

## Homogeneous [Ru<sup>III</sup>(Me<sub>3</sub>tacn)Cl<sub>3</sub>]-Catalyzed Alkene *cis*-Dihydroxylation with Aqueous Hydrogen Peroxide

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**Abstract:** A simple and green method that uses [Ru(Me<sub>3</sub>tacn)Cl<sub>3</sub>] (**1**; Me<sub>3</sub>tacn = *N,N,N'*-trimethyl-1,4,7-triazacyclononane) as catalyst, aqueous H<sub>2</sub>O<sub>2</sub> as the terminal oxidant, and Al<sub>2</sub>O<sub>3</sub> and NaCl as additives is effective in the *cis*-dihydroxylation of alkenes in aqueous *tert*-butanol. Unfunctionalized alkenes, including cycloalkenes, aliphatic alkenes, and styrenes (14 examples) were selectively oxidized to their corresponding *cis*-diols in good to excellent yield (70–96%) based on

substrate conversions of up to 100%. The preparation of *cis*-1,2-cycloheptanediol (119 g, 91% yield) and *cis*-1,2-cyclooctanediol (128 g, 92% yield) from cycloheptene and cyclooctene, respectively, on the 1-mol scale can be achieved by scaling up the reaction without modification. Results from

**Keywords:** alkenes • catalysis • dihydroxylation • oxidation • ruthenium

Hammett correlation studies on the competitive oxidation of *para*-substituted styrenes ( $\rho = -0.97$ ,  $R = 0.988$ ) and the detection of the cycloadduct [(Me<sub>3</sub>tacn)ClRuHO<sub>2</sub>(C<sub>8</sub>H<sub>14</sub>)<sup>+</sup> by ESI-MS for the **1**-catalyzed oxidation of cyclooctene to *cis*-1,2-cyclooctanediol are similar to those of the stoichiometric oxidation of alkenes by *cis*-[(Me<sub>3</sub>tacn)-(CF<sub>3</sub>CO<sub>2</sub>)Ru<sup>VI</sup>O<sub>2</sub>]<sup>+</sup> through [3+2] cycloaddition (W.-P. Yip, W.-Y. Yu, N. Zhu, C.-M. Che, *J. Am. Chem. Soc.* **2005**, *127*, 14239).

### Introduction

The use of O<sub>2</sub> or H<sub>2</sub>O<sub>2</sub> as a terminal oxidant for the selective oxidation of organic compounds is an area of immense interest in homogeneous catalysis because these oxidants are inexpensive and environmentally friendly.<sup>[1]</sup> Recently, several homogeneous transition-metal-catalyzed oxidation reactions have been reported to display high selectivity in the epoxidation of alkenes<sup>[2]</sup> and the oxidation of C=C bonds to carboxylic acids,<sup>[1e,3]</sup> but catalytic procedures that employ H<sub>2</sub>O<sub>2</sub> as a terminal oxidant for alkene *cis*-dihydroxylation remain sparse in the literature. With H<sub>2</sub>O<sub>2</sub> as a terminal oxidant, tungsten peroxo<sup>[4]</sup> and methyltrioxorhenium-(VII)<sup>[5]</sup> complexes were reported to catalyze the dihydroxy-

lation of alkenes by epoxidation–hydrolysis to give *trans*-diols. Que and co-workers reported biomimetic non-heme iron catalysts for the oxidation of unfunctionalized alkenes to the corresponding *cis*-diols with H<sub>2</sub>O<sub>2</sub> as the oxidant.<sup>[6]</sup> Heterogenized manganese complexes with cyclic triamine ligands could catalyze the oxidation of alkenes by H<sub>2</sub>O<sub>2</sub> to give a mixture of epoxides and diols.<sup>[7]</sup> Osmium-catalyzed alkene *cis*-hydroxylation by using *N*-methylmorpholine oxide (NMO)<sup>[8]</sup> and K<sub>3</sub>[Fe(CN)<sub>6</sub>]<sup>[9]</sup> as oxidants is the most reliable protocol in organic synthesis.<sup>[10]</sup> The use of H<sub>2</sub>O<sub>2</sub> instead of NMO and K<sub>3</sub>[Fe(CN)<sub>6</sub>] should be more desirable, but in most cases, direct addition of H<sub>2</sub>O<sub>2</sub> to a reaction mixture of alkenes and OsO<sub>4</sub> usually leads to *cis*-diols in low yields due to nonselective reactions and overoxidation.<sup>[11]</sup> In this regard, Bäckvall and co-workers reported an improvement of the reoxidation of Os<sup>VI</sup> to Os<sup>VIII</sup> by H<sub>2</sub>O<sub>2</sub> that gave *cis*-diols in high yields and high selectivities for the oxidation of various alkenes under mild conditions.<sup>[12a,b]</sup> Despite their remarkable success, this catalytic reaction requires *N*-methylmorpholine and flavin as cocatalysts to facilitate Os-catalyzed alkene *cis*-dihydroxylation by H<sub>2</sub>O<sub>2</sub>. Thus, the search for new metal catalysts that are able to dihydroxylate alkenes selectively by H<sub>2</sub>O<sub>2</sub> without organic cocatalysts remains a formidable challenge.

Ruthenium-catalyzed reactions have long been investigated as an alternative synthetic route to *cis*-diols. Using NaIO<sub>4</sub>

