

# Mechanistic Investigation of the Oxidation of Aromatic Alkenes by Monooxoruthenium(IV). Asymmetric Alkene Epoxidation by Chiral Monooxoruthenium(IV) Complexes

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Received April 21, 1998

The oxoruthenium(IV) complexes [Ru<sup>IV</sup>(terpy)(6,6'-Cl<sub>2</sub>-bpy)O](ClO<sub>4</sub>)<sub>2</sub> (**1a**; terpy = 2,2':6',2''-terpyridine; 6,6'-Cl<sub>2</sub>-bpy = 6,6'-dichloro-2,2'-bipyridine), [Ru<sup>IV</sup>(terpy)(tmeda)O](ClO<sub>4</sub>)<sub>2</sub> (**1b**; tmeda = *N,N,N,N*-tetramethylethylenediamine), [Ru<sup>IV</sup>(Cn)(bpy)O](ClO<sub>4</sub>)<sub>2</sub> (**1c**; Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane), and [Ru<sup>IV</sup>(PPz\*)(bpy)O](ClO<sub>4</sub>)<sub>2</sub> (**1d**; PPz\* = 2,6-bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methanoindazol-2-yl]pyridine) are effective for the epoxidation of aromatic alkenes in acetonitrile at ambient conditions. Their reactions with *cis*-alkenes such as *cis*- $\beta$ -methylstyrene and *cis*- $\beta$ -deuteriostyrene afford epoxides nonstereospecifically. The observation of the inverse secondary kinetic isotope effect for the  $\beta$ -d<sub>2</sub>-styrene oxidations [ $k_H/k_D = 0.87$  (**1b**), 0.86 (**1d**)], but not for  $\alpha$ -deuteriostyrene ( $k_H/k_D = 0.98$  for **1b** and **1d**), indicates that C–O bond formation is more advanced at the  $\beta$ -carbon atom than at the  $\alpha$  carbon, i.e., a stepwise mechanism. The second-order rate constants ( $k_2$ ) for the styrene oxidations are weakly dependent on the  $E^{\circ}$ (Ru<sup>IV/III</sup>) values of the oxoruthenium(IV) complexes, and both electron-withdrawing and -donating para substituents mildly accelerate the oxidation reaction of styrene. These findings discount strongly the intermediaries of an alkene-derived cation radical and a carbocation. A linear free-energy relationship between the second-order rate constants for the para-substituted styrene oxidations and the total substituent effect (TE) parameters has been established:  $\rho_{TE}^* = +0.43$  ( $R = 0.99$ ) for **1b**, +0.50 ( $R = 0.98$ ) for **1c**, and +0.37 ( $R = 0.99$ ) for **1d** (Wu, Y.-D.; Wong, C.-L.; Chan, K. W.; Ji, G.-Z.; Jiang, X.-K. *J. Org. Chem.* **1996**, *61*, 746). This suggests that the oxidation of aromatic alkenes by oxoruthenium(IV) complexes should proceed via the rate-limiting formation of a benzylic radical intermediate. Oxidation of styrene and *cis*- and *trans*- $\beta$ -methylstyrenes by the chiral oxoruthenium(IV) complex **1d** attains moderate enantioselectivities, in which the production of *cis*-epoxide is more enantioselective than the *trans* counterpart. The ligand dissymmetry of PPz\* together with the bipyridine ligand create a "chiral pocket" around the Ru<sup>IV</sup>=O moiety, leading to enantiofacial discrimination through nonbonding interaction. Because the acyclic benzylic radical intermediate would undergo *cis*–*trans* isomerization before the second C–O bond formation, the overall product enantioselectivity (% ee<sub>obs</sub>) cannot be determined exclusively by facial selectivity (ee<sub>facial</sub>) of the first irreversible C–O bond formation step. The extent of the isomerization, measured by the *cis*–*trans*-epoxide selectivity or diastereoselectivity of epoxide ring closure, is an important element in controlling the enantiomeric excess of the epoxides.

## Introduction

Catalytic enantioselective epoxidation of unfunctionalized alkenes, in which chiral recognition is based on nonbonding interaction between prochiral alkenes and chiral catalysts, has been receiving widespread attention.<sup>1,2</sup> This process provides a direct transformation of simple prochiral alkenes to enantio-enriched epoxides that are extremely versatile synthetic intermediates for construction of complex organic molecules.<sup>3</sup> Understanding the various factors affecting the enantioselectivity of the reactions will facilitate rational design for better catalysts. In recent years, significant advances in enantioselective epoxidation of simple alkenes by applying the chiral Mn–Schiff base systems have been made.<sup>4</sup> In these Mn-catalyzed reactions, a reactive chiral oxomanganese(V) intermediate (Mn<sup>V</sup>=O) is postulated, though its characterization remains elusive<sup>5</sup> and the mechanistic

details are still controversial.<sup>6</sup> Indeed, well-characterized and reactive chiral terminal oxo–metal complexes (M=

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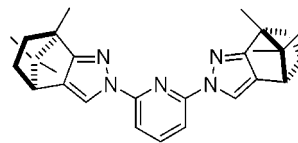
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O) capable of undergoing oxygen-atom transfer reactions to a C=C bond in an enantioselective manner are sparse in the literature.<sup>7</sup>

