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Relationship between structure, fluxionality and racemization activity in organometallic derivatives of polyoxometalates

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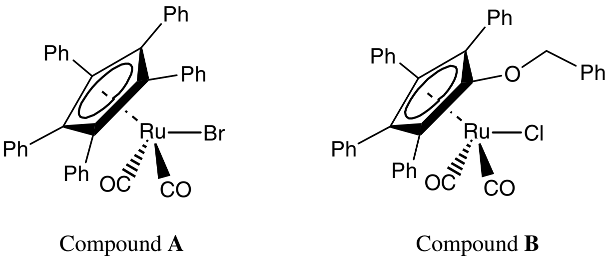
Abstract—The catalytic activity of several organometallic derivatives of polyoxometalates, especially those of general formula $[M_4O_{16}\{M'(\eta^6\text{-arene})\}_4]$ (M = Mo, W; M′ = Ru, Os), was evaluated in the racemization of secondary alcohols. A link between composition, fluxionality and catalytic activity was established.

1. Introduction

Due to their great importance in the pharmaceutical, agricultural and other fine chemical industries, several teams have focused over the past 10 years on the development of methods for preparing enantiomerically pure secondary alcohols.[1] Among the different routes which were explored, the Dynamic Kinetic Resolution (DKR) appears as a powerful tool for converting a racemic alcohol into one single enantiomer.[2] It combines the action of an enzyme, which catalyzes the enantioselective transformation of one of the enantiomers, with that of a metal catalyst, which catalyzes the isomerization of the other enantiomer.

Several Ru^{II} racemizing catalysts have thus been synthesized, some of which appeared to be particularly active and compatible with the enzymatic reaction (Fig. 1).[3–5] Nevertheless, with regards to industrial applications, one of the major drawbacks of these systems is that large quantities of additives or a special control of the experimental conditions are necessary, in order to obtain a high activity. For instance, compound **A** reacts best under an argon atmosphere and in the presence of 1 equiv of *t*-BuOK with respect to the catalyst,[3b] whereas compound **B** displays its highest activity in the presence of 1 equiv of K_3PO_4 with respect to the alcohol.[4e,5a] The search for readily accessible and more sustainable racemization catalysts, which do not require any additives, remains an important goal, on which a few teams have recently started to work, via the synthesis of heterogeneous ruthenium catalysts.[6]



Compound **A**
Compound **B**

Figure 1. Efficient Ru(II) racemization catalysts.[3b,4e]

Over the past 10 years, a great variety of Ru^{II}–arene derivatives of polyoxometalates have been synthesized,[7] in particular by our group. These compounds are constituted of one or several $\{Ru(arene)\}^{2+}$ fragments coordinated to an oxometallic core. They are tunable in composition; in charge (neutral or anionic species); in the mode of grafting of the organometallic fragment(s), and in their behaviour in solution (some compounds maintain their molecular structure, whereas others isomerize). They are easy to

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obtain in reasonable yields and are not sensitive to oxygen or humidity.

Given the special environment of the Ru^{II}–arene fragment in these architectures and the robustness of the compounds, they could be an alternative to the racemization catalysts described so far.[3–6] Herein, we report and discuss the activity of some of these organometallic oxides in the racemization of 1-phenylethanol.

2. Results and discussion

2.1. Study of the catalytic activity of $\{Ru(\eta^6\text{-arene})\}^{2+}$ derivatives of polyoxometalates

We concentrated our study on the racemization of enantiomerically pure 1-phenylethanol, which is commonly regarded as the gold standard in this area. The catalytic activity of several different organometallic derivatives of polyoxometalates in the racemization of (*S*)-1-phenylethanol was tested. In addition, the low-nuclearity oxometalates $(n\text{-}Bu_4N)_2[WO_4]$ and $(n\text{-}Bu_4N)_2[Mo_2O_7]$, and the $[Ru(arene)Cl_2]_2$ complexes (arene = toluene, *p*-cymene and hexamethylbenzene) were tested for comparison with the results reported in Table 1.