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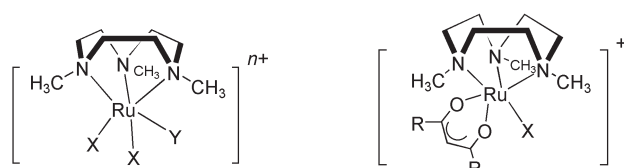
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as an oxidant, Shing et al. first reported that  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (7 mol %) was an effective catalyst for the dihydroxylation of various alkenes in  $\text{EtOAc}/\text{MeCN}/\text{H}_2\text{O}$  solvent systems.<sup>[13]</sup> However, the reaction conditions ( $0^\circ\text{C}$ , <30 s) have to be carefully controlled to prevent overoxidation. Recently, Plietker and Niggemann improved the  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}/\text{NaIO}_4$  system by the addition of Brønsted or Lewis acids, and the catalyst loading was decreased to 0.25–0.5 mol %.<sup>[14]</sup> We also reported a solid-supported ruthenium-nanoparticle catalyst for the *cis*-hydroxylation of alkenes.<sup>[15]</sup> Ruthenium oxo complexes are well-known to be active oxidants for alkene epoxidation and alkane hydroxylation.<sup>[16–19]</sup> Previously, we reported the stoichiometric oxidation of alkenes by *cis*- $[(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)\text{Ru}^{\text{VI}}\text{O}_2]\text{ClO}_4$  ( $\text{Me}_3\text{tacn} = N,N,N'$ -trimethyl-1,4,7-triazacyclononane) in aqueous *tert*-butanol to give the *cis*-1,2-diol in moderate to good yields.<sup>[20]</sup> We also mentioned that  $[\text{Ru}(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)_2(\text{OH}_2)]\text{CF}_3\text{CO}_2$  catalyzed the oxidation of cyclooctene to *cis*-1,2-cyclooctanediol and cyclooctene oxide in 50 and 42% yield, respectively, by using  $\text{H}_2\text{O}_2$  as a terminal oxidant, but only one example was reported.<sup>[20]</sup> Herein we report an environmentally friendly protocol for the *cis*-dihydroxylation of various unfunctionalized alkenes (14 examples) by using  $[\text{Ru}(\text{Me}_3\text{tacn})\text{Cl}_3]$  (**1**) as catalyst and  $\text{H}_2\text{O}_2$  as the terminal oxidant in the presence of  $\text{Al}_2\text{O}_3$  and  $\text{NaCl}$  additives. In a one-pot reaction, 128 g of *cis*-1,2-cyclooctanediol (92% yield) and 119 g of *cis*-1,2-cycloheptanediol (90% yield) were easily obtained from cyclooctene and cycloheptene, respectively, by using the “**1**+ $\text{H}_2\text{O}_2$ + $\text{Al}_2\text{O}_3$ + $\text{NaCl}$ ” protocol.

## Results and Discussion

### Synthesis and Characterization

The structures of the  $[\text{Ru}(\text{Me}_3\text{tacn})(\text{L})\text{X}]^+$  complexes **3a–d** ( $\text{L} = \text{acetylacetonato}$  (acac), hexafluoroacetylacetonato (hfacac), or 1,5-diphenylacetylacetonato ( $\text{Ph}_2\text{acac}$ );  $\text{X} = \text{Cl}$  or  $\text{CF}_3\text{CO}_2$ ) are depicted in Scheme 1.  $[\text{Ru}(\text{Me}_3\text{tacn})\text{Cl}_3]$ <sup>[21]</sup> (**1**) and  $[\text{Ru}(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)_2(\text{OH}_2)]\text{CF}_3\text{CO}_2$ <sup>[20]</sup> (**2**) were synthesized according to literature methods. Complexes **3a–c**



	X	Y	n		R	X
<b>1</b>	Cl	Cl	0	<b>3a</b>	CF <sub>3</sub>	Cl
<b>2</b>	CF <sub>3</sub> CO <sub>2</sub>	OH <sub>2</sub>	1	<b>3b</b>	CH <sub>3</sub>	Cl
				<b>3c</b>	Ph	Cl
				<b>3d</b>	CH <sub>3</sub>	CF <sub>3</sub> CO <sub>2</sub>

Scheme 1. Ruthenium catalysts **1–3**.

were prepared by the reaction of **1** (0.79 mmol) with an excess of the acetylacetonate ligands (2 mmol) in water for 72 h, followed by the addition of  $\text{NaClO}_4$  to afford the perchlorate salts in 60–80% yield. Likewise, treatment of **2** with excess acetylacetonate followed by the addition of  $\text{NaClO}_4$  gave **3d** in 75% yield. All the new complexes **3a–d** were characterized by UV/Vis and IR spectroscopy as well as FAB mass spectrometry.

The UV/Vis absorption spectra of **3a–d** in aqueous solution show two intense absorption peaks with  $\lambda_{\text{max}}$  at 261–299 and 322–386 nm. These spectral data are similar to that of  $[\text{Ru}^{\text{III}}(\text{Me}_3\text{tacn})(\text{acac})(\text{OH})]\text{PF}_6$ , which displays absorption peaks at 275 and 355 nm in acetonitrile.<sup>[22]</sup> The IR spectra of **3a–d** show intense absorption bands at approximately  $1550\text{ cm}^{-1}$ , which are assigned to  $\nu_{\text{C=O}}$  of the coordinated acetylacetonate ligand. The FAB mass spectra of **3a–d** show prominent peaks at  $m/z = 515, 407, 531,$  and  $485$ , which correspond to the  $[\text{Ru}^{\text{III}}(\text{Me}_3\text{tacn})(\text{hfacac})\text{Cl}]^+$  (**3a**),  $[\text{Ru}^{\text{III}}(\text{Me}_3\text{tacn})(\text{acac})\text{Cl}]^+$  (**3b**),  $[\text{Ru}^{\text{III}}(\text{Me}_3\text{tacn})(\text{Ph}_2\text{acac})\text{Cl}]^+$  (**3c**), and  $[\text{Ru}^{\text{III}}(\text{Me}_3\text{tacn})(\text{acac})\text{CF}_3\text{CO}_2]^+$  (**3d**) ions, respectively.

The structures of **3a**· $\text{ClO}_4$  and **3d**· $\text{ClO}_4$  were determined by X-ray crystallography. Perspective drawings of the complex cations are depicted in Figure 1. The crystal data and structure refinements are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

As shown in Figure 1, the  $\text{Me}_3\text{tacn}$  ligand in **3a** and **3d** is facially coordinated to the ruthenium atom, with the other auxiliary ligands being bidentate acetylacetonate and  $\eta^1$ -bound trifluoroacetate or  $\text{Cl}^-$ . The Ru–O(1) and Ru–O(2) bond lengths of **3a** and **3d** are virtually the same (**3a**: 2.030(3) and 2.029(3) Å; **3d**: 2.013(4) and 2.014(4) Å, respectively). These distances are comparable to the corresponding values for  $[\text{Ru}^{\text{III}}(\text{Me}_3\text{tacn})(\text{acac})(\text{OH})]\text{PF}_6$  (2.029(5) Å)<sup>[22]</sup> and other  $\text{Ru}^{\text{III}}$  acac complexes ( $[\text{Ru}^{\text{III}}(\text{acac})_2\text{Cl}_2]^-$ : 2.011(3) and 2.013(3) Å,<sup>[23a]</sup>  $[\text{Ru}(\text{acac})_2(\text{ProH}_2)]$ : 1.999(2) and 2.003(2) Å (Pro = proline),<sup>[23b]</sup>  $[\text{Ru}(\text{acac})_2(\text{NMelle})]$ : 2.010(2) and 2.003(2) Å (NMelle = *N*-methyl-*L*-isoleucine)<sup>[23b]</sup>). The Ru–Cl(1) bond length of 2.349(1) Å is close to the corresponding bond lengths found in *cis*- $[\text{Ru}^{\text{III}}(\text{Tet-Me}_6)\text{Cl}_2]\text{ClO}_4$  (2.343(4) and 2.346(4) Å; Tet-Me<sub>6</sub> = *N,N,N',N'*-tetramethyl-3,6-diazaoctane-1,8-diamine)<sup>[24]</sup> and *cis*- $[\text{Ru}^{\text{III}}(14\text{aneN}_4)\text{Cl}_2]\text{Cl}$  (2.369(1) and 2.373(1) Å; 14aneN<sub>4</sub> = 1,4,8,11-tetraazacyclotetradecane).<sup>[25]</sup>

