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Ruthenium(II) 2-(phenylazo)pyridine complexes as epoxidation catalysts

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Abstract

trans-Stilbene undergoes epoxidation with a two-fold excess of sodium periodate in the presence of 2 mol% ruthenium(II) 2-(phenylazo)pyridine complexes. Selectivities for epoxide are in the range 34–75%, depending on the structure of the complex. The byproduct, benzaldehyde, is derived from competing oxidative cleavage of the double bond.

Keywords: Alkenes; Epoxidation; Nitrogen ligands; Ruthenium

Epoxides, and more specifically chiral epoxides, are key intermediates in organic synthesis. Catalytic methods for their preparation fall into two major categories [1]. The first category [2] employs alkyl hydroperoxides or hydrogen peroxide in combination with early transition elements (Mo, W, V, Ti, etc.) as catalysts and involves peroxometal species as the active oxidant (pathway a in Fig. 1). The Katsuki–Sharpless method [3] for the asymmetric epoxidation of allylic alcohols with alkyl hydroperoxides, in the presence of titanium(IV)–tartrate complexes as chiral catalysts, is a well-known example of this category. The second category employs late transition elements (e.g. Fe and Mn) in combination with various single oxygen donors [4], such as iodosyl benzene and hypochlorite, and involves high-valent oxometal species as the active oxidant. An important difference is that the oxometal

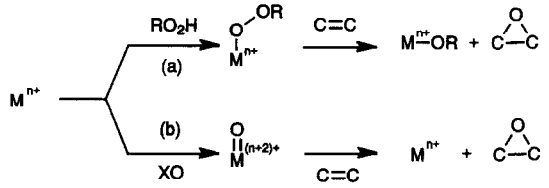

Fig. 1. Peroxometal vs. oxometal pathways in catalytic olefin epoxidation.

oxidants generally give selective epoxidation only when coordinated to certain organic ligands. In the biological systems this is accomplished with porphyrin ligands in combination with iron as the catalytic centre, e.g. in the ubiquitous cytochrome P450-dependent monooxygenases [5]. Hence, much effort has been devoted in recent years to developing biomimetic systems, mainly involving Fe or Mn as the catalytic centre, capable of emulating the regio- and enantioselective oxidations observed in Nature. The most well-known of these are the chiral manganese Schiff's base complexes used by both Katsuki [6] and Jacobsen [7] in combination with iodosyl benzene or hypochlorite

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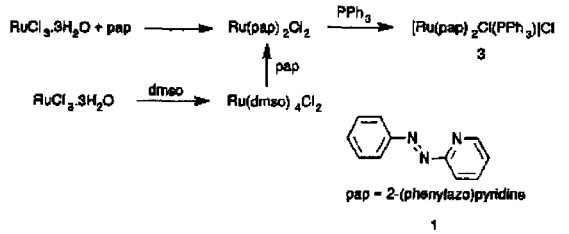

Scheme 1. Synthesis of $Ru(pap)_2Cl_2$.

and by Mukaiyama [8] with in situ formed percarboxylic acids.

In view of its close proximity to iron in the periodic table and its ability to readily form high-valent oxometal complexes, ruthenium would also be expected to be a candidate for epoxidation catalysis. In the absence of organic ligands high-valent oxoruthenium species effect the oxidative cleavage of olefins [9]. In contrast, Balavoine and coworkers showed [10] that $RuCl_3$ in the presence of bipyridyl or substituted phenanthroline ligands, catalyzed the epoxidation of olefins with sodium periodate as single oxygen donor. Recently it was shown that a ruthenium bipyridyl periodate complex was even more active [11]. Olefin epoxidation has also been observed with iodosyl benzene and heteroaromatic N-oxides, in the presence of ruthenium Schiff base complexes [12] and/or ruthenium porphyrins [13]. Similarly, chiral ruthenium Schiff's base complexes [14] and ruthenium pyridyl-oxazolines [15] have been reported to catalyze the asymmetric epoxidation of olefins, using iodosyl benzene and sodium periodate, respectively, as the oxygen donors. The best enantioselectivity (80% ee) was observed in the epoxidation of styrene using a

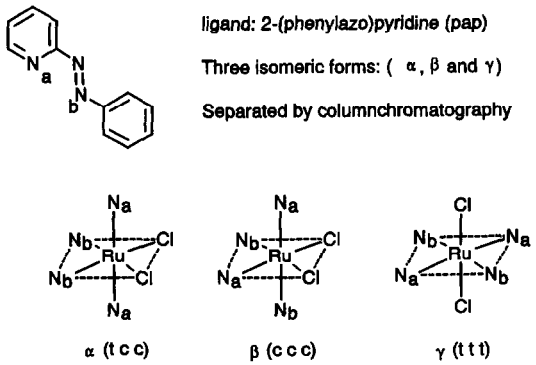

Fig. 2. Three isomers of $Ru(pap)_2Cl_2$.

tridentate Schiff's base ligand in combination with triphenylphosphine [14].

A prerequisite for the development of a more efficient ruthenium-based asymmetric epoxidation catalyst is the understanding of the nature of the active oxoruthenium species and the influence of ligand structure on its reactivity. The mechanism and the nature of the oxidative species is still not fully understood. Assuming that oxidative cleavage involves initial [3+2] cycloaddition of the olefin to a dioxoruthenium(VI) moiety, one would expect this to be possible only when the oxo ligands are disposed in a *cis* fashion. Ru(IV)oxo complexes have been reported to afford epoxides [16]. Both *trans*-Ru(VI)dioxo [17] and *cis*-Ru(VI)dioxo [c] complexes have also been shown to afford epoxides. Until now there has been no comparison of *cis*- and *trans*-ruthenium(VI)dioxo complexes with the same ligand(s). Hence, we have undertaken a study of the ruthenium-catalyzed epoxidation of olefins using a variety of nitrogen-containing ligands. Here we report our findings on the epoxidation of *trans*-stilbene with $NaIO_4$ as oxygen donor and ruthenium bis[2-(phenylazo)pyridine] (pap) complexes as catalyst. We expected to see a difference in selectivity to the epoxide for *cis*-complexes on the one hand, and *trans*-complexes on the other. These complexes were known in the literature [18], but have never been used for epoxidation reactions. Since the $Ru(pap)_2Cl_2$ complexes are easy to isolate and very stable we have used them to investigate the influence of the nature of the coordination on the selectivity to epoxide.