As expected,[8] in the absence of any additive, the ruthenium precursors are inactive in the racemization of (*S*)-1-phenylethanol (entries 3–5). Similarly, the low-nuclearity molybdate and tungstate anions display no catalytic activity (entries 1 and 2a), nor does the isopolyoxomolybdate $[Mo_6O_{19}]^{2-}$ (entry 2b).

Conversely, for most of the organometallic derivatives of polyoxometalates tested, the ee values were below 100%, meaning that these complexes, in the absence of additive, have evolved towards a catalytically active species. It thus appears that the grafting of $\{Ru(arene)\}^{2+}$ fragments onto a polyoxometalate framework leads to an activation of the ruthenium centre, allowing it to evolve more easily towards a catalytically active complex. Unfortunately, these cooperative effects between the polyoxoanion and the organometallic moiety are moderately efficient: the racemization activity of the compounds remains low, insofar as after 22 h of reaction, the ee has not yet reached the value of 0%.

Table 1. Racemization of (*S*)-1-phenylethanol by ruthenium derivatives of polyoxometalates

Entry	Catalyst[a]	ee[b,c] (%)
1	$(n\text{-}Bu_4N)_2[WO_4]$	100
2a	$(n\text{-}Bu_4N)_2[Mo_2O_7]$	100
2b	$(n\text{-}Bu_4N)_2[Mo_6O_{19}]$	100
3	$[Ru(toluene)Cl_2]_2$	96
4	$[Ru(p\text{-cymene})Cl_2]_2$	100
5	$[Ru(hmb)Cl_2]_2$[d]	100
6	$[Mo_4O_{16}\{Ru(toluene)\}_4]$	48
7	$[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$	60
8	$[Mo_4O_{16}\{Ru(hmb)\}_4]$[d]	80
9	$[W_4O_{16}\{Ru(p\text{-cymene})\}_4]$	59
10	$[W_4O_{16}\{Ru(hmb)\}_4]$[d]	57
11	$[\{Ru(hmb)\}_2W_5O_{18}\{Ru(hmb)(H_2O)\}]$[d]	96
12	$[\{Ru(hmb)\}_2Mo_5O_{18}\{Ru(hmb)(H_2O)\}]$[d]	100
13	$[\{Ru(p\text{-cymene})\}_2Mo_2O_4\{MeC(CH_2O)_3\}_2]$	100
14	$(n\text{-}Bu_4N)_xNa_{10-x}[Sb_2W_{20}O_{70}\{Ru(p\text{-cymene})\}_2]$	99
15	$(n\text{-}Bu_4N)_xCs_{5-x}[PW_{11}O_{39}\{Ru(p\text{-cymene})(H_2O)\}]$	67

[a] Reaction conditions: (*S*)-1-phenylethanol (0.50 mmol), catalyst: 5 mol % (W) (entry 1), 5 mol % (Mo) (entries 2a and 2b), 5 mol % (Ru) (entries 3–15) PhCl (5 mL), N_2 atm, 70 °C, 22 h.

[b] ee of the alcohol: $(\%) = 100 \times ([S] - [R])/([S] + [R])$.

[c] Measured by GC equipped with a chiral column, using an internal standard technique. The main by-product was acetophenone (<3%).

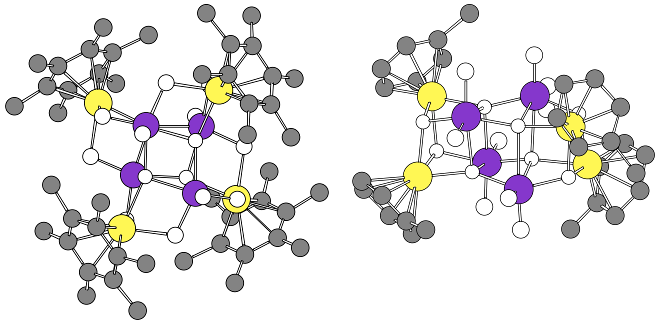
[d] hmb = hexamethylbenzene.