### Ruthenium-Catalyzed Alkene *cis*-Dihydroxylation

In the initial experiments, the catalytic activities of various ruthenium complexes in the oxidation of cycloheptene with aqueous  $\text{H}_2\text{O}_2$  as the terminal oxidant were examined (Table 3). Generally, aqueous  $\text{H}_2\text{O}_2$  (11 mmol, 17.5%) was slowly added over a period of 6 h to an aqueous solution of *tert*-butanol containing the alkene (5 mmol) and catalyst (1 mol %) at  $60^\circ\text{C}$ , and the reaction was allowed to proceed for a further 8 h. The yields of the corresponding *cis/trans*-diol product were determined based on  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data (*cis*-1,2-cycloheptanediol:  $\delta_{\text{H}} = 3.85$  ppm

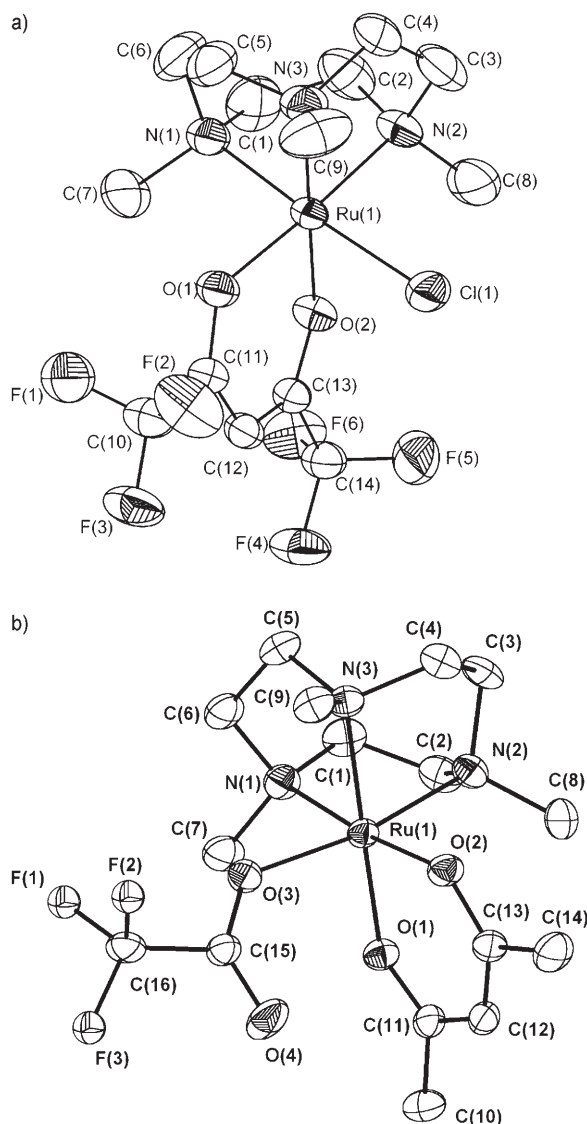


Figure 1. ORTEP drawing of the structures of a) **[3a]<sup>+</sup>** and b) **[3d]<sup>+</sup>**. Thermal ellipsoids drawn at the 30% probability level.

(d,  $J=9$  Hz, 2H),  $\delta_{\text{C}}=73.8$  ppm; *trans*-1,2-cycloheptanediol:  $\delta_{\text{H}}=3.42$  ppm (d,  $J=7.5$  Hz, 2H),  $\delta_{\text{C}}=77.9$  ppm). Without optimization of the reaction conditions, an excellent yield for *cis*-1,2-cycloheptanediol (91%) was obtained, together with a small amount of *trans*-cycloheptane-1,2-diol (5%), when 1 mol% of **1** was used as catalyst (Table 3, entry 1). Our earlier work showed that **2** can catalyze alcohol oxidation<sup>[26]</sup> and C=C bond-cleavage reactions.<sup>[3a]</sup> However, a mixture of *cis*- and *trans*-diols was obtained under the reaction conditions employed in this work (Table 3, entry 3). Interestingly, **3a–d**, which contain a chelating acetylacetonato ligand, also catalyzed the dihydroxylation of cycloheptene to give the *cis*-diol product in 60–80% yield (Table 3, entries 4–7). Previous studies of the stoichiometric oxidation of alkenes by *cis*-[(Me<sub>3</sub>tacn)(CF<sub>3</sub>CO<sub>2</sub>)Ru<sup>VI</sup>O<sub>2</sub>]<sup>+</sup> showed that the *cis*-dioxoruthenium moiety reacts with the C=C bond through a concerted [3+2] cycloaddition pathway.<sup>[20]</sup> Que

Table 1. Crystallographic data of **3a**·ClO<sub>4</sub> and **3d**·ClO<sub>4</sub>.

	<b>3a</b> ·ClO <sub>4</sub>	<b>3d</b> ·ClO <sub>4</sub>
Formula	C <sub>14</sub> H <sub>22</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>3</sub> O <sub>8</sub> Ru	C <sub>16</sub> H <sub>26</sub> ClF <sub>3</sub> N <sub>3</sub> O <sub>8</sub> Ru
$M_r$	615.32	584.94
Crystal symmetry	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$ (No. 2)
$a$ [Å]	13.187(3)	8.509(5)
$b$ [Å]	10.504(2)	17.749(5)
$c$ [Å]	16.929(3)	17.787(5)
$\alpha$ [°]	90	62.680(5)
$\beta$ [°]	103.36(3)	76.530(5)
$\gamma$ [°]	90	87.340(5)
$V$ [Å <sup>3</sup> ]	2281.5(8)	2315.3(16)
$Z$	4	4
Diffractometer	MAR	MAR
$D_c$ [g cm <sup>-3</sup> ]	1.791	1.678
No. of collected reflections	16323	10314
No. of reflections used	4082	7024
No. of parameters	291	572
$\mu$ (MoK $\alpha$ ) [mm <sup>-1</sup> ]	1.005	0.863
$F(000)$	1232	1192
$R_1$ <sup>[a]</sup>	0.045	0.080
$wR_2$ <sup>[a]</sup>	0.133	0.15
Goodness-of-fit	1.058	0.99

[a]  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$ , in which  $w = 4F_o^2 / \sigma^2(F_o^2)$ .

