deprotection steps often required in paths A and B. Group 8, 9 and 10 metal complexes have been predominantly employed as catalysts for this

transformation, with ruthenium and rhodium species showing the best performances.[3] Despite the great interest of the catalytic isomerization of allylic alcohols in synthesis, efforts devoted to develop such a reaction in aqueous medium have been scarce.[4,5] Moreover, to the best of our knowledge, the use of biphasic conditions allowing an efficient catalyst recycling has been only reported for a few rhodium complexes.[4d–f,h,6]

With these precedents in mind, we believe that there is a need to develop new efficient, cheap and readily available water-soluble catalysts for this important transformation. In this regard, ruthenium complexes are a cheaper alternative to rhodium.[7] Here we describe the synthesis of the novel water-soluble tris(hydroxymethyl)phosphine–ruthenium(II) derivatives [RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}] **2a–c** and [RuCl(η^6-arene){P(CH$_2$OH)$_3$}$_2$][Cl] **3a–c** (arene = benzene, *p*-cymene and hexamethylbenzene), and their application in catalytic isomerization of allylic alcohols under biphasic water/*n*-heptane conditions. The catalytic activity of complexes **2/3a–c** in hydration of terminal alkynes is also briefly presented.

Results and discussion

Synthesis and characterization of the water-soluble ruthenium(II) complexes [RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}] (arene = C$_6$H$_6$ 2a, *p*-cymene 2b, C$_6$Me$_6$ 2c) and [RuCl(η^6-arene){P(CH$_2$OH)$_3$}$_2$][Cl] (arene = C$_6$H$_6$ 3a, *p*-cymene 3b, C$_6$Me$_6$ 3c)

Introduction of hydrophilic ligands in the coordination sphere of a transition-metal is probably the most popular method for the preparation of water-soluble catalysts.[1,2] Thus, a wide variety of functionalized phosphine ligands containing highly polar sulfonated, hydroxyalkyl, ammonium, phosphonium, carboxylate, carbohydrate or phosphonate groups are actually known and their effectiveness in biphasic catalysis largely demonstrated.[1,2] In this context, tris(hydroxymethyl)phosphine P(CH$_2$OH)$_3$ is a simple, commercially available and moderately air-sensitive phosphine ligand successfully used for the preparation of a large number of water-soluble transition-metal complexes.[2,8]

The ability of dimers [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] to form mononuclear ruthenium(II) complexes of general formula [RuCl$_2$(η^6-arene)L] (L = 2e$^-$ donor ligand) *via* cleavage of the chloride bridges is well-known.[9] In polar solvents, these dimers can also add two basic ligands L per ruthenium atom to afford cationic
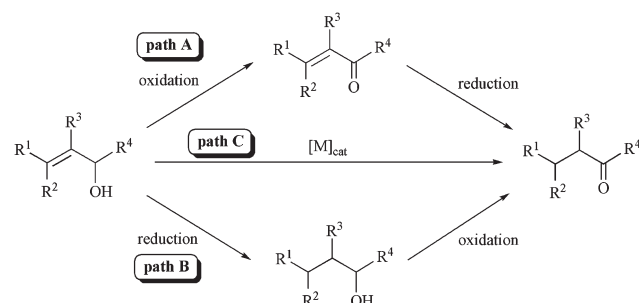
Scheme 1 Transformation of allylic alcohols into carbonyl compounds.

† Electronic supplementary information (ESI) available: Table S1: Isomerization of allylic alcohols catalyzed by the neutral complex [RuCl$_2$(η^6-C$_6$Me$_6$){P(CH$_2$OH)$_3$}] **2c** under biphasic water/*n*-heptane conditions. See http://www.rsc.org/suppdata/dt/b4/b411177j/

derivatives $[RuCl(\eta^6\text{-arene})L_2][Cl]$.[9] In accord, we have found that the reaction of $[\{Ru(\eta^6\text{-arene})(\mu\text{-Cl})Cl\}_2]$ (arene = C_6H_6 **1a**, *p*-cymene **1b**, C_6Me_6 **1c**) with two and four equivalents of tris(hydroxymethyl)phosphine, in a mixture dichloromethane/methanol at room temperature, leads to the selective formation of mononuclear compounds $[RuCl_2(\eta^6\text{-arene})\{P(CH_2OH)_3\}]$ **2a–c** and $[RuCl(\eta^6\text{-arene})\{P(CH_2OH)_3\}_2][Cl]$ **3a–c**, respectively (see Scheme 2).
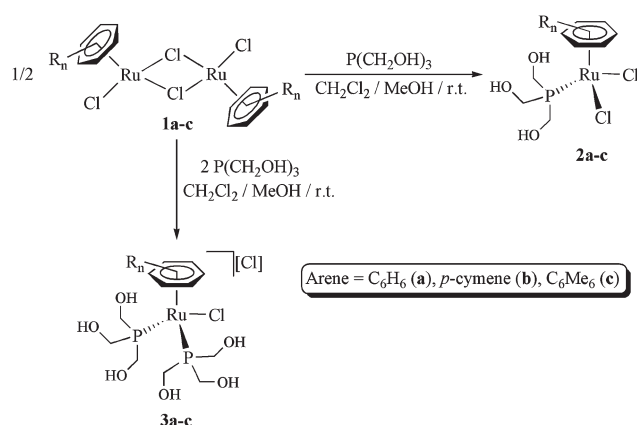
Scheme 2 Reactivity of ruthenium(II) dimers **1a–c** towards $P(CH_2OH)_3$.