Studies by various groups have established the rich oxidation chemistry of oxoruthenium (Ru=O) complexes,<sup>8</sup> which are competent oxidants for organic oxidations. In particular, their reactions with alkenes are usually accompanied by large and negative entropies of activation.<sup>9</sup> Therefore, it is possible that the introduction of chiral ligands to the metal coordination sphere could result in enantioselective epoxidations.<sup>7f,h,10</sup> Following the work by Meyer and co-workers on the [Ru<sup>IV</sup>(bpy)<sub>2</sub>(py)O]<sup>2+</sup> complex (bpy = 2,2'-bipyridine),<sup>11</sup> we studied the structures and reactivities of some related monooxoruthenium(IV) complexes: [Ru<sup>IV</sup>(terpy)(6,6'-Cl<sub>2</sub>-bpy)O]<sup>2+</sup> (**1a**;<sup>9b</sup> terpy = 2,2':6,2''-terpyridine; 6,6'-Cl<sub>2</sub>-bpy = 6,6'-dichloro-2,2'-bipyridine), [Ru<sup>IV</sup>(terpy)(tmeda)O]<sup>2+</sup> (**1b**;<sup>12</sup> tmeda = *N,N,N,N*-tetramethylethylenediamine), and [Ru<sup>IV</sup>(Cn)(bpy)O]<sup>2+</sup> (**1c**;<sup>13</sup> Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane); these complexes can effect stereoselective alkene epoxidations. Recently, we communicated that the chiral oxoruthenium(IV) complex, [Ru<sup>IV</sup>(PPz\*)-(bpy)O]<sup>2+</sup> (**1d**; PPz\* = 2,6-bis[(4*S*,7*R*)-7,8,8-trimethyl-



(+)-PPz\* =  
(+)-2,6-bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methanoindazol-2-yl]pyridine

**Figure 1.** (+)-PPz\* = (+)-2,6-bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methanoindazol-2-yl]pyridine.

4,5,6,7-tetrahydro-4,7-methanoindazol-2-yl]pyridine (Figure 1), can undergo enantioselective epoxidation of styrene to give styrene oxide in 56% enantiomeric excess (ee).<sup>7f</sup> Herein are described the results of a mechanistic investigation on the oxidation of aromatic alkenes by this complex and its related Ru<sup>IV</sup>=O derivatives (**1a–d**), and the participation of a benzylic radical intermediate is proposed. For asymmetric epoxidations by these chiral oxoruthenium(IV) complexes, the % ee of the epoxides is not established at the first irreversible C–O bond formation step, but it is also dependent upon the extent of the *cis*–*trans* isomerization which has taken place in the benzylic radical intermediate before ring closure.

## Results and Discussion

**Product Analysis and Kinetic Studies.** In acetonitrile, the oxoruthenium(IV) complexes **1a–d** react with aryl alkenes to yield epoxides as the major product, along with some carbonyl compounds (Table 1 and Scheme 1). The [Ru<sup>II</sup>(L<sup>1</sup>)(L<sup>2</sup>)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> (**2**) complexes were isolated and characterized spectroscopically. A small amount of phenylacetaldehyde was also detected when styrene was used as the substrate (entry 2). In the absence of organic substrates, **1** slowly converted to **2** over a period of 24 h in an acetonitrile solution at room temperature. We found that the C=C bond cleavage product formation can be retarded by more thorough drying of the ruthenium oxidant; less than 1% benzaldehyde and greater than 95% epoxide were obtained for the oxidation of styrene by [Ru<sup>IV</sup>(Cn)(bpy)O](ClO<sub>4</sub>)<sub>2</sub>, which had been predried over P<sub>2</sub>O<sub>5</sub> in a vacuum. However, applying similar pretreatment to the other oxoruthenium(IV) complexes led to complex deterioration, poor epoxide yield, and poor chemoselectivity.

The oxidation reactions of *cis*- $\beta$ -methylstyrene with **1a–d** produced mixtures of *cis*- and *trans*-epoxides (*cis*:*trans* ratios from 2:1 to 5:1; entry 6). Stirring of pure *cis*- $\beta$ -deuteriostyrene oxide with [Ru<sup>II</sup>(L<sup>1</sup>)(L<sup>2</sup>)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> in acetonitrile at room temperature led to the full recovery of the starting *cis*-epoxide after 12 h, and no *trans*-epoxide was detected. This finding confirms that the *cis*–*trans* isomerization associated with the *cis*-alkene oxidations is not a consequence of the epoxide isomerization catalyzed by the ruthenium(II) product.<sup>14</sup>

Figure 2 depicts the UV–vis spectral trace for the reaction of styrene with **1d**, which is similar to the oxidation reactions of the other oxoruthenium(IV) complexes employed in this study. This shows an isosbestic point at 375 nm and the emergence of [Ru<sup>II</sup>(PPz\*)(bpy)(MeCN)]<sup>2+</sup> (**2d**) manifested by the gradual growth of its metal-to-ligand charge-transfer (MLCT) absorption band