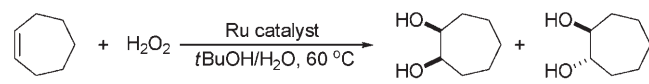
Table 2. Selected bond lengths (Å) and angles (°) for **3a**·ClO<sub>4</sub> and **3d**·ClO<sub>4</sub>.

	<b>3a</b> ·ClO <sub>4</sub>	<b>3d</b> ·ClO <sub>4</sub>
Ru–O(1)	2.030(3)	2.013(4)
Ru–O(2)	2.029(3)	2.014(4)
Ru–Cl(1)	2.349(1)	2.068(5) <sup>[a]</sup>
Ru–N(1)	2.102(4)	2.104(5)
Ru–N(2)	2.100(4)	2.089(6)
Ru–N(3)	2.086(4)	2.112(5)
O(1)–C(11)	1.280(5)	1.288(8)
O(2)–C(13)	1.264(5)	1.282(8)
C(11)–C(12)	1.379(6)	1.406(8)
C(12)–C(13)	1.391(6)	1.382(8)
C(13)–C(14)	1.516(6)	1.506(9)
O(1)–Ru–O(2)	90.3(1)	91.5(2)
Cl(1)–Ru–N(1)	176.8(1)	170.5(2) <sup>[b]</sup>
O(2)–Ru–N(3)	176.5(2)	174.8(2)
O(1)–Ru–N(2)	176.7(1)	176.2(2)
O(1)–C(11)–C(12)	128.5(4)	125.4(6)
O(2)–C(13)–C(12)	128.4(4)	126.2(6)
C(13)–C(12)–C(11)	123.0(4)	126.1(6)

[a] Ru–O(3). [b] O(3)–Ru–N(1).

and co-workers also suggested that at least two *cis*-labile sites are needed for the iron-catalyzed alkene *cis*-dihydroxylation by H<sub>2</sub>O<sub>2</sub>.<sup>[6]</sup> Thus, it is possible that partial dissociation of the bidentate acac ligand in **3a–d** could occur during the catalytic reactions. Monodentate-oxygen-bound diketonate metal complexes are known in the literature.<sup>[27]</sup>

We also examined other ruthenium(III) complexes that bear *cis*-coordinated chloride ligands, including K<sub>2</sub>[RuCl<sub>5</sub>(H<sub>2</sub>O)], *cis*-[Ru(Tet-Me<sub>6</sub>)Cl<sub>2</sub>ClO<sub>4</sub>], *cis*-[Ru(pyxn)Cl<sub>2</sub>ClO<sub>4</sub>] (pyxn = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)cyclohexane-1,2-diamine), [Ru(terpy)Cl<sub>3</sub>] (terpy = 2,2':6',2''-terpyridine), and RuCl<sub>3</sub>·*x*H<sub>2</sub>O, for their catalytic activities toward

Table 3. Catalytic alkene *cis*-dihydroxylation.<sup>[a]</sup>


Entry	Catalyst	Conv. [%]	Yield [%] <sup>[b]</sup>	
			<i>cis</i> -Diol	<i>trans</i> -Diol
1	<b>1</b>	100	91	5
2 <sup>[c]</sup>	<b>1</b>	100	44	50
3	<b>2</b>	100	62	30
4	<b>3a</b>	100	83	10
5	<b>3b</b>	100	73	25
6	<b>3c</b>	100	72	26
7	<b>3d</b>	100	62	30
8	K <sub>2</sub> [RuCl <sub>5</sub> (H <sub>2</sub> O)]	<1	n.d.	n.d.
9	<i>cis</i> -[Ru(Tet-Me <sub>6</sub> )Cl <sub>2</sub> ]ClO <sub>4</sub>	<1	n.d.	n.d.
10	<i>cis</i> -[Ru(pyxn)Cl <sub>2</sub> ]ClO <sub>4</sub>	<1	n.d.	n.d.
11	[Ru(terpy)Cl <sub>3</sub> ]	<1 <sup>[d]</sup>	n.d.	n.d.
12	RuCl <sub>3</sub> ·xH <sub>2</sub> O	<1	n.d.	n.d.

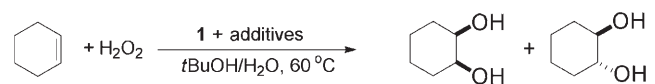
[a] Reaction conditions: cycloheptene (5 mmol), Ru catalyst (50 μmol), aqueous H<sub>2</sub>O<sub>2</sub> (11 mmol), *tert*-butanol/H<sub>2</sub>O = 6 mL:3 mL, 60 °C, 14 h, unless otherwise stated. [b] Yield of isolated product based on conversion. [c] Cyclohexene (5 mmol) was used. [d] Trace amount of cycloheptene oxide was detected. n.d. = not detected.

alkene *cis*-dihydroxylation using with H<sub>2</sub>O<sub>2</sub> under the same reaction conditions (Table 3, entries 8–12). However, all these ruthenium catalysts were inactive, and no diol products were detected. In the case of [Ru(terpy)Cl<sub>3</sub>], only a trace amount of cycloheptene oxide was detected.

#### Effects of Al<sub>2</sub>O<sub>3</sub> and Chloride

As shown in Table 3, dihydroxylation of cyclohexene catalyzed by **1** is nonselective, as an almost 1:1 mixture of *cis/trans*-diols was obtained (Table 3, entry 2). We attempted to optimize the reaction conditions by examining several conditions with cyclohexene as a model substrate, H<sub>2</sub>O<sub>2</sub> as the terminal oxidant, and **1** as a catalyst in aqueous *tert*-butanol. The results are depicted in Table 4. The addition of 5 mmol of basic Al<sub>2</sub>O<sub>3</sub> enhanced the *cis*-diol yield to 65% and improved the *cis/trans* ratio to 2:1 (Table 4, entry 2). No effect was observed when 1 mmol of basic alumina was used (Table 4, entry 1). A further increase in the amount of basic alumina to 10 mmol had a deleterious effect as the substrate conversion dropped dramatically to 15% (Table 4, entry 3). The use of acidic and neutral Al<sub>2</sub>O<sub>3</sub> did not improve the selectivity toward the *cis*-diol (Table 4, entries 4 and 5). At this moment, the reason for the improvement is not clear; however, the basic Al<sub>2</sub>O<sub>3</sub> became pale yellow during the reaction, which indicates that some ruthenium complexes were grafted onto the Al<sub>2</sub>O<sub>3</sub> surface.

