Ruthenium bis(bipyridine) sulfoxide complexes: new catalysts for alkene epoxidation

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The ruthenium bis(bipyridine) sulfoxide complexes Ru-1 and Ru-2 exhibit high catalytic activity for epoxidation of unfunctionalized olefins in the presence of [bis(acetoxy)-iodo]benzene; with the chiral catalyst, Ru-2, asymmetric induction up to 94% was observed for β-methylstyrene.

The development of new and efficient catalysts for alkene epoxidation is a subject that has recently attracted intensive research.[1] Ruthenium complexes with nitrogen ligands are recognized to be powerful oxidizing catalysts, which have been extensively investigated in oxidation transformations.[2]

Since the pioneering work of Balavoine and co-workers[3] on the epoxidation of olefins by the $RuCl_3$–2,2′-bipyridine–$NaIO_4$ system, different approaches were proposed and efforts have been spent to render this method more efficient.[4] Also, several attempts were made to present an enantioselective version of this simple system by using chiral nitrogen ligands. However, only low to moderate enantioselectivities have been obtained.[5]

We and Inoue and co-workers recently described the synthesis of chiral ruthenium bis(diimine) sulfoxide complexes.[6] These new complexes were successfully used as precursors in the preparation of optically pure ruthenium tris(diimine) complexes.[7] In order to extend the utility of these new chiral complexes, we investigated their application as catalysts in alkene epoxidation. Here, we present our preliminary results demonstrating the catalytic efficiencies of *rac*-**Ru-1**[7] and Δ-**Ru-2** acting as chiral catalysts in alkene epoxidation reactions.†

We first examined the epoxidation of *trans*-stilbene as a model substrate (runs 1–6). The use of racemic **Ru-1** applying Balavoine′s procedure ($NaIO_4$ in a two phase-system) gave only a 5% yield of the desired epoxide (Table 1, run 1). No reaction was observed when H_2O_2 (30% in water) was used, probably

due to the complexation of water on the ruthenium (run 2).[8] The use of *tert*-butylhydroperoxide (*t*BuOOH) as an oxidant gave 85% of *trans*-stilbene oxide (run 3). However, the use of [bis(acetoxy)iodo]benzene [$PhI(OAc)_2$]‡ under the same conditions led to the *trans*-stilbene oxide in a quasi-quantitative yield (run 4). We finally found that $PhI(OAc)_2$ served as an efficient oxygen donor in dichloromethane at reflux assisted by **Ru-1**. Thus, addition of $PhI(OAc)_2$ (1.0 mmol) to a solution of *trans*-stilbene (0.5 mmol) and 2% mol of **Ru-1** in CH_2Cl_2 at 40 °C for 40 h resulted in the formation of *trans*-stilbene oxide in a quantitative yield (run 5). The use of *t*BuOOH under these conditions gave a lower yield of the desired epoxide (run 6). We have also observed that in the presence of $PhI(OAc)_2$ without catalyst, the reaction provided only 8% yield of the desired epoxide. To further explore the potential of **Ru-1**, we examined its aptitude to induce epoxidation of various olefins under the optimized conditions. Epoxidation of styrene substrates proceeded smoothly with high yields (runs 8–11). More interestingly, the catalyst seems to be very active in aliphatic and cyclic olefin epoxidations (runs 12 and 13). In contrast, when allylic alcohol or α,β-unsaturated carbonyl compounds were
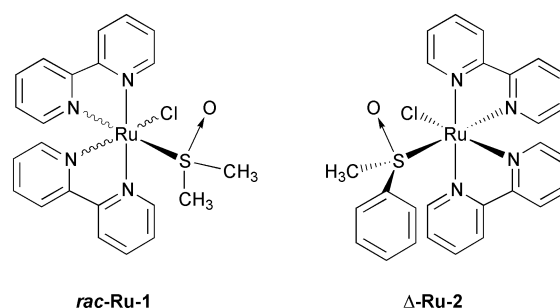

rac-**Ru-1**   Δ-**Ru-2**

Table 1 Catalytic epoxidation of different olefins with *rac*-**Ru-1**[a]

Run	Olefin	Oxidant	T/°C	t/h[b]	Conversion (%)	Yield (%)[c]
1	*trans*-stilbene	$NaIO_4$	25	40	98	5
2	*trans*-stilbene	H_2O_2	25	48	—	—
3	*trans*-stilbene	*t*BuOOH	25	100	95	85
4	*trans*-stilbene	$PhI(OAc)_2$	25	100	99	95
5	*trans*-stilbene	$PhI(OAc)_2$	40	40	98	94
6	*trans*-stilbene	*t*BuOOH	40	48	90	85
7	*trans*-stilbene	$PhI(OAc)_2$	40	48	12	8
8	Styrene	$PhI(OAc)_2$	40	48	99	92
9	*p*-MeO-styrene	$PhI(OAc)_2$	40	38	99	75
10	β-Me-styrene	$PhI(OAc)_2$	40	48	95	92
11	α-Me-styrene	$PhI(OAc)_2$	40	45	96	83
12	Cyclopentene	$PhI(OAc)_2$	40	40	>99	>99
13	1-Hexene	$PhI(OAc)_2$	40	40	>99	>98

[a] Catalyst (2% mol), olefin (0.5 mmol), and oxidant (1.25 mmol; 2.5 equiv.). CH_2Cl_2 (4 mL). [b] t/h refers to time in hours. [c] The yields are determined by GC using nonane as an internal standard and they refer to the used olefin.