Complexes **2/3a–c** have been isolated as air-stable orange (**2a**–**c**) or yellow (**3a**–**c**) solids in 85–91% yield. They are soluble in water and alcohols but insoluble in *n*-alkanes and diethyl ether. The formulation proposed for these species is based on analytical data, conductance measurements, and IR and NMR ($^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$) spectroscopy (details are given in the Experimental section). Thus, the $^{31}P\{^1H\}$ NMR spectra of all these derivatives exhibit at room-temperature the expected singlet signal at δ_P 24.14–34.97. Resonances for complexes **3a–c** appear at lower fields (*ca.* $\Delta\delta$ 3–6 ppm) than those of the corresponding neutral derivatives **2a–c** reflecting their cationic character (conductance values in methanol unequivocally confirm that **3a–c** are 1:1 electrolytes ($\Lambda_M = 96$–101 Ω^{-1} cm^2 mol^{-1})). Their ^1H and $^{13}C\{^1H\}$ NMR spectra in CD_3OD show, in addition to the corresponding arene ligand resonances, typical signals for the methylenic PCH_2 units: (*i*) (^1H NMR) a broad singlet at *ca.* 4.4 ppm, and (*ii*) ($^{13}C\{^1H\}$ NMR) a doublet ($^1J(CP) = 29.8$–33.8 Hz; **2a–c**) or an unresolved multiplet (second order system; **3a–c**) at δ_C 55.77–57.28. Although OH protons were not detected by ^1H NMR spectroscopy, the presence of these groups was confirmed by the appearance of a strong $\nu(OH)$ absorption band at 3263–3393 cm^{-1} in the IR spectra.

We note that, despite the burgeoning role of ruthenium(II) species in catalytic organic transformations,[10] the synthesis and catalytic activity of only three tris(hydroxymethyl)-phosphine–ruthenium(II) complexes, namely $[RuCl(\eta^5\text{-}C_5Me_5)(CO)\{P(CH_2OH)_3\}]$,[11] $[Ru_4H_4(CO)_8\{P(CH_2OH)_3\}_4]$,[12] and $[RuCl_2\{PH(CH_2OH)_2\}_2\{P(CH_2OH)_3\}_2]$,[13] has been reported to date.[14]

Catalytic isomerization of allylic alcohols into carbonyl compounds

The catalytic activity of dimer $[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ **1b** in the isomerization of allylic alcohols has been reported by Bäckvall and co-workers.[15] Although **1b** itself catalyzes the reaction very slowly, they found that a dramatic rate enhancement takes place upon addition of a catalytic amount of K_2CO_3 as co-catalyst.[16] For example, using 1 mol% of **1b** and 3 mol% of K_2CO_3, 1-octen-3-ol is converted into octan-3-one in 99% yield after 3 h at 65 °C in THF (TOF = 33 h^{-1}). More recently, we have reported that the catalytic performance of **1b** can be improved by using Cs_2CO_3 (2 equiv. per Ru) as co-catalyst instead of K_2CO_3 (TOF up to 333 h^{-1}).[4i]

Table 1 Ruthenium-catalyzed isomerization of 1-octen-3-ol into octan-3-one[a]

Entry	Catalyst	Yield[b] (%) (time)	TOF[c]/h^{-1}
1	$[\{Ru(\eta^6\text{-}C_6H_6)(\mu\text{-Cl})Cl\}_2]$ **1a**	100 (1 h)	500
2	$[\{Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl\}_2]$ **1b**	100 (1.5 h)	333[d]
3	$[\{Ru(\eta^6\text{-}C_6Me_6)(\mu\text{-Cl})Cl\}_2]$ **1c**	100 (4 h)	125
4	$[Ru(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})Cl_2]$	100 (1.2 h)	429[d]
5	$[RuCl_2(PPh_3)_3]$	92 (22 h)	21[d]
6	$[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$	38 (22 h)	9[d]
7	$[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$	1 (22 h)	<1[d]

[a] Reactions performed under N_2 atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (0.2 M in THF). Substrate/Ru/Cs_2CO_3 ratio: 500:1:2. [b] Yield of octan-3-one determined by GC (octan-3-one and 1-octen-3-ol were the only compounds detected). [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. [d] See ref. 4*i*.

In order to evaluate the influence of the arene ligand, we have firstly checked the catalytic activity of dimers **1a** and **1c** in the isomerization of 1-octen-3-ol into octan-3-one under the same reaction conditions (see Scheme 3). Thus, in a typical experiment, the ruthenium precursor (0.2 mol% of Ru) and Cs_2CO_3 (0.4 mol%) were added to a 0.2 M solution of 1-octen-3-ol (4 mmol) in THF a 75 °C, the reaction being monitored by gas chromatography. Results are summarized in Table 1.
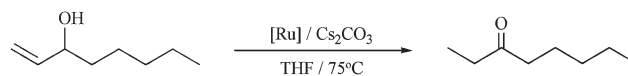
Scheme 3 Isomerization of 1-octen-3-ol into octan-3-one.