We found that the addition of 1 mmol of NaCl and 5 mmol of Al<sub>2</sub>O<sub>3</sub> to the **1**-catalyzed alkene dihydroxylation further improved the yield of the *cis*-diol to 75% and increased the product *cis/trans* ratio to 3.9:1 (Table 4, entry 6). A similar *cis/trans* ratio (4:1) was obtained when 2 mol of NaCl was used, but the substrate conversion decreased to 20% (Table 4, entry 7). The use of KCl gave similar selectivity and substrate conversion (Table 4, entry 8). Replacement

Table 4. Effect of additives on **1**-catalyzed alkene *cis*-dihydroxylation.<sup>[a]</sup>


Entry	Additive(s) [(mmol)]	Conv. [%]	Yield [%] <sup>[b]</sup>	
			<i>cis</i> -Diol	<i>trans</i> -Diol
1	basic alumina (1)	100	43	50
2	basic alumina (5)	100	65	30
3	basic alumina (10)	15	68	26
4	acidic alumina (5)	100	33	62
5	neutral alumina (5)	100	43	52
6	basic alumina (5)+NaCl (1)	100	78	20
7	basic alumina (5)+NaCl (2)	20	80	20
8	basic alumina (5)+KCl (1)	100	75	21
9 <sup>[c]</sup>	basic alumina (5)+NaCl (1)	15	20	75
10 <sup>[d]</sup>	basic alumina (5)+NaCl (1)	30	28	68
11 <sup>[e]</sup>	basic alumina (5)+NaCl (1)	13	n.d.	88

[a] Reaction conditions: cyclohexene (5 mmol), **1** (50 μmol), aqueous H<sub>2</sub>O<sub>2</sub> (11 mmol), *tert*-butanol/H<sub>2</sub>O = 6 mL:3 mL, 60 °C, 14 h, unless otherwise stated. [b] Yield of isolated product based on conversion. [c] Urea/H<sub>2</sub>O<sub>2</sub> (11 mmol). [d] TBHP (11 mmol). [e] Oxone (11 mmol).

of aqueous H<sub>2</sub>O<sub>2</sub> by urea/H<sub>2</sub>O<sub>2</sub> or *tert*-butyl hydroperoxide (TBHP) led to decreased substrate conversion and *cis*-diol selectivity (Table 4, entries 9 and 10). When oxone was used as the oxidant, only the *trans*-diol was obtained (Table 4, entry 11).

#### Catalytic *cis*-Dihydroxylation of Various Alkenes

Using the optimized conditions (Table 4, entry 6), we investigated the substrate scope and limitations of the “**1**+H<sub>2</sub>O<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+NaCl” protocol (Table 5). Cyclic alkenes were efficiently converted into their corresponding *cis*-diols in good to excellent yield (Table 5, entries 1–7). Oxidation of cyclooctene, cycloheptene, and cyclopentene afforded the corresponding *cis*-diols as single products in 93–96% yield with complete substrate conversion and no *trans*-diols being detected by NMR spectroscopic analysis of the reaction mixture (Table 5, entries 1–3). With styrenes, the **1**-catalyzed dihydroxylation gave the corresponding *cis*-diol in 77–91% yield without C=C bond-cleavage products being detected (Table 5, entries 8–11). Likewise, terminal and internal alkenes were oxidized to the corresponding *cis*-diols in up to 96% yield with substrate conversions of greater than 60% (Table 5, entries 12–14). Notably, in the literature, the RuCl<sub>3</sub>·xH<sub>2</sub>O/NaIO<sub>4</sub> protocol gave only moderate to good yields of *cis*-diols (58–70%) when unfunctionalized alkenes such as 1-decene, cyclohexene, cyclooctene, and  $\alpha$ -methyl styrene were used as substrates.<sup>[13c]</sup>

Good yields of *cis*-diols (based on conversion) were also obtained when allylic alcohols and acetyl-protected allylic alcohols were used as substrates (Table 5, entries 15–18). The protocol was ineffective for ethyl cinnamate, which contains an electron-deficient C=C bond, and the substrate was recovered completely after the reaction, in contrast to the case when the RuCl<sub>3</sub>·xH<sub>2</sub>O/NaIO<sub>4</sub> protocol was employed.<sup>[113]</sup> On the other hand, stoichiometric oxidation of ethyl cinnamate

Table 5. Catalytic alkene *cis*-dihydroxylation with the “**1**+H<sub>2</sub>O<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+NaCl” protocol.<sup>[a]</sup>

Entry	Alkenes	Conv. [%]	Yield of <i>cis</i> -diol <sup>[b,c]</sup> [%]
1		100	93 (n.d.) <sup>[d]</sup>
2		100	96 (n.d.) <sup>[d]</sup>
3		100	95 (n.d.) <sup>[d]</sup>
4		100	78 (20)
5		100	59 (38)
6		100	72 (23)
7		100	68 (28)
8		100	91
9		100	77 (17)
10		100	89 (9)
11		100	89
12		80	92
13		83	90
14		60	96 (n.d.)
15		43	63 (28) <sup>[d]</sup>
16		40	58 (32) <sup>[d]</sup>
17		43	82 (15)
18		44	85 (n.d.)

[a] Reaction conditions: alkene (5 mmol), **1** (50 μmol), basic Al<sub>2</sub>O<sub>3</sub> (5 mmol), NaCl (1 mmol), aqueous H<sub>2</sub>O<sub>2</sub> (17.5%, 11 mmol), *tert*-butanol/H<sub>2</sub>O=6 mL:3 mL, 60 °C, 14 h. [b] Yield of isolated product based on conversion. [c] Yield of *trans*-diol is shown in parentheses. [d] The corresponding aldehydes were obtained instead of the *trans*-diol.

mate by *cis*-[(Me<sub>3</sub>tacn)(CF<sub>3</sub>CO<sub>2</sub>)Ru<sup>VI</sup>O<sub>2</sub>]<sup>+</sup> was reported to give (±)-*threo*-ethyl 2,3-dihydroxy-3-phenylpropanoate in 72% yield.<sup>[20]</sup>

### Scaled-Up Reactions

Previously, we reported that the **2**-catalyzed oxidation of cyclohexene to adipic acid by H<sub>2</sub>O<sub>2</sub> could be scaled up to the 1-mol scale in a one-pot process.<sup>[3a]</sup> We also examined the feasibility of scaling up the “**1**+H<sub>2</sub>O<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+NaCl” protocol by using 1 mol of alkene substrate. Dropwise addition over a period of 6 h of 17.5% aqueous H<sub>2</sub>O<sub>2</sub> (1.1 mol) to aqueous *tert*-butanol (1800 mL, *tert*-butanol/H<sub>2</sub>O=2:1) containing cycloheptene (96.2 g, 1 mol), **1** (3.8 g, 0.01 mol), Al<sub>2</sub>O<sub>3</sub> (101.9 g, 1 mol), and NaCl (11.7 g, 0.2 mol) at 60 °C gave a homogeneous yellow solution. After the reaction mixture was stirred for a further 8 h at 60 °C, 119 g of *cis*-1,2-cycloheptanediol was isolated as a single product, corresponding to 91% yield. Under the same conditions, cyclooctene (110.2 g, 1 mol) was oxidized to *cis*-1,2-cyclooctanediol (128 g) in 92% yield. We also found that, for this scaled-up oxidation, *cis*-1,2-cycloheptanediol was obtained in 89% yield (115.7 g) from the **1**-catalyzed oxidation of cycloheptene by H<sub>2</sub>O<sub>2</sub> (1.1 mol) even in the absence of NaCl and

Al<sub>2</sub>O<sub>3</sub> as additives, and the *cis*-/*trans*-1,2-cycloheptanediol ratio was 90:5 as determined by <sup>1</sup>H NMR spectroscopy.