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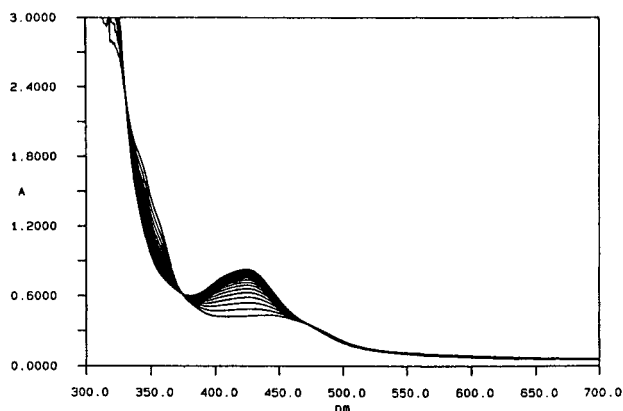
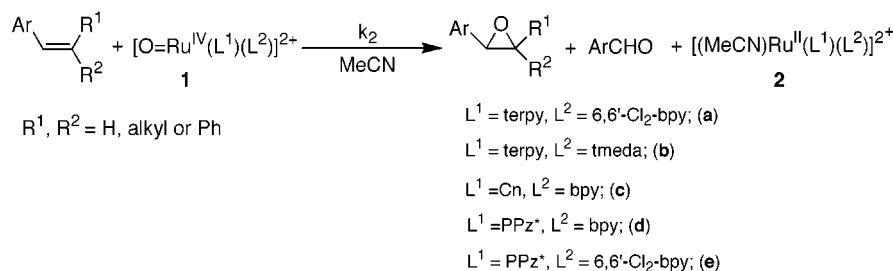
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**Table 1.** Stoichiometric Alkene Oxidations by Oxoruthenium(IV) Complexes<sup>a</sup>

entry	alkenes	products	% yield			
			<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>
1	norbornene	<i>exo</i> -2,3-epoxynorbornane	83	79	79	
2	styrene	styrene oxide	65	64	62	58
		benzaldehyde	16	12	12	10
		phenylacetaldehyde	8	7	2	10
3	<i>trans</i> -stilbene	<i>trans</i> -stilbene oxide	0	33	18	0
		benzaldehyde	32	0	0	12
		<i>cis</i> -stilbene oxide	0	37	45	0
4	<i>cis</i> -stilbene oxide	<i>trans</i> -stilbene oxide	0	3	4	0
		benzaldehyde	24	0	0	15
		<i>trans</i> - $\beta$ -methylstyrene oxide	40	41	14	33
5	<i>trans</i> - $\beta$ -methylstyrene oxide	benzaldehyde	34	42	54	45
		<i>cis</i> - $\beta$ -methylstyrene oxide	30	47	23	33
		<i>trans</i> - $\beta$ -methylstyrene oxide	10	9	5	17
6	<i>cis</i> - $\beta$ -methylstyrene	benzaldehyde	32	32	34	31

<sup>a</sup> Reaction conditions: Stoichiometric oxidation was performed by dissolving the oxoruthenium(IV) complex (50  $\mu$ mol) in degassed MeCN (4 mL) containing an alkene (1 mmol) at room temperature. The reaction mixture was stirred for 12 h. After the addition of an internal standard, an aliquot was taken for analysis by either GC or <sup>1</sup>H NMR for product identification and quantification. Percent yield is based on the oxidant used.

**Scheme 1.** Oxidation of Aromatic Alkenes by Oxoruthenium(IV) Complexes

**Figure 2.** UV-vis spectral trace (300–700 nm) for the reaction of styrene (0.1 M) with [Ru<sup>IV</sup>(PPz\*)(bpy)O](ClO<sub>4</sub>)<sub>2</sub> (**1d**) (0.15 mM) in acetonitrile at room temperature under pseudo-first-order conditions.

at 424 nm (the MLCT bands of the other Ru<sup>II</sup> complexes were 477 nm for **2a**, 480 nm for **2b**, and 458 nm for **2c**). All of the olefinic substrates utilized here—*para*-substituted styrenes, *cis*- $\beta$ -methylstyrene, *trans*- $\beta$ -methylstyrene,  $\alpha$ -methylstyrene, and norbornene—exhibit isosbestic spectral changes and follow clean first-order kinetics for their reactions with **1** under pseudo-first-order conditions, i.e., [alkene]  $\gg$  [Ru]. Therefore, the accumulation of any long-lived intermediates is untenable for these reactions.

The pseudo-first-order rate constants,  $k_{\text{obs}}$ , were determined by monitoring the growth of the MLCT band of **2** in acetonitrile. The second-order rate constants,  $k_2$ , were evaluated from the slope of the plots of  $k_{\text{obs}}$  versus [alkene]. For all the reactions studied, the  $k_{\text{obs}}$  versus

[alkene] plots are linear, and rate saturation has not been observed over the concentration ranges employed in this work. The  $k_2$  values are listed in Table 2.

The temperature effect on the  $k_2$  values for the oxidation of some representative alkenes has been studied. The Eyring plots are linear over a temperature range of 19–42 °C. The activation enthalpy  $\Delta H^\ddagger$  and entropy  $\Delta S^\ddagger$  for the styrene, *trans*- $\beta$ -methylstyrene, *cis*- $\beta$ -methylstyrene,  $\alpha$ -methylstyrene, and norbornene oxidations by **1b** and **1d** are listed in Table 3. The large and negative  $\Delta S^\ddagger$  values are consistent with association of reactants at the transition states. Similar  $\Delta S^\ddagger$  values among the aromatic alkenes indicate that these substrates should have experienced similar steric demand for their reactions with the oxoruthenium(IV) complexes.