As expected, dimers **1a** and **1c** are also active catalysts for this reaction, leading to the quantitative formation of octan-3-one in 1 or 4 h, respectively. Interestingly, the catalytic efficiency of compounds $[\{Ru(\eta^6\text{-arene})(\mu\text{-Cl})Cl\}_2]$ is strongly dependent on the arene ligand. The rate order observed, *i.e.* C_6H_6 (TOF = 500 h^{-1}) > *p*-cymene (TOF = 333 h^{-1}) > C_6Me_6 (TOF = 125 h^{-1}), indicates clearly that the less sterically demanding and electron-rich arene the higher performances are found (see entries 1–3 in Table 1). We note also that, under these reaction conditions, complex **1a** is much more active than the classical ruthenium(II) catalysts $[RuCl_2(PPh_3)_3]$,[15] $[Ru(\eta^5\text{-}C_9H_7)Cl(PPh_3)_2]$[17] and $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$[17] (entries 5–7 *vs* entry 1 in Table 1), its activity being even better than that of the bis(allyl)–ruthenium(IV) complex $[Ru(\eta^3:\eta^2:\eta^3\text{-}C_{12}H_{18})Cl_2]$ described recently by us (entry 4 *vs* entry 1 in Table 1).[4i]

The solubility of the novel tris(hydroxymethyl)phosphine–ruthenium(II) complexes $[RuCl_2(\eta^6\text{-arene})\{P(CH_2OH)_3\}]$ **2a–c** and $[RuCl(\eta^6\text{-arene})\{P(CH_2OH)_3\}_2][Cl]$ **3a–c** in water, allowed us to study the isomerization of 1-octen-3-ol in a biphasic water/*n*-heptane medium. Thus, with a catalyst loading of 1 mol% of Ru (2 mol% of Cs_2CO_3 as co-catalyst), quantitative conversions of 1-octen-3-ol into octan-3-one were in all cases observed (results are collected in Table 2). We note that the use of 0.2 mol% of ruthenium results in longer or incomplete reactions. Octan-3-one can be isolated in pure form from the reaction media by simple organic-phase separation, evaporation, and distillation of the crude (>90% yield).

The results depicted in Table 2 show that the catalytic performances of the neutral complexes **2a–c** (TOF = 29–67 h^{-1}) are, in all cases, much better than their cationic counterparts **3a–c** (TOF = 4–6 h^{-1}) (see entries 1–3 *vs* 4–6). Assuming that this catalytic transformation proceeds through the mechanism proposed by Trost and co-workers, in which the chelate coordination of the allylic alkoxide to the metal is the initial step in the catalytic cycle,[17] dissociation not only of chloride but also of the arene ligand is required in the case of **3a–c** to furnish the required free coordination sites. In accord with this proposal, we note that free benzene, *p*-cymene and C_6Me_6 could be detected by GC/MS (no free arene was observed in the case of **2a–c**). This

Table 2 Isomerization of 1-octen-3-ol into octan-3-one catalyzed by complexes **2/3a–c** under biphasic water/*n*-heptane conditions[a]

Entry	Catalyst	Yield[b] (%) (time)	TOF[c]/h^{-1}
	[RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}]		
1	**2a**	100 (1.5 h)	67
2	**2b**	100 (2.25 h)	44
3	**2c**	100 (3.5 h)	29
	[RuCl(η^6-arene){P(CH$_2$OH)$_3$}$_2$][Cl]		
4	**3a**	100 (18 h)	6
5	**3b**	100 (21 h)	5
6	**3c**	100 (24 h)	4

[a] Reactions performed under N$_2$ atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (0.2 M in a mixture H$_2$O/*n*-heptane; V_{org}/V_{aq} = 1). Substrate : Ru : Cs$_2$CO$_3$ ratio: 100 : 1 : 2. [b] Yield of octan-3-one determined by GC (octan-3-one and 1-octen-3-ol were the only compounds detected). [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.

Table 3 Isomerization of 1-octen-3-ol into octan-3-one catalyzed by complexes **2/3a–c** under biphasic water/*n*-heptane conditions: Catalyst recycling[a]

Entry	Catalyst	Cycle	Yield[b] (%) (time)	TOF[c]/h^{-1}	TON[d]
1	**2a**	1	100 (1.5 h)	67	100
		2	100 (24 h)	4	200
		3	100 (64 h)	2	300
		4	67 (94 h)	<1	367
2	**2b**	1	100 (2.25 h)	44	100
		2	93 (53 h)	2	193
3	**2c**	1	100 (3.5 h)	29	100
		2	93 (43 h)	2	193
4	**3a**	1	100 (18 h)	6	100
		2	91 (70 h)	1	191
5	**3b**	1	100 (21 h)	5	100
		2	86 (24 h)	4	186
6	**3c**	1	100 (24 h)	4	100
		2	89 (54 h)	2	189