Nevertheless, it is noteworthy that the catalytic activity differs from one organometallic oxide to the other, meaning that all oxoanionic cores do not have the same efficiency in activating the ruthenium. Apart from the complex $(n\text{-}Bu_4N)_xCs_{5-x}[PW_{11}O_{39}\{Ru(p\text{-cymene})(H_2O)\}]$ (entry 15), the family of compounds $[M_4O_{16}\{Ru(arene)\}_4]$ (M = Mo, W; entries 6–10) displayed the highest activity. However, even within this family of complexes, different racemization activities were observed. We thus proceeded to a more detailed analysis of the catalytic tests, in order to rationalize the differences observed, and with the prospect of understanding better as to which factors are likely to enhance the racemization activity of organometallic derivatives of polyoxometalates.

2.2. Comparison of the catalytic activity of the $[M_4O_{16}\{Ru(\eta^6\text{-arene})\}_4]$ (M = Mo, W) complexes

The family of complexes of general formula $[M_4O_{16}\{Ru(arene)\}_4]$ (M = Mo, W; arene = toluene, *p*-cymene, hexamethylbenzene) has drawn our attention over the past six years.[7b–e] In the solid state, two isomeric forms have been evidenced, as shown in Figure 2. These differ by the arrangement of the four $\{Ru(arene)\}^{2+}$ fragments around a central cubic $[M_4O_{16}]^{8-}$ core, and are referred to as the 'Triple Cubane' and 'Windmill' forms, a terminology initially proposed by Süss-Fink et al.[7a] In solution, some of the species maintain their solid state structure, whereas others isomerize, a process during which coordination sites on the ruthenium are temporarily released (Fig. 3).[7b,e]

Based on our previous studies of the fluxionality of these species in $CHCl_3$ and CH_2Cl_2,[7b,e] we have determined the behaviour of the different complexes in chlorobenzene by various spectroscopic techniques (Table 2, entries 6–10).



$[Mo_4O_{16}\{Ru(hexamethylbenzene)\}_4]$[7c] $[Mo_4O_{16}\{Ru(toluene)\}_4]$[7e]

Figure 2. Molecular structures of 'Windmill' (left) and 'Triple Cubane' (right) compounds.

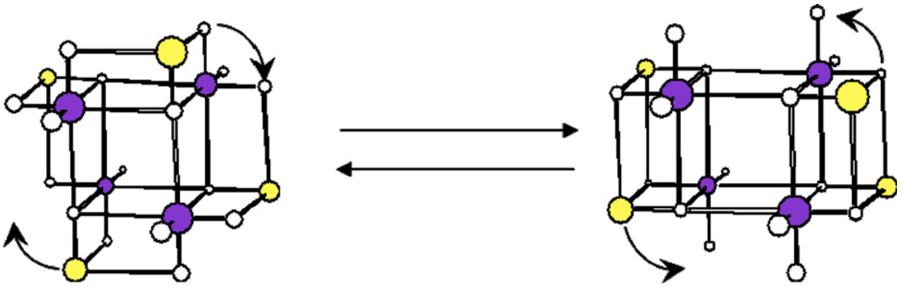


Figure 3. Schematic representation of the isomerization between the 'Windmill' (left) and 'Triple Cubane' (right) oxometallic structures.

Table 2. Influence of the isomerization process on the racemization activity of $[M_4O_{16}\{M'(arene)\}_4]$ (M = Mo, W; M′ = Ru, Os)

Entry	Catalyst[a]	Isomer (in the solid state)	Isomerization in PhCl[b]	ee (%)
6	$[Mo_4O_{16}\{Ru(toluene)\}_4]$	Triple Cubane or Windmill	Yes	48
7	$[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$	Windmill	Yes	60
8	$[Mo_4O_{16}\{Ru(hmb)\}_4]$	Windmill	No	80
9	$[W_4O_{16}\{Ru(p\text{-cymene})\}_4]$	Windmill	No	59
10	$[W_4O_{16}\{Ru(hmb)\}_4]$	Windmill	No	57
16	$[Mo_4O_{16}\{Os(p\text{-cymene})\}_4]$	Windmill	Yes	91

[a] Reaction conditions: (*S*)-1-phenylethanol (0.50 mmol), catalyst: 5 mol % (Ru) (entries 6–10), 5 mol % (Os) (entry 16), PhCl (5 mL), N_2 atm, 70 °C, 22 h.
[b] Determined by IR (entry 6), ^{95}Mo NMR (entries 7, 8 and 16), ^{1}H and ^{13}C NMR (entries 9 and 10).