A noticeable exception has been found for the oxidation of *cis*-*trans*-stilbenes; the reactions displayed complicated kinetics even when the alkenes were present in large excess. From the UV-vis spectral traces of the reactions, at least two distinct steps can be recognized. Meyer and co-workers have recently proposed a multistep reaction scheme for analogous reactions by the [Ru<sup>IV</sup>-(bpy)<sub>2</sub>(py)O]<sup>2+</sup> complex using a global kinetic analysis technique.<sup>11b</sup>

**Concerted versus Nonconcerted Reaction Pathways.** The use of *cis*-alkenes such as *cis*-stilbene to probe the concertedness of the oxo-metal-mediated epoxidation reactions is well-documented.<sup>15</sup> If the epoxidation of *cis*-alkene involves breakage of the C=C  $\pi$  bond resulting in the formation of an acyclic intermediate, i.e., a

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**Table 2.** Second-Order Rate Constants ( $k_2$ ) for the Oxidation of Aromatic Alkenes by Oxoruthenium(IV) Complexes

entry	alkenes	$k_2/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$		
		<b>1b</b> ( $\times 10^{-2}$ )	<b>1c</b> ( $\times 10^{-4}$ )	<b>1d</b> ( $\times 10^{-1}$ )
1	styrene	1.95 $\pm$ 0.10	13.0 $\pm$ 1.1	1.71 $\pm$ 0.05
2	4-methoxystyrene	5.62 $\pm$ 0.08	45.1 $\pm$ 2.6	4.19 $\pm$ 0.09
3	4-methylstyrene	2.65 $\pm$ 0.10	16.9 $\pm$ 1.4	2.23 $\pm$ 0.03
4	4-fluorostyrene	1.60 $\pm$ 0.03	15.9 $\pm$ 0.6	1.16 $\pm$ 0.03
5	4-chlorostyrene	2.25 $\pm$ 0.07	15.0 $\pm$ 0.7	1.94 $\pm$ 0.10
6	4-(trifluoromethyl)styrene	2.06 $\pm$ 0.10	12.0 $\pm$ 0.5	1.17 $\pm$ 0.04
7	<i>cis</i> - $\beta$ -methylstyrene	3.01 $\pm$ 0.07	20.0 $\pm$ 1.3	2.41 $\pm$ 0.08
8	<i>trans</i> - $\beta$ -methylstyrene	5.55 $\pm$ 0.01	33.1 $\pm$ 1.8	3.43 $\pm$ 0.02
9	$\alpha$ -methylstyrene	0.741 $\pm$ 0.005		0.455 $\pm$ 0.006
10	norbornene	0.319 $\pm$ 0.021	2.52 $\pm$ 0.2	
11	$\alpha$ - <i>d</i> <sub>1</sub> -styrene	2.00 $\pm$ 0.09 ( $k_H/k_D = 0.98$ )		1.74 $\pm$ 0.08 ( $k_H/k_D = 0.98$ )
12	$\beta$ - <i>d</i> <sub>2</sub> -styrene	2.24 $\pm$ 0.09 ( $k_H/k_D = 0.87$ )		1.99 $\pm$ 0.06 ( $k_H/k_D = 0.86$ )

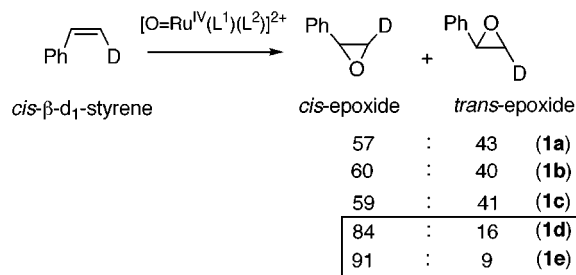
**Table 3.** Activation Parameters for the Oxidation of Styrene, *cis*- $\beta$ -Methylstyrene, *trans*- $\beta$ -Methylstyrene,  $\alpha$ -Methylstyrene and Norbornene

alkenes	<b>1b</b>		<b>1d</b>	
	$\Delta H^\ddagger/(\text{kcal mol}^{-1})$	$\Delta S^\ddagger/\text{eu}$	$\Delta H^\ddagger/(\text{kcal mol}^{-1})$	$\Delta S^\ddagger/\text{eu}$
styrene	9.06 $\pm$ 0.66	-(35.8 $\pm$ 2.2)	9.52 $\pm$ 0.34	-(30.2 $\pm$ 2.0)
$\alpha$ -methylstyrene	12.5 $\pm$ 0.2	-(26.5 $\pm$ 0.8)	10.8 $\pm$ 0.4	-(28.4 $\pm$ 1.5)
<i>trans</i> - $\beta$ -methylstyrene	9.21 $\pm$ 0.38	-(33.3 $\pm$ 1.3)	8.77 $\pm$ 0.36	-(31.2 $\pm$ 1.2)
<i>cis</i> - $\beta$ -methylstyrene	9.48 $\pm$ 0.38	-(33.8 $\pm$ 1.2)	9.26 $\pm$ 0.43	-(30.3 $\pm$ 1.4)
norbornene	14.9 $\pm$ 0.9	-(19.7 $\pm$ 3.0)		