[a] Reactions performed under N$_2$ atmosphere at 75 °C using 4 mmol of 1-octen-3-ol (0.2 M in a mixture H$_2$O/*n*-heptane; V_{org}/V_{aq} = 1). Substrate : Ru : Cs$_2$CO$_3$ ratio: 100 : 1 : 2. [b] Yield of octan-3-one determined by GC (octan-3-one and 1-octen-3-ol were the only compounds detected). [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. [d] Cumulative TON values.

fact could be responsible of their lower activity. As observed for dimers **1a–c**, the rate order C$_6$H$_6$ > *p*-cymene > C$_6$Me$_6$ has been also found in both series of catalysts.

We were interested to know whether the active ruthenium species could be recycled from the aqueous phase after separation of the organic phase. Thus, high conversions were obtained in all cases in a second catalytic run (≥86%; see Table 3) but only the neutral complex [RuCl$_2$(η^6-C$_6$H$_6$){P(CH$_2$OH)$_3$}] **2a** showed good performances in a third and fourth cycle (cumulative TON = 367; see entry 1 in Table 3). Although the homogeneity of the aqueous solutions is maintained after each cycle, partial decomposition of the catalysts has been observed after prolonged periods in solution at 75 °C (inferred by ^{31}P{^{1}H} NMR spectroscopy).

In order to investigate the scope of the reaction, the isomerization of a number of other allylic alcohols has been studied using the most active catalysts [RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}] **2a–c**. Results using **2a** (arene = C$_6$H$_6$) and **2b** (arene = *p*-cymene) are summarized in Tables 4 and 5, respectively (data for the hexamethylbenzene derivative **2c** have been deposited as ESI†). Simple allylic alcohols bearing terminal C=C bonds (entries 1–4) are readily isomerized into the corresponding ketones by **2a–c**. In general, the activity of our catalysts decreases in function of the length of the hydrocarbon chain from C$_4$ to C$_8$ (see Tables 3–5 and ESI†). Thus, the highest TOF values have been obtained for the isomerization of 1-buten-ol into butan-2-one (TOF = 600 h^{-1} (**2a**), 200 h^{-1} (**2b**) and 153 h^{-1} (**2c**) in the first

cycle). This behaviour, which has been previously observed by de Bellefon and co-workers using the RhCl$_3$/TPPTS and Rh$_2$(SO$_4$)$_3$/TPPTS (TPPTS = P(*m*-C$_6$H$_4$SO$_3$Na)$_3$) catalytic systems under biphasic water/*n*-heptane conditions,[4e] can be rationalized in terms of both steric hindrance and decreasing solubility of the substrates in the aqueous phase for the heavier allylic alcohols.

A strong dependence of the catalysts recycling on the length of the hydrocarbon chain has been also observed (see Tables 3–5 and ESI†). Thus, the deactivation of **2a–c** is more severe when bulky allylic alcohols are used (see TOF and cumulative TON values). We note also that, although [RuCl$_2$(η^6-C$_6$H$_6$){P(CH$_2$OH)$_3$}] **2a** is in all cases the most active catalyst in the first cycles, the highest cumulative TON values for the isomerization of 1-buten-3-ol, 1-penten-3-ol and 1-hexen-3-ol were attained using [RuCl$_2$(η^6-*p*-cymene){P(CH$_2$OH)$_3$}] **2b** as catalyst (782 (8 runs), 489 (5 runs) and 341 (4 runs), respectively, to be compared with 625 (7 runs), 484 (5 runs) and 294 (3 runs) using **2a**; entries 1–3 in Tables 4 and 5). In contrast, as observed for 1-octen-3-ol (Table 3), **2a** leads to the best results in the isomerization of the bulkier 1-hepten-3-ol into heptan-3-one (cumulative TON = 345 (4 cycles) *vs* 260 (3 cycles) using **2b**; entry 4 in Tables 4 and 5).

Complexes **2a–c** are also active catalysts in the isomerization of allylic alcohols bearing an inner C=C bond such as 2-buten-1-ol (it is well-known that the isomerization of allylic alcohols becomes more difficult as the number of substituents increases on the double bond).[3] In particular, **2a** is able to catalyze this transformation in a quantitative manner after 23 h (TOF = 4 h^{-1}) and can be reused a second time (93% of conversion after 72 h; see entry 5 in Table 4).