The following conclusions thus stem from the analysis of their racemization activity:

1. The nature of the arene ligand coordinated to the ruthenium hardly influences the catalytic activity of the complexes, as can be shown by comparing the ee's for compounds $[W_4O_{16}\{Ru(hexamethylbenzene)\}_4]$ and $[W_4O_{16}\{Ru(p\text{-cymene})\}_4]$, which both maintain the 'Windmill' form in PhCl (entries 9 and 10).
2. The nature of the metal, which constitutes the $[M_4O_{16}]^{8-}$ core has an effect on the racemization activity of the complexes: compounds with tungsten are more active than those with molybdenum, given the results obtained for complexes $[Mo_4O_{16}\{Ru(hexamethylbenzene)\}_4]$ and $[W_4O_{16}\{Ru(hexamethylbenzene)\}_4]$, which both maintain the 'Windmill' form in PhCl (entries 8 and 10).
3. The complexes which isomerize in solution give rise to the highest activity; indeed, according to the first point of this list, given the poor activity of $[Mo_4O_{16}\{Ru(hexamethylbenzene)\}_4]$, one would also have expected a low racemization activity for $[Mo_4O_{16}\{Ru(toluene)\}_4]$ and $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$; the higher activity of the latter compounds could thus be attributed to the fact that they isomerize in solution (entries 6 and 7).

Consequently, chemical composition and intrinsic behaviour in solution are two factors which shed light on the differences observed in the catalytic activity of the compounds of the $[M_4O_{16}\{Ru(arene)\}_4]$ family. The complexes which evolve towards more active species are either those for which tungsten is the metal constituent of the oxoanionic core (entries 9 and 10), or those which isomerize in solution and thus easily release coordination sites on the ruthenium (entries 6 and 7). Nevertheless, their racemization activity remains low compared to that reported in the literature for other Ru^{II} complexes, which can achieve the racemization in less than 30 min.[3b,d] We thus tried to improve the catalytic activity of the most active species ($[Mo_4O_{16}\{Ru(toluene)\}_4]$, $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$, $[W_4O_{16}\{Ru(p\text{-cymene})\}_4]$ and $[W_4O_{16}\{Ru(hexamethylbenzene)\}_4]$), by varying the experimental conditions.

2.3. Attempts to enhance the catalytic activity of the $[M_4O_{16}\{Ru(\eta^6\text{-arene})\}_4]$ complexes (M = Mo, arene = toluene, *p*-cymene; M = W, arene = *p*-cymene, hexamethylbenzene)

2.3.1. Influence of the nature of the solvent. Previous studies have shown that the nature of the solvent often plays an important role with regards to the efficiency of racemization catalysts.[4b,c,5a] We thus tested the activity of the complexes in two other solvents often used in racemization reactions: toluene and *t*-amylalcohol. The results obtained in the case of $[W_4O_{16}\{Ru(hexamethylbenzene)\}_4]$ and $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$ are reported in Table 3.

In both cases, the catalytic activity appeared to be much lower in toluene and *t*-amylalcohol than in chlorobenzene. In toluene, the lower solubility of the catalysts could explain the decrease in racemization activity. In *t*-amylalcohol, the competitive coordination of the solvent on the ruthenium could account for the loss of efficiency in the racemization of 1-phenylethanol.

Consequently, chlorobenzene appeared as the most appropriate solvent for these catalysts, and was thus used in the majority of the following studies.