nonconcerted pathway, then isomerization via the unhindered C–C bond rotation to form *trans*-epoxide product would occur. In the case of *cis*-stilbene oxidation, the supposed acyclic intermediate is particularly prone to *cis*–*trans* isomerization because of severe steric interaction between the two phenyl rings. In this work, the reactions of **1b** and **1c** with *cis*-stilbene are almost completely stereoretentive (the *cis*–*trans*-epoxide ratio = 93:7), albeit in rather poor overall epoxide yields (Table 1, entry 4). A high degree of stereoretention for the oxidation of *cis*-stilbene by the [Ru<sup>IV</sup>(bpy)<sub>2</sub>(py)O]<sup>2+</sup> complex had previously been observed,<sup>11b</sup> and an oxene insertion mechanism was suggested (Scheme 3, pathway a). The isomerization of *cis*- to *trans*-stilbene catalyzed by a Ru<sup>II</sup> complex prior to oxidation was proposed to account for the minor production of *trans*-stilbene oxide.<sup>11b</sup>

Stereoselectivities for *cis*-alkene oxidations vary with both the *cis*-alkenes and the ruthenium oxidants. Unlike the *cis*-stilbene oxidations, the reactions of *cis*- $\beta$ -methylstyrene with oxoruthenium(IV) complexes gave mixtures of *cis*- and *trans*-epoxides (*cis*:*trans* ratios = 84:16 for **1b** and **1c**, 75:25 for **1a**, and 66:34 for **1d**, Table 1, entry 6). However, [Ru<sup>IV</sup>(PPz\*)(6,6'-Cl<sub>2</sub>-bpy)O]<sup>2+</sup> (**1e**) can oxidize *cis*- $\beta$ -methylstyrene with greater than 99% stereoretention, and *cis*-epoxide and benzaldehyde were obtained in 58 and 25% yield, respectively (Table 6, entry 7). Moreover, while the *cis*- $\beta$ -deuteriostyrene oxidations by **1a**–**c** at room temperature in acetonitrile are almost nonstereoselective (*cis*–*trans*-epoxide ratio  $\approx$ 60:40; see Scheme 2); similar reactions with the chiral ruthenium oxidants **1d** and **1e** maintained relatively high *cis*–*trans*-epoxide selectivities of 84:16 and 91:9, respectively, based on <sup>1</sup>H NMR analyses (see the Experimental Section). These reactions were repeated at least three times, and their *cis*–*trans* selectivities were obtained in a reproducible manner and reported as average values. The purity of the *cis*-alkenes (>99%) was checked by gas chromatography before use, and *trans*-alkenes were not detected at the end of the reactions.

Because the styrene and *cis*- $\beta$ -methylstyrene oxidations follow clean second-order kinetics, a simple bimolecular kinetic scheme should be applicable. Complica-

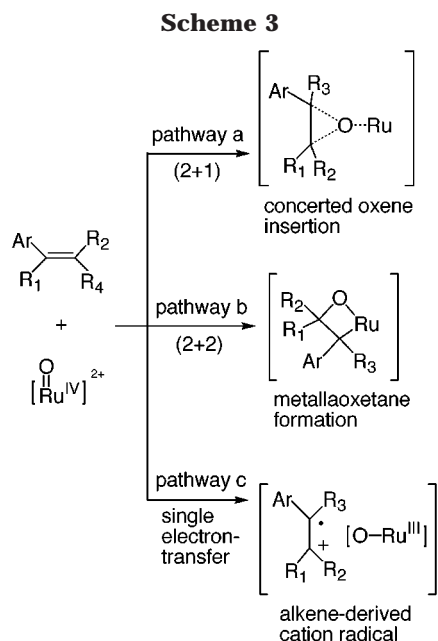
**Scheme 2.** Nonstereoselective Oxidation of *cis*- $\beta$ -Deuteriostyrene by Oxoruthenium(IV) Complexes

tions such as the participation of several reactive species in the production of the *cis*–*trans*-epoxides and benzaldehyde, as happens for the stilbene oxidations, are not anticipated in our case. Evidently, the concerted insertion of Ru<sup>IV</sup>=O to the C=C bond (Scheme 3, pathway a) cannot explain the loss of stereospecificity/selectivity; hence, a nonconcerted mechanism is in operation.