**Catalytic hydration of terminal alkynes**

The hydration of terminal alkynes catalyzed by transition-metal complexes represents an appealing atom economical and environmentally benign method for the preparation of carbonyl compounds.[18] Since these catalytic additions of water across terminal alkynes follow the Markovnikov's rule, ketones are exclusively obtained in most cases. In particular, arene–ruthenium(II) complexes [RuCl$_2$(η^6-arene)(PPh$_2$CH=CH$_2$)] (arene = C$_6$Me$_6$, MeC$_6$H$_5$, *p*-Me$_2$C$_6$H$_4$, *p*-cymene, 1,3,5-Me$_3$C$_6$H$_3$, 1,2,4,5-Me$_4$C$_6$H$_2$)[19] and [RuCl(η^6-arene)(Me–Duphos)][Cl] (arene = C$_6$H$_6$, *p*-cymene; Me–Duphos = 1,2-bis((2*R*,5*R*)-2,5-dimethylpholano)benzene)[20] have proven to be active catalysts for the hydration of terminal alkynes into the corresponding ketones. Nevertheless, it has been recently demonstrated that a few ruthenium(II) complexes can invert the regioselectivity of the reaction yielding mainly aldehydes (anti-Markovnikov addition).[21] Thus, Tokonuga and Wakatsuki have reported that the arene–ruthenium(II) complexes [RuCl$_2$(η^6-C$_6$H$_6$)(PR$_3$)] (PR$_3$ = PPh$_2$(C$_6$F$_5$), P(*m*-C$_6$H$_4$SO$_3$Na)$_3$) are able to favor the anti-Markovnikov hydration of terminal alkynes in alcoholic aqueous media.[21a] All these results point out the crucial role of the ancillary phosphine ligands on the regioselectivity of the process.

The easy access to complexes **2/3a–c** prompted us to check their catalytic activity in alkyne hydration (see Scheme 4). Thus, in a typical experiment, a solution of the corresponding alkyne (1 mmol) and the ruthenium catalyst precursor (5 mol%) in a mixture of propan-2-ol–water (3 cm³/1 cm³) was heated at 90 °C, the reaction being monitored by gas chromatography. Results are summarized in Table 6.
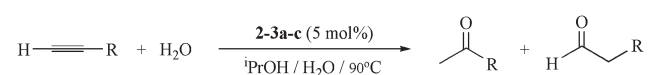
**Scheme 4** Hydration of terminal alkynes.

In the presence of the neutral complexes [RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}] **2a–c** phenylacetylene and 1-octyne are readily hydrated affording exclusively the corresponding

Table 4 Isomerization of various allylic alcohols catalyzed by the neutral complex [RuCl$_2$(η^6-C$_6$H$_6$){P(CH$_2$OH)$_3$}] **2a** under biphasic water/n-heptane conditions[a]

Entry	Substrate	Product	Cycle	Yield[b] (%) (time)	TOF[c]/h⁻¹	TON[d]
1			1	100 (10 min)	600	100
			2	100 (15 min)	400	200
			3	100 (20 min)	300	300
			4	100 (45 min)	133	400
			5	100 (1 h)	100	500
			6	100 (1.75 h)	57	600
			7	25 (24 h)	1	625
2			1	100 (20 min)	300	100
			2	100 (25 min)	240	200
			3	100 (30 min)	200	300
			4	100 (45 min)	133	400
			5	84 (24 h)	4	484
3			1	100 (30 min)	200	100
			2	100 (1.25 h)	80	200
			3	94 (24 h)	4	294
4			1	100 (45 min)	133	100
			2	100 (1.5 h)	67	200
			3	100 (2 h)	50	300
			4	45 (24 h)	2	345
5			1	100 (23 h)	4	100
			2	93 (72 h)	1	193

[a] Reactions performed under N$_2$ atmosphere at 75 °C using 4 mmol of the corresponding allylic alcohol (0.2 M in a mixture H$_2$O/n-heptane; V_{org}/V_{aq} = 1). Substrate : Ru : Cs$_2$CO$_3$ ratio: 100 : 1 : 2. [b] Yield of the aldehyde or ketone determined by GC (the alcohol and the carbonyl compound were the only species detected). [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. [d] Cumulative TON values.

Table 5 Isomerization of various allylic alcohols catalyzed by the neutral complex [RuCl$_2$(η^6-p-cymene){P(CH$_2$OH)$_3$}] **2b** under biphasic water/n-heptane conditions[a]

Entry	Substrate	Product	Cycle	Yield[b] (%) (time)	TOF[c]/h⁻¹	TON[d]
1			1	100 (30 min)	200	100
			2	100 (35 min)	171	200
			3	100 (40 min)	150	300
			4	100 (45 min)	133	400
			5	100 (50 min)	120	500
			6	100 (1 h)	100	600
			7	100 (1.75 h)	57	700
			8	82 (24 h)	3	782
2			1	100 (30 min)	200	100
			2	100 (35 min)	172	200
			3	100 (40 min)	150	300
			4	100 (50 min)	120	400
			5	89 (24 h)	4	489
3			1	100 (1 h)	100	100
			2	100 (2 h)	50	200
			3	100 (16 h)	6	300
			4	41 (24 h)	2	341
4			1	100 (45 min)	133	100
			2	100 (8 h)	13	200
			3	60 (24 h)	2	260
5			1	85 (72 h)	1	85

[a] Reactions performed under N$_2$ atmosphere at 75 °C using 4 mmol of the corresponding allylic alcohol (0.2 M in a mixture H$_2$O/n-heptane; V_{org}/V_{aq} = 1). Substrate : Ru : Cs$_2$CO$_3$ ratio: 100 : 1 : 2. [b] Yield of the aldehyde or ketone determined by GC (the alcohol and the carbonyl compound were the only species detected). [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. [d] Cumulative TON values.