2.3.2. Influence of irradiation. Due to positive influence of the Triple Cubane/Windmill isomerization in chlorobenzene on the racemization activity of $[Mo_4O_{16}\{Ru(toluene)\}_4]$ and $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$, we decided to

Table 3. Influence of the solvent on the racemization activity of $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$ and $[W_4O_{16}\{Ru(hmb)\}_4]$

Catalyst[a]	Solvent	ee (%)
$[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$	PhCl	60
	Toluene	90
	t-Amylalcohol	89
$[W_4O_{16}\{Ru(hmb)\}_4]$	PhCl	57
	Toluene	88
	t-Amylalcohol	85

[a] Reaction conditions: (*S*)-1-phenylethanol (0.50 mmol), catalyst: 5 mol % (Ru), solvent (5 mL), N_2 atm, 70 °C, 22 h.

favour even more the release of coordination sites on the metal by irradiating the reaction medium,[7g,9] in order to decoordinate the arene ligand.

Results were similar for the different compounds tested, and those obtained in the case of $[Mo_4O_{16}\{Ru(toluene)\}_4]$ are reported in Table 4. A clear enhancement of the racemization activity was observed under irradiation: the ee reached a value close to 35% in only 5 h, even though the irradiation had been carried out in toluene rather than chlorobenzene.[10] Consequently, the catalytic activity is higher under irradiation, because of the efficient release of coordination sites on the ruthenium.

Nevertheless, a high percentage of acetophenone simultaneously formed in solution, in a way which appeared difficult to control, as shown by the difference in the figures observed for two reactions performed under the same conditions (7.9% vs 15%). This prohibitively high yield in acetophenone and the problem of reproducibility of the experiments under irradiation led us to look for other means of activation of the racemization catalysts.

2.3.3. Influence of additives. For an important number of racemization catalysts, the addition of molecules such as *t*-BuOK or TEMPO, favours the evolution of the Ru^{II} complexes towards an active species.[3b,4d,5a] We thus tried to evaluate if these molecules were also able to enhance the catalytic activity of complexes such as $[W_4O_{16}\{Ru(hexamethylbenzene)\}_4]$ or $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$. The results are given in Table 5.

The effect of TEMPO and *t*-BuOK varies from one catalyst to the other. On one hand, in the case of $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$, adding *t*-BuOK not only considerably accelerates the racemization process, but also strongly increases the quantity of acetophenone formed, whereas adding TEMPO only enhances the percentage of acetophenone. On the other hand, in the case of $[W_4O_{16}\{Ru(hexamethylbenzene)\}_4]$, adding TEMPO only slightly increases the racemization activity, whereas the addition of *t*-BuOK strongly decreases it.

Table 4. Effect of the irradiation on the racemization activity

Irradiation	Solvent	*T* (°C)	Time[a] (h)	ee (%)	$\eta_{(ACP)}$[b] (%)
No	PhCl	70	22	48	2.8
Yes	Toluene	≈110	5	32	7.9
Yes	Toluene	≈110	5	36	>15

[a] Reaction conditions: (*S*)-1-phenylethanol (0.50 mmol), $[Mo_4O_{16}\{Ru(toluene)\}_4]$ (5 mol % (Ru)), solvent (5 mL), inert atmosphere (N_2 or Ar).

[b] Yield in acetophenone.

Table 5. Influence of *t*-BuOK and TEMPO on the racemization activity

Catalyst[a]	Additive[b]	ee (%)	$\eta_{(ACP)}$ (%)
$[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$	—	60	2.9
	t-BuOK	0.3	23.5
	TEMPO	58	8.7
$[W_4O_{16}\{Ru(hmb)\}_4]$	—	57	2.9
	t-BuOK	96	6.8
	TEMPO	52	2.6

[a] Reaction conditions: (*S*)-1-phenylethanol (0.50 mmol), catalyst: 5 mol % (Ru), PhCl (5 mL), N_2 atm, *T* = 70 °C, 22 h.

[b] Quantities of additive: 1 equiv/Ru.