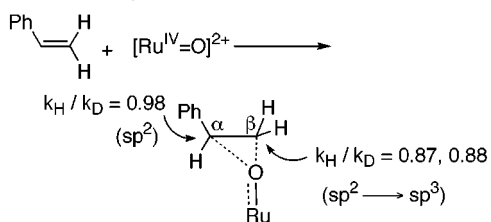
The rate-limiting formation of a metallaoxetane intermediate (Scheme 3, pathway b) by (2 + 2) cycloaddition between the Ru<sup>IV</sup>=O and C=C bonds is unlikely. Both the  $\alpha$  and  $\beta$  olefinic carbon atoms would simultaneously rehybridize from sp<sup>2</sup> to sp<sup>3</sup> upon metallaoxetane formation, and this is inconsistent with the fact that the inverse secondary kinetic isotope effect (KIE) was only observed for the  $\beta$ -*d*<sub>2</sub>-styrene oxidations ( $k_H/k_D = 0.87$  for **1b** and 0.86 for **1d**) but not for  $\alpha$ -deuteriostyrene ( $k_H/k_D = 0.98$  for **1b** and **1d**; see Scheme 4).<sup>16</sup> The KIE results actually favor a nonsymmetrical transition state in which more C–O bonding is forming at the  $\beta$ -carbon atom with concomitant rehybridization from sp<sup>2</sup> to sp<sup>3</sup> and the  $\alpha$ -carbon atom remains more or less sp<sup>2</sup> hybridized on progressing to the transition state, implying the formation of an acyclic intermediate at the rate-limiting step.

The concerted oxene insertion mechanism for the styrene oxidation can be excluded by the same token. In

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**Scheme 4. Secondary KIE for Styrene Oxidation by Oxoruthenium(IV)**



regard to the high stereoselectivity for the oxidation of *cis*- $\beta$ -deuteriostyrene by  $[\text{Ru}^{\text{IV}}(\text{PPz}^*)(6,6'\text{-Cl}_2\text{-bpy})\text{O}]^{2+}$  (>90% *cis*-epoxide), secondary KIE experiments have been carried out using **1e** as the oxidant, resulting in  $k_H/k_D = 0.87$  for  $\beta$ - $d_2$ -styrene and  $k_H/k_D = 1.02$  for  $\alpha$ -deuteriostyrene. These results indicate that the apparent stereoretention cannot possibly be due to a concerted oxene insertion reaction.

**Nature of the Rate-Limiting Step.** At pH 1.1, the  $E^\circ(\text{Ru}^{\text{IV/III}})$  values of the oxoruthenium(IV) complexes span over a 230-mV range: 1.13 V for **1a**,<sup>9b</sup> 0.93 V for **1b**,<sup>12</sup> 0.90 V for **1c**,<sup>13</sup> 0.98 V for **1d**,<sup>7f</sup> and 0.99 V for the  $[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})\text{O}]^{2+}$  complex<sup>17</sup> versus SCE. The second-order rate constants ( $\log k_2$ ) for the stoichiometric styrene oxidations by complexes **1a–c** and  $[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})\text{O}]^{2+}$  do not correlate linearly with their  $E^\circ(\text{Ru}^{\text{IV/III}})$  values. A very narrow variation in the  $k_2$  values (within 1.5-fold) is observed for the terpyridine- and bipyridine-based oxoruthenium complexes, despite over a 200 mV change in their  $E^\circ(\text{Ru}^{\text{IV/III}})$  values. However, the Cn-based derivative **1c** undergoes a nearly 10-fold decrease in reactivity (which is merely 30-mV less oxidizing than **1b**; see Table 4). This abrupt change in the reactivity pattern is attributed to the enhanced steric hindrance of the tertiary amine macrocycle. The weak dependence of the  $k_2$  values on the electrochemical potentials contrasts sharply to the linear  $\log k_2$  versus  $E^\circ(\text{Ru}^{\text{VI/V}})$  relationship observed for the *trans*- $[\text{Ru}^{\text{VI}}(\text{N}_4)\text{O}_2]^{2+}$  systems ( $\text{N}_4$  = tetraamine macrocycles),<sup>9d</sup> where an increase

**Table 4. Variation of  $k_2$  for the Styrene Oxidations with the  $E^\circ(\text{Ru}^{\text{IV/III}})$  Values<sup>a</sup>**

entry	oxidant	$E^\circ(\text{Ru}^{\text{IV/III}})$ vs SCE	$k_2/(\text{M}^{-1} \text{s}^{-1})$	ref
1	$[\text{Ru}^{\text{IV}}(\text{terpy})(6,6\text{-Cl}_2\text{bpy})\text{O}]^{2+}$	1.13	$2.79 \times 10^{-2}$	9b
2	$[\text{Ru}^{\text{IV}}(\text{terpy})(\text{tmeda})\text{O}]^{2+}$	0.93	$1.95 \times 10^{-2}$	12
3	$[\text{Ru}^{\text{IV}}(\text{Cn})(\text{bpy})\text{O}]^{2+}$	0.90	$1.30 \times 10^{-3}$	13
4	$[\text{Ru}^{\text{IV}}(\text{bpy})_2(\text{py})\text{O}]^{2+}$	0.99	$1.48 \times 10^{-2}$	11, 17

<sup>a</sup>  $E^\circ(\text{Ru}^{\text{IV/III}})$  is defined by  $[\text{Ru}^{\text{IV}}(\text{L}^1)(\text{L}^2)\text{O}]^{2+} \xrightarrow{\text{H}^+/\text{e}^-} [\text{Ru}^{\text{III}}(\text{L}^1)(\text{L}^2)\text{OH}]^{2+}$  at pH 1.1.

in  $\sim 150$  mV brings about a 10-fold acceleration of the oxidation rate. Therefore, the rate-limiting formation of an alkene-derived cation radical intermediate (Scheme 3, pathway c) cannot be correct. In fact, a one-electron reduction of  $\text{Ru}^{\text{IV}}=\text{O}$  to  $\text{Ru}^{\text{III}}$  would disrupt the  $d_\pi\text{-p}_\pi$  metal-oxo bond and must be accompanied by Lewis acid coordination; therefore, in a nonaqueous solution without Lewis acid, the  $\text{Ru}^{\text{IV}}=\text{O}$  species is unlikely to function as an outer-sphere one-electron oxidant.