### Mechanistic Aspects

To obtain information on the reaction mechanism, competitive oxidation of *para*-substituted styrenes (*p*-Y-C<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub>; Y=Me, H, Cl, Br, or CF<sub>3</sub>) with the “**1**+H<sub>2</sub>O<sub>2</sub>+NaCl+Al<sub>2</sub>O<sub>3</sub>” protocol was studied by gas chromatography (see Experimental Section). Figure 2 shows the plot of

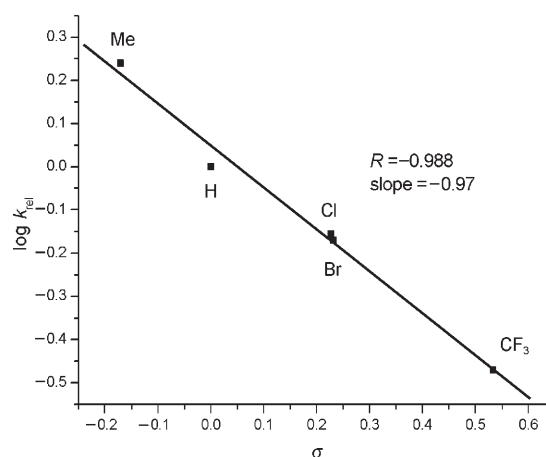


Figure 2. Hammett plot ( $\log k_{\text{rel}}$  vs.  $\sigma$ ) for the **1**-catalyzed oxidation of *para*-substituted styrenes by H<sub>2</sub>O<sub>2</sub>.

$\log k_{\text{rel}}$  ( $k_{\text{rel}} = k(p\text{-Y-C}_6\text{H}_4\text{CH=CH}_2)/k(\text{C}_6\text{H}_5\text{CH=CH}_2)$ ) versus the substituent constant  $\sigma$ , in which a linear correlation is observed with gradient  $\rho^+ = -0.97$ . Such a small negative value indicates that a small positive charge is present on the  $\alpha$ -carbon atom in the transition state. This  $\rho^+$  value is comparable to that of the stoichiometric oxidation of styrenes by *cis*-[(Me<sub>3</sub>tacn)(CF<sub>3</sub>CO<sub>2</sub>)Ru<sup>VI</sup>O<sub>2</sub>]<sup>+</sup> ( $\rho^+ = -1.05$ ,  $R = 0.95$ ),<sup>[20]</sup> but is very different from those of reactions that involve the formation of carbocations, for example, bromination ( $\rho^+ = -4.1$ )<sup>[28]</sup> and hydration ( $\rho^+ = -3.5$ )<sup>[29]</sup> of alkenes.

Slow addition of H<sub>2</sub>O<sub>2</sub> (11 mmol) to a reaction mixture containing cyclohexene oxide (5 mmol), **1** (1 mol %), Al<sub>2</sub>O<sub>3</sub> (5 mmol), and NaCl (1 mmol) in aqueous *tert*-butanol at 60 °C gave the corresponding *trans*-diol in over 96% yield. This finding suggests that formation of the *cis*-diol through epoxidation followed by ring opening in the **1**-catalyzed *cis*-dihydroxylation of alkenes by aqueous H<sub>2</sub>O<sub>2</sub> is unlikely.

Recently, we reported that *cis*-[(Me<sub>3</sub>tacn)(CF<sub>3</sub>CO<sub>2</sub>)Ru<sup>VI</sup>O<sub>2</sub>]<sup>+</sup> reacts with alkenes by a [3+2] cycloaddition to give the corresponding Ru<sup>III</sup> cycloadducts, which eventually decompose to give the *cis*-diols and [(Me<sub>3</sub>tacn)<sub>2</sub>Ru<sup>III</sup>(μ-O)(μ-O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>.<sup>[20]</sup> In this work, we monitored the reaction of **1** with H<sub>2</sub>O<sub>2</sub> in the absence/presence of organic substrates by using ESI-MS. When H<sub>2</sub>O<sub>2</sub> (11 mmol) was added to aqueous *tert*-butanol (*tert*-butanol/H<sub>2</sub>O=2:1 v/v) containing **1** (5 mM) at 60 °C/room temperature, no oxygen was evolved over a period of 6 h, which sug-