2-(Phenylazo)pyridine (pap) has a higher reduction potential than 2,2′-bipyridyl, is a stronger π-acceptor and gives stable ruthenium complexes. It was synthesized from nitrosobenzene and 2-aminopyridine [19]. The synthesis of the complexes is depicted in Scheme 1. $Ru(DMSO)_2Cl_2$ was synthesized from $RuCl_3 \cdot 3H_2O$ and dimethyl sulfoxide (DMSO) [20].

$Ru(pap)_2Cl_2$ can give five possible isomeric forms, three of which can be isolated from the synthesized material; *trans–trans–trans* (γ),

Table 1
Results of epoxidation of *trans*-stilbene with $NaIO_4$

Entry	Complex	Conversion (%)	Selectivity (%)
1	$RuCl_3$/–	100	<2
2	$RuCl_3$/pap **1**	100	48
3	$RuCl_3$/4-NO_2–pap **2**	100	42
4	α,β,γ-Ru(pap)$_2Cl_2$	100	47
5	α-Ru(pap)$_2Cl_2$	75	34
6	β-Ru(pap)$_2Cl_2$	100	75
7	γ-Ru(pap)$_2Cl_2$	100	65
8	[γ-Ru(pap)$_2$P(Ph)$_3$Cl]Cl **3**	6	26

Selectivity is % epoxide vs. % aldehyde (from oxidative cleavage of the double bond).

trans–cis–cis (α) and *cis–cis–cis* (β) (Fig. 2). The isomers were separated by column chromatography over silica gel. The α- and the β-isomers are blue while the γ-isomer is green.

Both the mixture and the three isolated isomers were tested in the epoxidation of *trans*-stilbene using $NaIO_4$ as the primary oxidant. A two-fold excess of oxidant was used in order to obtain complete conversion of the *trans*-stilbene. The only byproduct observed was benzaldehyde, derived from oxidative cleavage of the stilbene. In the absence of the 2-(phenylazo)pyridine ligands benzaldehyde was the only product observed. Interestingly, the different isomers showed different activity and selectivity (Table 1, entries 2 and 5–7). 2-(4-Nitrophenylazo)pyridine **2** [21], a derivative of 2-(phenylazo)pyridine was also synthesized and tested (entry 3). One additional complex with only one vacant position at the ruthenium metal was also tested (entry 8). This complex ([Ru(pap)$_2$(P(Ph)$_3$)Cl]Cl **3**) contained an additional triphenylphosphine ligand [22].

The *cis*-β- and the *trans*-γ-isomer gave good selectivities. The most stable *cis*-α-isomer gave both lower conversion and selectivity. Complex **3** with only one vacant coordination site gave a low conversion and selectivity (Table 1, entry 8). This suggests that a Ru(VI)-dioxo compound is the active oxidant as was postulated by others [23]. Alternatively, the electronic and/or steric effects of the triphenyl phosphine group may also cause the large decrease in activity. The similar selectivity observed with both a *trans*- and a *cis*-complex, with the same bidentate ligand, cannot be reconciled with a mechanism in which only the *cis*-dioxo moiety is responsible for oxidative cleavage. The different selectivity, observed for the two *cis*-isomers (α and β) could possibly be due to a steric effect. X-ray structures of both the α and the β-isomer have been determined [24]. The α-isomer appears to be more sterically hindered, which was confirmed by constructing molecular models.

General procedure for epoxidation of stilbene with $RuCl_3 \cdot nH_2O/NaIO_4$: (a) with in situ formation of complex; To a vigorously stirred solution of 14 mg (0.059 mmol) of $RuCl_3 \cdot nH_2O$ (42.3% Ru assay) in 8 ml of distilled water was added 0.26 mmol (2.2 equiv.) of ligand. The solution was stirred for 30 min. Then, 0.5 g (2.78 mmol) of *trans*-stilbene in 12 ml of CH_2Cl_2 was added, followed by 1.2 g (5.66 mmol) of $NaIO_4$. The mixture was stirred at room temperature and monitored by GLC. The reaction was stopped when GLC showed complete conversion (18–24 h). Then 25 ml of CH_2Cl_2 and 25 ml of water was added. The layers were separated and the aqueous layer was extracted twice with 25 ml of CH_2Cl_2. The combined organic layers were washed with water (25 ml) and brine (50 ml), dried on Na_2SO_4, filtered over silica gel and evaporated under reduced pressure. The amount of epoxide and aldehyde (byproduct) was determined by ^1H NMR and GLC.

For epoxidation with preformed complexes the same procedure was followed, except that 0.059 mmol complex was added instead of ruthenium salt and free ligand.

In summary, ruthenium pap complexes have been found to be new catalysts for epoxidation reactions. Both a *cis*- and a *trans*-isomer showed good selectivity which suggests that both ruthenium *cis*- and *trans*-dioxo species can give epoxidation. Interestingly, both the α- and β-isomer of Ru(pap)$_2Cl_2$, are chiral. Since the β-isomer gave the highest selectivity for epoxide we are currently investigating the possibility of using optically

active β-Ru(pap)$_2$Cl$_2$ for asymmetric epoxidation.

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