On the other hand, the alkene-derived cation radical intermediate is susceptible to skeletal rearrangement. This is the case for the oxidation of norbornene by hypervalent oxometalloporphyrins which produce *exo*- and *endo*-epoxynorbornane, norcamphor, and cyclohexene-4-carboxyaldehyde. Traylor and co-workers<sup>18</sup> have suggested that such a finding can be explained by the presence of a cation radical intermediate. In this work, *exo*-epoxynorbornane was found to be the exclusive product of the norbornene oxidation (Table 1, entry 1), suggesting that a cation radical species is not necessarily the intermediate of the reaction.

**Oxidation of Para-Substituted Styrenes.** The effect of para substituents on the rate of styrene oxidations by **1b–d** has been investigated (Table 2, entries 1–6). Both electron-releasing and -withdrawing substituents can accelerate the reaction, although the variation of the  $k_2$  values is small ( $\sim 3.5$ -fold for 4-methoxystyrene and  $\sim 1.05$ -fold for 4-(trifluoromethyl)styrene), and the correlation of  $\log k_{\text{rel}}$  vs  $\sigma^+$  [ $k_{\text{rel}} = k_2(\text{para-substituted styrene})/k_2(\text{styrene})$ ] gives rise to concave Hammett curves resembling the case involving  $[\text{Ru}^{\text{IV}}(\text{terpy})(6,6'\text{-Cl}_2\text{-bpy})\text{O}]^{2+}$  as the oxidant.<sup>9b</sup> This finding is contrary to the styrene oxidations by the  $[\text{Ru}^{\text{VI}}(\text{N}_4)\text{O}_2]^{2+}$  systems wherein linear Hammett correlations of  $\log k_{\text{rel}}$  versus  $\sigma^+$  ( $\rho^+ = -2.1$ ) were obtained.<sup>9d,e</sup> The minor influence of the electronic substituent effect on the  $k_2$  values discounts the participation of either an alkene-derived cation radical or a carbocation intermediate. Given that the rate-limiting carbocation formation for the electrophilic addition to the C=C bond would have  $\rho^+$  values as large as  $-3.5$  (hydration)<sup>19</sup> and  $-4.1$  (bromination),<sup>20</sup> the insensitivity of the  $k_2$  values to the para-substituent effect is, in fact, more compatible with the rate-limiting formation of a carboradical intermediate.

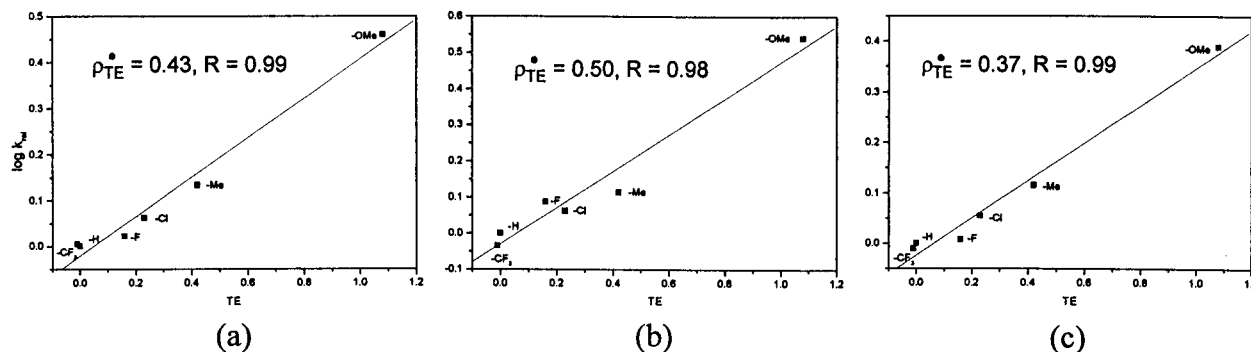
We have attempted to fit the relative reactivity data ( $\log k_{\text{rel}}$ ) to some carboradical  $\sigma^\bullet$  parameters. In the literature, there have been several studies concerning the establishment of  $\sigma^\bullet$  scales using spectroscopic and kinetic methods. The three most complete studies are by Arnold (ESR studies of para-substituted benzylic radicals),<sup>21</sup>

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**Figure 3.** Linear free-energy correlations [ $\log k_{\text{rel}}$  vs TE] for the ruthenium oxidation of para-substituted styrenes: (a)  $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{tmEDA})\text{O}](\text{ClO}_4)_2$ , (b)  $[\text{Ru}^{\text{IV}}(\text{Cn})(\text{bpy})\text{O}](\text{ClO}_4)_2$ , and (c)  $[\text{Ru}^{\text{IV}}(\text{PPz}^*)(\text{bpy})\text{O}](\text{ClO}_4)_2$ .