carbonyl compounds in excellent yields (≥88%; see entries 1–6 in Table 6). In contrast, using the cationic complexes [RuCl(η^6-arene){P(CH$_2$OH)$_3$}$_2$][Cl] **3a–c** longer reaction times are required and the formation of several uncharacterized by-products, along with the expected carbonyl compounds (≤74% yield), was observed (entries 7–12 in Table 6). Within both series of catalysts, no appreciable differences in activity were observed as a function of the arene ligand used. Remarkably, GC/MS analysis of the crude reaction mixtures show in all the cases the presence of the corresponding free arene. This could indicate a mechanism similar to that proposed by Tokonuga and Wakatsuki using [RuCl$_2$(η^6-C$_6$H$_6$)(PR$_3$)] (PR$_3$ = PPh$_2$(C$_6$F$_5$), P(m-C$_6$H$_4$SO$_3$Na)$_3$) as catalysts which postulate that the ac-

tive catalytic species are of the type [RuCl$_2$(PR$_3$)$_x$].[21a] Similar intermediates have been also proposed starting from complexes [RuCl$_2$(η^6-arene)(PPh$_2$CH=CH$_2$)].[19]

Concerning the regioselectivity of the hydration process, in our systems the addition of water across the terminal alkyne seems to follow the Markovnikov's rule to produce the corresponding ketone as the major (entries 3–12) or unique (entries 1 and 2) product.

The hydration of phenylacetylene and 1-octyne catalyzed by complex **2/3a–c** in a biphasic water/n-heptane medium has been also studied. Unfortunately, very low yields (≤20%) were in all cases observed due probably to the insolubility of the terminal alkynes in the aqueous phase.

Table 6 Hydration of terminal alkynes catalyzed by complexes **2/3a–c**[a]

Entry	Alkyne	Catalyst	Conversion[b] (%) (time)	Yield of ketone[b] (%)	Yield of aldehyde[b] (%)
[RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}]					
1	Ph–C≡C–H	**2a**	88 (24 h)	88	0
2	Ph–C≡C–H	**2b**	89 (24 h)	89	0
3	Ph–C≡C–H	**2c**	89 (24 h)	88	1
4	^{n}Hex–C≡C–H	**2a**	100 (8 h)	84	16
5	^{n}Hex–C≡C–H	**2b**	100 (8 h)	69	31
6	^{n}Hex–C≡C–H	**2c**	100 (8 h)	72	28
[RuCl(η^6-arene){P(CH$_2$OH)$_3$}$_2$][Cl]					
7	Ph–C≡C–H	**3a**	88 (48 h)	42	6
8	Ph–C≡C–H	**3b**	90 (48 h)	60	6
9	Ph–C≡C–H	**3c**	89 (48 h)	41	4
10	^{n}Hex–C≡C–H	**3a**	100 (48 h)	46	9
11	^{n}Hex–C≡C–H	**3b**	100 (48 h)	47	27
12	^{n}Hex–C≡C–H	**3c**	100 (48 h)	46	9

[a] Reactions performed under N$_2$ atmosphere at 90 °C using 1 mmol of the corresponding alkyne (0.25 M in a mixture ^{i}PrOH–H$_2$O (3 : 1)). Substrate : Ru ratio: 100 : 5. [b] Determined by GC.

Conclusions

The novel water-soluble ruthenium(II) complexes [RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}] **2a–c** and [RuCl(η^6-arene){P(CH$_2$OH)$_3$}$_2$]-[Cl] **3a–c** have been easily prepared from the readily available precursors [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] and tris(hydroxymethyl)-phosphine. Complexes **2/3a–c** are efficient catalysts for the isomerization of allylic alcohols into carbonyl compounds in a biphasic water/n-heptane medium. Excellent results in terms of both activity and catalyst recycling (up to 8 consecutive runs) have been obtained using the neutral complexes [RuCl$_2$(η^6-C$_6$H$_6$){P(CH$_2$OH)$_3$}] **2a** and [RuCl$_2$(η^6-p-cymene){P(CH$_2$OH)$_3$}] **2b** (TOF values up to 600 h^{-1}; TON values up to 782), representing appealing alternatives to the known rhodium-based systems.[4d–f,h] Further studies concerning the application of these species in other aqueous/biphase catalytic transformations are currently underway.

Experimental

General comments

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification with the exception of compounds [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] (arene = C$_6$H$_6$ **1a**, p-cymene **1b**, C$_6$Me$_6$ **1c**) which were prepared following the methods reported in literature.[22] Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer. Conductivities were measured at room temperature, in ca. 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C and H analyses were carried out with a Perkin-Elmer 2400 micro-analyzer. GC measurements were made on a Hewlett-Packard HP6890 equipment using a HP-INNOWAX cross-linked poly(ethyleneglycol) (30 m, 250 μm) or Supelco Beta-Dex™ 120 (30 m, 250 μm) column. GC/MS measurements were performed on a Agilent 6890N equipment coupled to a 5973 mass detector (70-eV electron impact ionization) using a HP-1MS column. NMR spectra were recorded on a Bruker DPX300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using SiMe$_4$ or 85% H$_3$PO$_4$ as standards. DEPT experiments have been carried out for all compounds reported in this paper.

