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Dichloro(dodeca-2,6,10-triene-1,12-diyl)ruthenium(IV): a highly efficient catalyst for the isomerization of allylic alcohols into carbonyl compounds in organic and aqueous media

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The catalytic activity of the bis(allyl)-ruthenium(IV) complex [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2] in the transposition of allylic alcohols into carbonyl compounds, both in THF and H_2O as solvent, is reported.

The conversion of allylic alcohols into the corresponding saturated aldehydes or ketones is a useful synthetic process which conventionally requires a two-step sequence of oxidation and reduction reactions. An appealing alternative is the *one-pot* internal redox process catalyzed by a variety of transition-metal complexes (Scheme 1).[1]

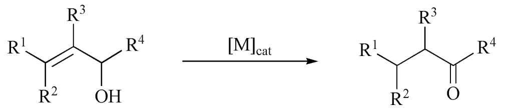
Despite the great interest of this atom economical and catalytic transformation in synthesis, efforts devoted to develop such a reaction in water have been scarce.[2] We have found that the readily available bis(allyl)-ruthenium(IV) complex [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2] ($C_{12}H_{18}$ = dodeca-2,6,10-triene-1,12-diyl; see Fig. 1)[3] (**1**) is an efficient catalyst for the isomerization of allylic alcohols into carbonyl compounds, both in THF and in water as solvent, representing the first example of a Ru(IV) catalyst for this transformation.[1]

Firstly, we checked the activity of [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2] (**1**) in the isomerization of 1-octen-3-ol as a model reaction. Thus, when a 0.2 M THF solution of 1-octen-3-ol was refluxed for 24 h with a catalytic amount of **1** (0.2 mol%), octan-3-one was obtained only in 6% yield. A dramatic rate-enhancement was observed upon addition of 0.4 mol% of Cs_2CO_3 resulting in the quantitative transformation of the alcohol into the saturated ketone in 70 min (Table 1; entry 1).[4] We note that, under these reaction conditions, complex **1** is much more active than the classical ruthenium(II) catalysts [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$],[4] [$RuCl_2(PPh_3)_3$],[4] [Ru(η^5-C_9H_7)Cl$(PPh_3)_2$][5] and [Ru(η^5-C_5H_5)Cl$(PPh_3)_2$][5] (entries 2–5 *vs.* entry 1 in Table 1).[6] The exceptional high activity of **1** is retained at lower catalyst loadings. As an example, using 10^{-4} mol% of **1**, 1-octen-3-ol (0.2 M in THF; substrate/Ru/Cs_2CO_3 ratio: 1000000 : 1 : 2) can be quantitatively isomerized within 18 hours leading to the highest turnover number value (TON = 10^6; see entry 6 in Table 1) reported to date for this catalytic transformation.[1,7]

Taking advantage of the known stability of complex **1** towards water,[8] the isomerization of 1-octen-3-ol was studied in aqueous medium.[9] Thus, we have found that the reaction proceeds at higher rates than those observed in THF either in the presence or absence of Cs_2CO_3 (Table 2; entry 1). Moreover, the effect of the co-catalyst is in this case not so marked since in the absence of Cs_2CO_3 octan-3-one was quantitatively obtained in only 50 min. These observations could be explained on the basis of the higher polarity of water *vs.* THF which favors the dissociation of the chloride ligands in complex **1** and therefore the coordination of the substrate to the metal. In order to check whether Cs_2CO_3 acts exclusively as a chloride abstractor, the isomerization of 1-octen-3-ol was studied in THF using $AgSbF_6$ as co-catalyst (substrate/Ru/$AgSbF_6$ ratio: 500 : 1 : 2). In this case only 27% of conversion was attained after 24 h of reflux (6% without co-catalyst). This seems to indicate that Cs_2CO_3 is acting not only as a chloride abstractor but also as a base. Thus, the formation of the 1-octen-3-olate ruthenium complex, after deprotonation of the substrate, could be envisaged as the first step of the catalytic process.[10]