gests that no decomposition of H<sub>2</sub>O<sub>2</sub> occurred. Aliquots of the reaction mixture before and after addition of H<sub>2</sub>O<sub>2</sub> were taken for MS analysis, but no significant difference in the ESI mass spectra was noted. Both spectra showed a prominent ion cluster peak at  $m/z = 361.0$  that could be attributed to  $[\text{Ru}(\text{Me}_3\text{tacn})\text{Cl}_2(\text{H}_2\text{O})]^+$ . Cluster peaks located at  $m/z = 343.1$ ,  $325.3$ , and  $307.1$  were assigned to  $[\text{Ru}(\text{Me}_3\text{tacn})\text{Cl}_2]^+$ ,  $[\text{Ru}(\text{Me}_3\text{tacn})(\text{OH})\text{Cl}]^+$ , and  $[\text{Ru}(\text{Me}_3\text{tacn})(\text{OH})_2]^+$ , respectively, thus revealing that aquoruthenium species of Me<sub>3</sub>tacn were present in the reaction mixture. No peaks arising from  $[(\text{Me}_3\text{tacn})\text{ClRu}^{\text{VI}}\text{O}_2]^+$  ( $m/z = 340$ ) were detected. Notably, addition of cyclooctene (5 mmol) to this reaction mixture gave a peak at  $m/z = 451.2$  after 0.5 h that matches the  $[(\text{Me}_3\text{tacn})\text{ClRu}^{\text{III}}\text{HO}_2(\text{C}_8\text{H}_{14})]^+$  formulation. After 6 h, the reaction mixture turned purple, and dimeric ruthenium species with relatively low abundance at  $m/z = 704.3$  (40%, formulated as  $[\text{Ru}_2(\text{Me}_3\text{tacn})_2\text{Cl}_4(\text{H}_2\text{O})]^+$ ) and  $684.3$  (15%, formulated as  $[\text{Ru}_2(\text{Me}_3\text{tacn})_2\text{Cl}_4]^+$ ) were detected. Similar observations were made for cycloheptene ( $m/z = 437.2$  corresponding to  $[(\text{Me}_3\text{tacn})\text{ClRu}^{\text{III}}\text{HO}_2(\text{C}_7\text{H}_{12})]^+$ ). However, attempts to detect oxoruthenium species in the reaction mixture were not successful, probably due to their high reactivity and instability, although H<sub>2</sub>O<sub>2</sub> is known to be an oxidant in the preparation of dioxoruthenium complexes such as *trans*- $[(14\text{-tmc})\text{Ru}^{\text{VI}}\text{O}_2]^{2+}$  [18b] (14-TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and *cis*- $[(\text{Tet-Me}_6)\text{Ru}^{\text{VI}}\text{O}_2]^{2+}$ . [24] Based on the Hammett correlation and the detection of cycloadducts  $[(\text{Me}_3\text{tacn})\text{ClRu}^{\text{III}}\text{HO}_2(\text{C}_8\text{H}_{14})]^+$  and  $[(\text{Me}_3\text{tacn})\text{ClRu}^{\text{III}}\text{HO}_2(\text{C}_7\text{H}_{12})]^+$  by ESI-MS analysis, we propose that the reaction between **1** and H<sub>2</sub>O<sub>2</sub> may generate a *cis*-dioxo-, *cis*-oxo(aquo)-, or *cis*-oxo-(hydroxy)ruthenium species, which reacts with alkenes by cycloaddition.

## Conclusions

In summary, an environmentally friendly protocol that adopts aqueous H<sub>2</sub>O<sub>2</sub> as a terminal oxidant and  $[\text{Ru}(\text{Me}_3\text{tacn})\text{Cl}_3]$  (**1**) as catalyst for the *cis*-dihydroxylation of alkenes has been presented. Unfunctionalized alkenes, including cycloalkenes, aliphatic alkenes, and styrenes, were selectively oxidized to their corresponding *cis*-diols as the major products. As  $[\text{Ru}(\text{Me}_3\text{tacn})\text{Cl}_3]$  is a stable complex that can be easily prepared by the reaction of  $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$  (DMSO = dimethyl sulfoxide) with Me<sub>3</sub>tacn in 60% yield, [21] we anticipate that the “[Ru(Me<sub>3</sub>tacn)Cl<sub>3</sub>] + H<sub>2</sub>O<sub>2</sub> + additives” protocol could be developed into a useful method for the practical synthesis of *cis*-diols from unfunctionalized alkenes.

## Experimental Section

### General

All solvents and hydrocarbon substrates were purified by standard procedures. [30] Me<sub>3</sub>tacn, [21]  $[\text{Ru}(\text{Me}_3\text{tacn})\text{Cl}_3]$  (**1**), [21]  $[\text{Ru}(\text{Me}_3\text{tacn})(\text{CF}_3\text{CO}_2)_2$

$(\text{OH}_2)]\text{CF}_3\text{CO}_2$  (**2**), [26] *cis*- $[\text{Ru}(\text{Tet-Me}_6)\text{Cl}_2]\text{ClO}_4$ , [19d] *cis*- $[\text{Ru}(\text{pyxn})\text{Cl}_2]\text{ClO}_4$ , [31] and  $[\text{Ru}(\text{terpy})\text{Cl}_3]$  [32] were prepared according to previously published procedures. RuCl<sub>3</sub>·xH<sub>2</sub>O (Aldrich), K<sub>2</sub>[RuCl<sub>5</sub>(H<sub>2</sub>O)] (Aldrich), hexafluoroacetylacetone (Aldrich), 1,3-diphenyl-1,3-propanedione (Aldrich), silver trifluoromethanesulfonate (99+%, Acros), and trifluoromethanesulfonic acid (Acros) were used as received. Dropwise addition of aqueous H<sub>2</sub>O<sub>2</sub> was carried out with a syringe pump.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker spectrometer (<sup>1</sup>H: 400 MHz; <sup>13</sup>C: 100 MHz). Chemical shifts (δ) are given in parts per million relative to tetramethylsilane (δ = 0 ppm). Gas chromatography was performed on a Hewlett-Packard model HP 5890 Series II chromatograph equipped with an HP 17 column (cross-linked 50% phenyl methyl silicone, 0.2 μm film thickness) and equipped with a flame ionization detector. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. Electrospray ionization mass spectra were obtained with a Finnigan MAT LCQ spectrometer. The sheath (compressed air) and auxiliary (nitrogen) gases were operated at 100 and 40 psi, respectively. Typical operating voltages were 3.0 V for capillary voltage and 3.5 kV for spray voltage. All spectra were collected at a capillary temperature of 180 °C. Elemental analysis was performed by the Institute of Chemistry of the Chinese Academy of Sciences.

All X-ray diffraction data were collected on a MAR diffractometer with a 300-mm image plate detector with graphite-monochromated MoK<sub>α</sub> radiation (λ = 0.71073 Å) at 253 K. The images were interpreted and the intensities integrated by using the program DENZO. [33] The structures were solved by direct methods with the SIR-97 program on a PC. [34] Structure refinements were performed by full-matrix least squares with the program SHELXL-97 [35] on a PC. CCDC-656309 (**3d**) and -656310 (**3a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data\_request.cif.

### Syntheses

**Warning!** Perchlorate salts of complexes with organic ligands are potentially explosive and should be handled in small quantities with great care. General procedure for the synthesis of **3a-c**: Compound **1** (0.79 mmol, 0.3 g) HL (L = acac, hfacac, or Phacac; 2 mmol), and distilled water (10 mL) was added to a 100-mL round-bottomed flask. Continuous stirring of the mixture for 72 h at ambient temperature gave a clear red solution. Any insoluble solid was removed by filtration, and the filtrate was washed with diethyl ether (3 × 10 mL) to remove any unreacted organic ligands. After addition of saturated aqueous NaClO<sub>4</sub> (5 mL), the solution was kept in a refrigerator (4 °C) for 36 h to obtain a red solid. The solid was collected on a frit and recrystallized in acetone/diethyl ether.