Such differences observed in the effect of *t*-BuOK and TEMPO can be related to the difference in behaviour of these two complexes in chlorobenzene, and suggests that they evolve towards different catalytically active species. In the case of $[Mo_4O_{16}\{Ru(p\text{-cymene})\}_4]$, it is unfortunately not possible to exploit the great increase in the racemization activity by adding *t*-BuOK, given the substantial quantity of acetophenone which forms simultaneously.

2.3.4. Racemization activity of $[Mo_4O_{16}\{Os(\eta^6\text{-}p\text{-cymene})\}_4]$. Since neither the solvent, nor the irradiation of the medium, nor the addition of cocatalysts appeared to lead to active racemization catalysts without increasing in parallel the quantity of acetophenone formed, we tried to obtain better activity by changing the nature of the metal implied in the catalysis.

Having recently synthesized the Os^{II} compound $[Mo_4O_{16}\{Os(\eta^6\text{-}p\text{-cymene})\}_4]$, which, like its ruthenium analogue, displays the windmill form in the solid state and isomerizes in chlorobenzene - thus releasing coordination sites on the osmium,[11] we tested its racemization activity. Unfortunately, as shown in Table 2 (entry 16), the catalytic activity of the osmium derivative is much lower than that of the ruthenium complex (entry 7). Consequently, it appears that ruthenium is the most appropriate metal for catalyzing these reactions.

Finally, it is noteworthy that when used as racemization catalysts in the conditions of the DKR, that is, in the presence of a lipase (such as CALB) and of an acylating agent (such as isopropenylacetate), the catalytic activity of the different $[M_4O_{16}\{Ru(arene)\}_4]$ compounds appeared to be even lower. The different tests performed seem to show that they are deactivated by both the enzyme and the acylating agent.

3. Conclusion

The catalytic activity of several $\{Ru(arene)\}^{2+}$ derivatives of polyoxometalates in the racemization of 1-phenylethanol was tested, with the prospect of finding new efficient catalysts for the DKR of secondary alcohols.

The racemization activity of the compounds tested was higher than that of the precursors used for their synthesis, thus underscoring the presence of cooperative effects between the oxometallic core and the organometallic moiety. So far, the ability of polyoxometalates to enhance the catalytic activity of organometallic fragments had only been tested in oxidation catalysis, and evidenced in a small number of cases.[12] For the first time, we have thus shown that some oxoanionic cores are likely to favour the evolution of $\{Ru(arene)\}^{2+}$ organometallic moieties towards species which are active in the racemization of 1-phenylethanol. Moreover, the activity of these catalysts does not rely on the presence of additional molecules in the reaction medium.

The comparison of the catalytic activity of the different compounds tested revealed the importance of the nature of the oxoanionic moiety on the catalytic activity. More specifically, in the case of the $[M_4O_{16}\{Ru(arene)\}_4]$ compounds ($M = Mo$, W; arene = toluene, *p*-cymene, hexamethylbenzene), which were among the most efficient racemization catalysts tested here, it was shown that the nature of the arene had little influence on the catalytic activity, and that the most active species were those containing tungsten and those which isomerize in solution. For these compounds, the relationship between structure, fluxionality and racemization activity was thus established.

Unfortunately, the $[M_4O_{16}\{Ru(arene)\}_4]$ compounds were less efficient racemization catalysts than other Ru^{II} complexes described so far. Attempts to enhance their activity by changing the nature of the solvent, adding cocatalysts (*t*-BuOK, TEMPO), or replacing ruthenium by osmium were unsuccessful. Nevertheless, by irradiating the reaction medium, a better racemization activity could be reached. Although irradiation also led to the formation of more oxidation by-product, we believe that this means of activation of the racemization catalyst would deserve to be exploited in the case of other ruthenium complexes.

Despite their globally moderate catalytic activity, $\{Ru(arene)\}^{2+}$ derivatives of polyoxometalates appear as a new class of racemization catalysts in which the environment of the Ru^{II} moiety is very different from that of the other catalysts described so far. This suggests that by looking at a greater variety of ruthenium complexes, better racemization catalysts are likely to be encountered.

Acknowledgement

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10. Toluene was chosen as the solvent for the irradiations because it is more inert under UV-light than chlorobenzene.
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