Preparation of complexes [RuCl$_2$(η^6-arene){P(CH$_2$OH)$_3$}] (arene = C$_6$H$_6$ 2a, p-cymene 2b, C$_6$Me$_6$ 2c). General procedure. To a solution of the corresponding dimer [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] **1a–c** (0.5 mmol) in 30 cm^3 of CH$_2$Cl$_2$ was added, at room temperature, a solution of P(CH$_2$OH)$_3$ (0.124 g, 1 mmol) in 10 cm^3 of methanol, and the reaction mixture stirred at room temperature for 1 h. The solvents were then removed under

vacuum, and the residue washed with diethyl ether (2 × 10 cm^3) and dried in vacuo to give complexes **2a–c** as orange solids. **2a:** Yield: 0.337 g, 90% (Found: C, 28.98; H, 3.90. RuC$_9$H$_{15}$O$_3$Cl$_2$P requires C, 28.89; H, 4.04%); IR (KBr)/cm^{-1} 525m, 600w, 625w, 669w, 761w, 800m, 823s, 867m, 886m, 1027s, 1173m, 1294w, 1395m, 1436s, 1507w, 1559w, 1653m, 2902m, 2927w, 3069m, 3267s; δ$_P$ (CD$_3$OD) 30.92 (s); δ$_H$ (CD$_3$OD) 4.40 (br, 6H, CH$_2$), 5.85 (s, 6H, C$_6$H$_6$); δ$_C$ (CD$_3$OD) 56.27 (d, ^{1}J(CP) = 33.8 Hz, CH$_2$), 87.36 (d, ^{2}J(CP) = 2.9 Hz, C$_6$H$_6$). **2b:** Yield: 0.366 g, 85% (Found: C, 36.12; H, 5.28. RuC$_{13}$H$_{23}$O$_3$Cl$_2$P requires C, 36.29; H, 5.39%); IR (KBr)/cm^{-1} 569m, 597w, 669w, 798m, 870s, 925w, 1031s, 1178m, 1259w, 1386s, 1434m, 1467m, 1498w, 1631m, 2879w, 2922m, 2958m, 3059w, 3393s; δ$_P$ (CD$_3$OD) 27.48 (s); δ$_H$ (CD$_3$OD) 1.23 (d, 6H, ^{3}J(HH) = 6.9 Hz, CH(CH$_3$)$_2$), 2.03 (s, 3H, CH$_3$), 2.74 (sept, 1H, ^{3}J(HH) = 6.9 Hz, CH(CH$_3$)$_2$), 4.42 (br, 6H, CH$_2$), 5.90 and 5.95 (d, 2H each, ^{3}J(HH) = 4.7 Hz, CH of p-cymene); δ$_C$ (CD$_3$OD) 18.32 (s, CH$_3$), 22.29 (s, CH(CH$_3$)$_2$), 31.77 (s, CH(CH$_3$)$_2$), 57.19 (d, ^{1}J(CP) = 32.1 Hz, CH$_2$), 86.14 (d, ^{2}J(CP) = 4.9 Hz, CH of p-cymene), 90.50 (d, ^{2}J(CP) = 3.7 Hz, CH of p-cymene), 95.15 and 107.50 (s, C of p-cymene). **2c:** Yield: 0.398 g, 87% (Found: C, 39.19; H, 5.90. RuC$_{15}$H$_{27}$O$_3$Cl$_2$P requires C, 39.31; H, 5.94%); IR (KBr)/cm^{-1} 475w, 503m, 539w, 604w, 715w, 731w, 799w, 868m, 898m, 1031s, 1182m, 1258w, 1385s, 1441m, 1496w, 1631m, 2872w, 2910m, 2980w, 3030w, 3323s; δ$_P$ (CD$_3$OD) 24.14 (s); δ$_H$ (CD$_3$OD) 2.15 (s, 18H, CH$_3$), 4.39 (br, 6H, CH$_2$); δ$_C$ (CD$_3$OD) 16.24 (s, CH$_3$), 57.25 (d, ^{1}J(CP) = 29.8 Hz, CH$_2$), 97.79 (s, C$_6$Me$_6$).