The catalytic activity of [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2] (**1**) was tested for a number of other allylic alcohols (results are summarized in Table 2). As a general trend, the isomerization process was found to take place faster in water (see columns 7 and 8 *vs.* 5 and 6, respectively, in Table 2). As far as the allylic alcohols are concerned, there is a strong dependence upon the substitution of the carbon–carbon double bond as previously observed with other catalytic systems.[1] Thus, monosubstituted secondary alcohols (see entries 1–4 in Table 2) are readily isomerized in aqueous medium into the corresponding ketones using 0.2 mol% of **1** (TOF values 300–2000 h^{-1} without Cs_2CO_3 or 1500–2000 h^{-1} with Cs_2CO_3).[11] The high catalytic activity of **1** at a lower loading (10^{-4} mol%) is also confirmed for the isomerization of 3-buten-2-ol (0.2 M in water) into butan-2-one (without Cs_2CO_3; 100% yield in 20 h; TON = 10^6; TOF = 50000 h^{-1}). In contrast, when 1,1- and 1,2-disubstituted allylic alcohols are used longer reaction times and higher catalyst loadings (5–10 mol%) are required to achieve total conversions (see entries 6–9 in Table 2).

The catalyst recycling was also examined. Thus, we have found that **1** can be recycled at least for three times after the conversion of 3-buten-2-ol in butan-2-one (0.2 M in water; 0.2 mol% of **1** and 0.4 mol% of Cs_2CO_3; separation of butan-2-one by distillation). No



Scheme 1 Isomerization of allylic alcohols into carbonyl compounds.

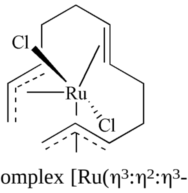


Fig. 1 Structure of complex [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2] (**1**).

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

Entry	Catalyst	Yield (%)[b] (time)	TOF/h^{-1}[c]
1	[Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2]	100 (70 min)	429
2	[{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$]	100 (90 min)	333
3	[$RuCl_2(PPh_3)_3$]	92 (22 h)	21
4	[Ru(η^5-C_9H_7)Cl$(PPh_3)_2$]	38 (22 h)	9
5	[Ru(η^5-C_5H_5)Cl$(PPh_3)_2$]	1 (22 h)	< 1
6	[Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2][d]	100 (18 h)	55556

[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. [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. [d] Reaction performed with a substrate/Ru/Cs_2CO_3 ratio: 1000000 : 1 : 2.

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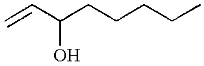
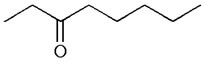
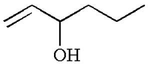
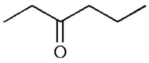
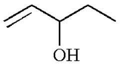
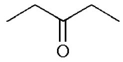
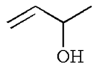
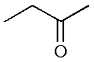
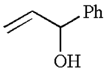
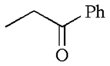
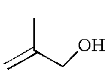
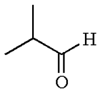
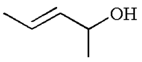
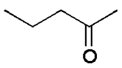
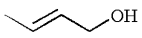
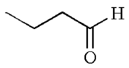
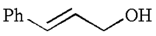
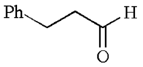
Table 2 Isomerization of various allylic alcohols catalyzed by complex [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2] (**1**) in THF and H_2O[a]

Entry	Substrate	Product	Catalyst concentration	THF Yield (%)^b (time) TOF/h^{-1c}	THF/Cs_2CO_3 Yield (%)^b (time) TOF/h^{-1c}	H_2O Yield (%)^b (time) TOF/h^{-1c}	H_2O/Cs_2CO_3 Yield (%)^b (time) TOF/h^{-1c}
1			0.2 mol%	6 (24 h) 1	100 (70 min) 429	100 (50 min) 600	100 (15 min) 2000
2			0.2 mol%	97 (24 h) 20	100 (65 min) 462	100 (15 min) 2000	100 (20 min) 1500
3			0.2 mol%	100 (22 h) 23	100 (20 min) 1500	100 (15 min) 2000	100 (15 min) 2000
4			0.2 mol%	100 (18 h) 28	100 (45 min) 667	100 (100 min) 300	100 (20 min) 1500
5			5 mol%	3 (24 h) < 1	100 (6 h) 3	100 (75 min) 16	100 (10 min) 120
6			5 mol%	65 (24 h) < 1	100 (15 h) 1	100 (10 h) 2	100 (3 h) 7
7			5 mol%	2 (24 h) < 1	100 (9 h) 2	92 (24 h) < 1	100 (3 h) 7
8			10 mol%	69 (24 h) < 1	100 (13 h) < 1	100 (7 h) 1	100 (3 h) 3
9			10 mol%	63 (24 h) < 1	100 (16 h) < 1	100 (9 h) 1	100 (4.5 h) 2

[a] Reactions performed under N_2 atmosphere at 75 °C using 4 mmol of the corresponding allylic alcohol (0.2 M). When Cs_2CO_3 was used as co-catalyst it was added in a 2 : 1 molar ratio with respect to complex **1**. [b] Yield of the aldehyde or ketone determined by GC. [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.

appreciable loss of activity was observed in the first and second runs (100% yield in 20 min). However, deactivation of the catalyst takes place in the third and fourth runs (100% and 43% yields in 24 h, respectively).