**3a**-ClO<sub>4</sub>: Yield: 60%. UV/Vis (H<sub>2</sub>O): λ<sub>max</sub> (ε<sub>max</sub>) = 299 (5930), 386 (3200), 495 nm (1250 M<sup>-1</sup> cm<sup>-1</sup>); IR (KBr): ν̄ = 1581, 1467 cm<sup>-1</sup>; MS (FAB):  $m/z = 515$  [M]<sup>+</sup>; elemental analysis: calcd (%) for C<sub>14</sub>H<sub>22</sub>Cl<sub>2</sub>F<sub>6</sub>N<sub>5</sub>O<sub>6</sub>Ru: C 27.37, H 3.61, N 6.84; found: C 27.72, H 3.69, N 6.64.

**3b**-ClO<sub>4</sub>: Yield: 73%. UV/Vis (H<sub>2</sub>O): λ<sub>max</sub> (ε<sub>max</sub>) = 284 (6100), 324 (4200), 565 nm (1150 M<sup>-1</sup> cm<sup>-1</sup>); IR (KBr): ν̄ = 1519, 1459 cm<sup>-1</sup>; MS (FAB):  $m/z = 407$  [M]<sup>+</sup>; elemental analysis: calcd (%) for C<sub>14</sub>H<sub>22</sub>Cl<sub>2</sub>F<sub>6</sub>N<sub>5</sub>O<sub>6</sub>Ru: C 27.37, H 3.61, N 6.84; found: C 26.83, H 3.47, N 7.04.

**3c**-ClO<sub>4</sub>: Yield: 80%. UV/Vis (H<sub>2</sub>O): λ<sub>max</sub> (ε<sub>max</sub>): 261 (12600), 338 nm (19900 M<sup>-1</sup> cm<sup>-1</sup>); IR (KBr): ν̄ = 1553, 1482 cm<sup>-1</sup>; MS (FAB):  $m/z = 531$  [M]<sup>+</sup>; elemental analysis: calcd (%) for C<sub>24</sub>H<sub>32</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>6</sub>Ru: C 45.72, H 5.12, N 6.66; found: C 46.08, H 5.02, N 6.93.

**3d**-ClO<sub>4</sub>: Compound **2** (160 μmol, 0.1 g) was added to an aqueous solution (10 mL) of 2,4-pentanedione (2 mmol, 0.2 g), and the mixture was stirred overnight at room temperature to give a purple solution. Any insoluble solid was removed by filtration, and saturated aqueous NaClO<sub>4</sub> (4 mL) was added to the filtrate. The resultant mixture was kept in a refrigerator (4 °C) for 36 h, and the purple crystalline solid obtained was collected on a sintered glass funnel and washed with diethyl ether (50 mL). Yield: 75%. UV/Vis (H<sub>2</sub>O): λ<sub>max</sub> (ε<sub>max</sub>): 283 (3800), 322 (3050), 595 nm (700 M<sup>-1</sup> cm<sup>-1</sup>); IR (KBr): ν̄ = 1703, 1529, 1186 cm<sup>-1</sup>; MS (FAB):  $m/z = 485$  [M]<sup>+</sup>; elemental analysis: calcd (%) for C<sub>16</sub>H<sub>28</sub>ClF<sub>3</sub>N<sub>3</sub>O<sub>8</sub>Ru: C 32.91, H 4.83, N 7.20; found: C 33.21, H 4.73, N 6.89.

General procedure for catalytic organic oxidations by aqueous H<sub>2</sub>O<sub>2</sub>: A reaction mixture containing *tert*-butanol (6 mL), distilled water (3 mL), substrate (5 mmol), Al<sub>2</sub>O<sub>3</sub> (5 mmol), NaCl (1 mmol), and the ruthenium catalyst (50 μmol) was heated at 60 °C. Aqueous H<sub>2</sub>O<sub>2</sub> (11 mmol, 17.5%) was added over a period of 6 h. After the reaction mixture was stirred for a further 8 h, it was cooled in an iced salt bath, and the unreacted H<sub>2</sub>O<sub>2</sub> was removed by adding saturated aqueous sodium bisulfite (3 mL). After addition of the internal standard, the products were extracted with diethyl ether (5 × 20 mL), and the combined extracts were dried over anhydrous MgSO<sub>4</sub> and filtered. Aliquots were taken for product identification and quantification with GC or NMR spectroscopic analysis.

For the 1-mol-scale reaction, a mixture containing substrate (1 mol), **1** (0.01 mol), Al<sub>2</sub>O<sub>3</sub> (1 mol, 101.9 g), and NaCl (0.2 mol, 11.7 g) in *tert*-butanol (1200 mL) and distilled water (600 mL) was heated to 60 °C. Aqueous H<sub>2</sub>O<sub>2</sub> (17.5%, 213 mL) was then added over a period of 6 h, and the reaction mixture was stirred for a further 8 h. Unreacted H<sub>2</sub>O<sub>2</sub> was removed by adding saturated aqueous sodium bisulfite (100 mL). *tert*-Butanol was recycled by simple distillation at 83 °C, and water was further distilled out to give a viscous layer containing residual solvent and crude product. The product was extracted with diethyl ether (5 × 200 mL), and the combined extracts were dried over anhydrous MgSO<sub>4</sub> and filtered. The ethereal layer was evaporated to dryness by a rotary evaporator to give the corresponding diol product.

#### Determination of Relative Reactivities ( $k_{\text{rel}}$ ) in the Catalytic Oxidation of *para*-Substituted Styrenes

An aqueous solution of *tert*-butanol (*tert*-butanol/H<sub>2</sub>O = 6 mL:3 mL) containing styrene (2.5 mmol), the *para*-substituted styrene (2.5 mmol), 1,4-dichlorobenzene (0.5 mmol as the internal standard), Al<sub>2</sub>O<sub>3</sub> (5 mmol), NaCl (1 mmol), and **1** (50 μmol) was heated to (60 ± 1) °C with vigorous stirring. Aqueous H<sub>2</sub>O<sub>2</sub> (1.1 mmol) was added over a period of 1 h, and the reaction mixture was stirred for a further 8 h. The amounts of styrenes before and after the reaction were determined by GC. The relative reactivities were determined by [Eq. (1)]:

$$k_{\text{rel}} = k_{\text{V}}/k_{\text{H}} = \log(Y_{\text{f}}/Y_{\text{i}})/\log(H_{\text{f}}/H_{\text{i}}) \quad (1)$$

in which  $Y_{\text{f}}$  and  $Y_{\text{i}}$  are the final and initial quantities of the substituted styrenes, respectively, and  $H_{\text{f}}$  and  $H_{\text{i}}$  are the final and initial quantities of styrene, respectively.

### Acknowledgements

This work was supported by the Areas of Excellence Scheme established under the University Grants Committee of the Hong Kong Special Administrative Region, China (AoE/P-10/01), The University of Hong Kong (University Development Fund), and the Hong Kong Research Grants Council (HKU7009-06P and CityU 2/06C).

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Received: August 3, 2007  
Published online: November 5, 2007