Table 2 Use of Δ-**Ru-2** in the asymmetric epoxidation of different olefins[a]

Run	Olefin	T/°C	t/h	Conversion (%)	Yield (%)	ee (%)[b]	Abs. Config.[c]
1	*trans*-stilbene	40	40	>99	0	—	—
2	*trans*-stilbene	0	100	0	0	—	—
3	*trans*-stilbene	25	80	>98	97	33	(R,R)
4	*trans*-stilbene[d]	25	100	>99	82	27	(R,R)
5	Styrene	25	72	95	85	66	(R)
6	*trans*-β-Me-styrene	25	75	>99	92	94	(R,R)
7	1-Hexene	25	80	—	—	—	

[a] Catalyst (2% mol), olefin (0.5 mmol), and oxidant (1.25 mmol; 2.5 equiv.). CH_2Cl_2 (4 mL). The isolated yields are referred to the starting material. [b] The ee values were determined by chiral HPLC (Pharmachir 7C; *i*PrOH : hexane (0.1 : 99.9); 0.7 mL min^{-1}) and are an average of three similar reactions. [c] Absolute configurations were determined by HPLC using the authentic samples. [d] The oxidant was *t*BuOOH.

used, only products of over-oxidation were observed under these reaction conditions.

We then examined the asymmetric epoxidation of different olefins using Δ-**Ru-2**. To our surprise, the reaction of *trans*-stilbene with PhI(OAc)$_2$ in the presence of **Ru-2** under the same conditions as for **Ru-1** resulted exclusively in the cleavage of the double bond with the benzaldehyde isolated as the product (Table 2, run 1). No reaction was observed at 0 °C with this catalytic system (run 2). However, at room temperature this reaction gave the *trans*-stilbene oxide in a high yield and a moderate enantiomeric excess (33% ee, run 3). Epoxidation with *t*BuOOH as an oxygen donor proceeded with approximately the same level of enantioselectivity (run 4). The epoxidation of styrene in the presence of **Ru-2** in combination with PhI(OAc)$_2$ gave the styrene oxide with high enantioselectivity (66% ee, run 5). More interestingly, a 94% ee was obtained in the case of *trans*-β-methyl styrene (run 6). This is the best result obtained so far in ruthenium-catalyzed alkene epoxidations. Unfortunately, no reaction was observed with 1-hexene (run 7).

In comparison, oxo complexes of ruthenium with polypyridine ligands as *cis*-[Ru(bpy)$_2$(py)O]$^{2+}$ have been investigated as stoichiometric and catalytic oxidants in a variety of organic and inorganic reactions.[9] Optically pure *cis*-Δ-[Ru(bpy)$_2$(py)O] was also used in the stoichiometric oxidation of methyl *p*-tolyl sulfide.[10] According to this, we assume that in our case the oxygen atom transfer occurs *via* the *in situ* formation of the oxo–ruthenium complex (Ru=O). The formation of this Ru=O intermediate could occur either by displacement of the chlorine ligand giving a catalyst with two different chiralities (sulfoxide and metal center), or by displacement of the chiral sulfoxide providing the catalyst with chirality only on the metal center. In order to confirm the proposed metal–oxo reactive intermediate in this oxidation reaction, the stoichiometric reaction of PhI(OAc)$_2$ with **Ru-1** was monitored by UV-Vis spectroscopy. The color changed from orange (λ_{max} = 426 nm) to yellow (λ_{max} = 404 nm), indicating the expected formation of [Ru^{IV}=O](X).[9] The IR spectrum of this solution is very similar to that of **Ru-1**, with the presence of the *S*-Ru sulfoxide stretching frequency at 1120 cm^{-1} and the occurrence of a $\nu_{(Ru=O)}$ stretch at 788 cm^{-1}, confirming the formation of Ru=O[5] by displacement of the chlorine ligand. Preliminary kinetic studies of the reaction of **Ru-1** with an excess of *trans*-stilbene in dichloromethane at 40 °C using an excess of PhI(OAc)$_2$ revealed that this reaction is pseudo-first order with respect to the *trans*-stilbene (K_{obs} = 0.06 h^{-1}).

In conclusion, we have found that the new ruthenium bis(bipyridine) sulfoxide complexes are efficient catalysts for alkene epoxidation. The results obtained with the chiral version of this catalyst are very promising even if they might not be generally applicable. Our work now is focused on the study of the mechanism involved, and the scope and limitations of this alkene epoxidation. In the case of **Ru-2**, we are also investigating the role of the chiral sulfoxide in the asymmetric induction.

Notes and references

† The **Ru-1** and **Ru-2** complexes are slightly unstable upon prolonged exposure to light. For this reason, all the reactions described here are carried out under dark conditions. Dichloromethane was also distilled and degassed before use.

‡ For the use of PhI(OAc)$_2$ see: *Encyclopedia of Reagents for Organic Synthesis*, ed. L. A. Paquette, Wiley, New York, 1995, vol. 2, p. 1479 and ref. 5.

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