We have also found that [Ru(η^3:η^2:η^3-$C_{12}H_{18}$)Cl_2] (**1**) remains active in the presence of isoprene.[12] It should be mentioned that almost all known catalysts able to perform allylic alcohol isomerization fail in the presence of conjugated dienes.[1] Since allylic alcohols can be obtained by hydration of dienes, complex **1** can be envisaged as a catalyst for the direct *one-pot* transformation of dienes into saturated ketones.[13]

In summary, these promising preliminary results open the possibility to develop a biphasic catalytic system based on complex **1**. Efforts in this direction, as well as studies concerning the mechanism of this catalytic process, are now in progress.

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Notes and references

1 For reviews see: R. C. van der Drift, E. Bouwman and E. Drent, *J. Organomet. Chem.*, 2002, **650**, 1; R. Uma, C. Crévisy and R. Grée, *Chem. Rev.*, 2003, **103**, 27.

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4 Addition of 0.4 mol% of Na_2CO_3 or K_2CO_3 results also in quantitative formation of octan-3-one in 4 or 2.5 h, respectively. The use of co-catalysts is well documented. See for example: (*a*) J.-E. Bäckvall and U. Andreasson, *Tetrahedron Lett.*, 1993, **34**, 5459; (*b*) R. Uma, M. K. Davies, C. Crévisy and R. Grée, *Eur. J. Org. Chem.*, 2001, 3141.

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6 The highest TOF values reported for the isomerization of 1-octen-3-ol, by using K_2CO_3 as co-catalyst, are the following: 33 h^{-1} [{Ru(η^6-*p*-cymene)(μ-Cl)Cl}$_2$], 285 h^{-1} [$RuCl_2(PPh_3)_3$] and 8 h^{-1} [Ru(η^5-C_5H_5)Cl$(PPh_3)_2$] (see ref. 4*a*).

7 (*a*) TON values up to 3000 (TOF up to 36000 h^{-1}) have been reported for the isomerization of 2-propen-1-ol into propionaldehyde using complexes [Ru(η^5-C_5H_5)(PR_3)$(NCMe)_2$][PF_6] (PR_3 = PPh_3, PCy_3) as catalysts: C. Slugovc, E. Rüba, R. Schmid and K. Kirchner, *Organometallics*, 1999, **18**, 4230; (*b*) TON values up to 6000 have been also reported for the isomerization of 3-buten-2-ol into butan-2-one using complex [RuCl(η^5-C_5H_5)$(PPh_3)_2$] as catalyst and AgOTs (silver *p*-toluenesulfonate) as co-catalyst (a TOF value > 200000 h^{-1} has been claimed): R. C. van der Drift, M. Vailati, E. Bouwman and E. Drent, *J. Mol. Catal. A*, 2000, **159**, 163.

8 J. W. Steed and D. A. Tocher, *J. Chem. Soc., Chem. Commun.*, 1991, 1609.

9 Although complex **1** itself is insoluble in water, it readily becomes soluble in the presence of the allylic alcohol.

10 The chelate coordination of the allylic alkoxide has been proposed as the initial step in the catalytic isomerization of allylic alcohols by the complexes [Ru(η^5-C_9H_7)Cl$(PPh_3)_2$] and [Ru(η^5-C_5H_5)Cl$(PPh_3)_2$] (see ref. 5).

11 In contrast, due probably to steric reasons, the isomerization of 1-phenyl-2-propen-1-ol requires 5 mol% of the catalyst to achieve 100% of conversion in reasonable reaction times (entry 5 in Table 2).

12 As an example, in the presence of 15 mmol of isoprene, 4 mmol of 1-octen-3-ol (0.2 M in H_2O) can be quantitatively isomerized within 65 min using 0.2 mol% of **1** (without Cs_2CO_3; TOF = 461 h^{-1} to be compared with entry 1 in Table 2).

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