Preparation of complexes [RuCl(η^6-arene){P(CH$_2$OH)$_3$}$_2$][Cl] (arene = C$_6$H$_6$ 3a, p-cymene 3b, C$_6$Me$_6$ 3c). General procedure. To a solution of the corresponding dimer [{Ru(η^6-arene)(μ-Cl)Cl}$_2$] **1a–c** (0.5 mmol) in 30 cm^3 of CH$_2$Cl$_2$ was added, at room temperature, a solution of P(CH$_2$OH)$_3$ (0.248 g, 2 mmol) in 15 cm^3 of methanol, and the reaction mixture stirred at room temperature for 2 h. The solvents were then removed under vacuum, and the residue washed with diethyl ether (5 × 10 cm^3) and dried in vacuo to give complexes **3a–c** as yellow solids. **3a:** Yield: 0.453 g, 91% (Found: C, 28.81; H, 4.92. RuC$_{12}$H$_{24}$O$_6$Cl$_2$P$_2$ requires C, 28.93; H, 4.86%); conductivity (MeOH, 20 °C) 101 Ω^{-1} cm^2 mol^{-1}; IR (KBr)/cm^{-1} 535m, 608w, 640w, 669w, 731m, 765w, 813s, 834m, 865m, 884m, 1037s, 1184m, 1316w, 1386m, 1438s, 1521w, 1635m, 2907m, 2924w, 3087m, 3300s; δ$_P$ (CD$_3$OD) 34.97 (s); δ$_H$ (CD$_3$OD) 4.39 (br, 12H, CH$_2$), 6.33 (s, 6H, C$_6$H$_6$); δ$_C$ (CD$_3$OD) 57.28 (m, CH$_2$), 92.68 (t, ^{2}J(CP) = 1.7 Hz, C$_6$H$_6$). **3b:** Yield: 0.515 g, 93% (Found: C, 34.51; H, 5.95. RuC$_{16}$H$_{32}$O$_6$Cl$_2$P$_2$ requires C, 34.67; H, 5.82%); conductivity (MeOH, 20 °C) 96 Ω^{-1} cm^2 mol^{-1}; IR (KBr)/cm^{-1} 559m, 608w, 669m, 772m, 793w, 867s, 923w, 1029s, 1181m, 1306w, 1398m, 1441m, 1480w, 1509w, 1635m, 2908w, 2924m, 2956w, 3069m, 3355s; δ$_P$ (CD$_3$OD) 30.17 (s); δ$_H$ (CD$_3$OD) 1.23 (d, 6H,

^3J(HH) = 6.8 Hz, CH(CH_3)$_2$), 2.07 (s, 3H, CH$_3$), 2.61 (sept, 1H, ^3J(HH) = 6.8 Hz, CH(CH$_3$)$_2$), 4.37 (br, 12H, CH$_2$), 6.20 and 6.56 (d, 2H each, ^3J(HH) = 3.8 Hz, CH of *p*-cymene); δ_C (CD$_3$OD) 16.34 (s, CH$_3$), 19.58 (s, CH(CH_3)$_2$), 29.76 (s, CH(CH$_3$)$_2$), 55.77 (m, CH$_2$), 86.44 and 92.88 (s, CH of *p*-cymene), 92.88 and 124.17 (s, C of *p*-cymene). **3c:** Yield: 0.518 g, 89% (Found: C, 37.33; H, 6.09. RuC$_{18}$H$_{36}$O$_6$Cl$_2$P$_2$ requires C, 37.12; H, 6.23%); conductivity (MeOH, 20 °C) 99 Ω^{-1} cm^2 mol^{-1}; IR (KBr)/cm^{-1} 460w, 547w, 576m, 668w, 721w, 758m, 798w, 878s, 1013s, 1037s, 1177m, 1294w, 1388s, 1441s, 1636m, 2906w, 2925m, 2972w, 3059m, 3263s; δ_P (CD$_3$OD) 30.29 (s); δ_H (CD$_3$OD) 2.26 (s, 18H, CH$_3$), 4.35 (br, 12H, CH$_2$); δ_C (CD$_3$OD) 16.33 (s, CH$_3$), 57.22 (m, CH$_2$), 106.08 (t, ^2J(CP) = 1.5 Hz, C$_6$Me$_6$).

General procedure for the catalytic isomerization of allylic alcohols under biphasic conditions. In a Schlenk tube, the ruthenium catalyst precursor (0.04 mmol) and Cs$_2$CO$_3$ (0.026 g, 0.08 mmol) were dissolved, under inert atmosphere, in water (10 cm^3). A solution of the corresponding allylic alcohol (4 mmol) in *n*-heptane (10 cm^3) was then added and the reaction mixture stirred at 75 °C for the indicated time. The course of the reaction was monitored by regular sampling and analysis of the organic phase by gas chromatography. The identity of the resulting saturated carbonyl compound was assessed by comparison with commercially available pure samples and by their fragmentation in GC/MS. *Catalyst recycling*: the reaction mixture was allowed to reach room temperature, the aqueous phase was then separated under inert atmosphere and washed twice with 5 cm^3 of *n*-heptane. To the aqueous phase a new solution of the corresponding allylic alcohol (4 mmol) in *n*-heptane (10 cm^3) was added.

General procedure for the catalytic hydration of terminal alkynes. A solution of the corresponding alkyne (1 mmol) and the appropriate ruthenium precursor (0.05 mmol) in a mixture of propan-2-ol and water (3 cm^3/1 cm^3) was heated, under inert atmosphere at 90 °C in a sealed tube, for the indicated time. The course of the reaction was monitored by gas chromatography. The identity of the resulting ketones and aldehydes was assessed by comparison with commercially available pure samples and by their fragmentation in GC/MS.

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