Jiang and Ji (kinetic studies of the thermal cycloaddition reaction of  $\alpha,\beta,\beta$ -trifluorostyrenes),<sup>22</sup> and Creary (kinetic studies of the rearrangement of methylenearcylcyclopropanes).<sup>23</sup> Radical reactivities are often influenced to differing degrees by both polar and spin delocalization effects of the substituents in both ground and radical states, efforts to set up a pure radical  $\sigma^*$  scale which reflects only the spin delocalization effect of the substituents in radicals have met with limited success thus far.

Recently, Wu and co-workers<sup>24</sup> proposed a series of total substituent effect (TE) parameters for the correlation of the para-substituent effect on the benzylic C–H bond dissociation energies of toluenes. By use of the density functional method (BLYP/6-31G\*), the ground-state effect was eliminated, and the calculation revealed that the influence of the TE on the relative stabilities of the benzylic radicals can be linearly correlated ( $R = 0.995$ ) by the change of spin ( $\Delta s$ ) and charge ( $\Delta c$ ) densities at the radical centers:  $\text{TE} = -29.9\Delta s - 11.7\Delta c$ . Accordingly, the spin delocalization effect is a more dominant factor than the polar effect in determining the radical stabilities in homolytic scission of the benzylic C–H bonds of toluenes. We applied the TE radical parameters to our correlation studies, and Figure 3 depicts the linear free-energy correlations of  $\log k_{\text{rel}}$  versus TE for the oxidation of the para-substituted styrenes; the slopes ( $\rho_{\text{TE}}^*$ ) are +0.43 ( $R = 0.99$ ) for **1b**, +0.50 ( $R = 0.98$ ) for **1c**, and +0.37 ( $R = 0.99$ ) for **1d**. The linear free-energy relationship suggests that the styrene oxidation should involve the rate-limiting formation of a benzylic radical intermediate, which is stabilized mainly by the spin delocalization effect.

**Proposed Mechanism.** We can conclude that the oxidation of aromatic alkenes by oxoruthenium(IV) complexes would generate a benzylic radical intermediate at the rate-determining step, possibly preceded by a rapid and reversible charge-transfer complex formation (Scheme 5).<sup>25</sup> A weakly polar complex in which less than 0.1 electron is transferred from the C=C bond to  $\text{Ru}^{\text{IV}}=\text{O}$  had previously been suggested by Drago and co-workers based on their theoretical calculations.<sup>26</sup> The carboradical

intermediate would undergo ring closure to produce epoxide, and the isomerized epoxide would form via C–C rotation followed by cyclization. Benzaldehyde, the C=C bond cleavage product, should arise from the reaction of the carboradical species with dissolved dioxygen.<sup>27</sup>

On the basis of magnetic susceptibility measurements, the oxoruthenium(IV) complexes **1a–e** ( $\mu_{\text{eff}} \sim 2.9\mu_{\text{B}}$ ) have a triplet electronic ground state: a  $[(d_{xy})^2(d_{xz})^1(d_{yz})^1]$  configuration. Studies by Meyer and co-workers revealed that a very small activation barrier of  $56\text{ cm}^{-1}$  exists for conversion to a singlet excited state; therefore, a rapid triplet–singlet interconversion is expected in solution at room temperature.<sup>28</sup> The singlet  $[\text{Ru}^{\text{IV}}=\text{O}]^1$  species was believed to behave like an oxene: a priori and able to effect concerted oxygen atom insertion to alkene, whereas the triplet  $[\text{Ru}^{\text{IV}}=\text{O}]^3$  form would react via a stepwise radical pathway. In this study, we do not recognize the involvement of two reactive species with distinctively different reactivity patterns since biexponential kinetics are not observed. However, kinetic studies on the alkene epoxidation by  $d^2$  dioxoruthenium(VI) porphyrin complexes suggest a similar stepwise, radical mechanism;<sup>29</sup> therefore, a singlet electronic state for oxoruthenium complexes does not necessarily warrant oxene-like reactivity.

**Stoichiometric Asymmetric Epoxidation by Chiral Oxoruthenium(IV) Complexes.** Reactions of  $[\text{Ru}^{\text{IV}}(\text{PPz}^*)(\text{Y}_2\text{-bpy})\text{O}](\text{ClO}_4)_2$  [ $\text{Y} = \text{H}$  (**1d**);  $\text{Y}_2 = 6,6'\text{-Cl}_2$  (**1e**)] with aryl alkenes in acetonitrile afforded epoxides as the major product, and the corresponding  $[\text{Ru}^{\text{II}}(\text{PPz}^*)(\text{Y}_2\text{-bpy})(\text{MeCN})](\text{ClO}_4)_2$  (**2d,e**) series was also isolated and characterized. The oxidation of styrene gave styrene oxide in 58% yield with 37% ee (Table 5, entry 1), and *cis*- $\beta$ -methylstyrene was oxidized to a mixture of *cis*- and *trans*- $\beta$ -methylstyrene oxides (*cis*:*trans* = 66:34) in 30% ee and 1% ee, respectively (entry 7). *trans*- $\beta$ -Methylstyrene oxide (33% yield) in 12% ee was produced from the oxidation of *trans*- $\beta$ -methylstyrene (entry 8). The electronic substituent effect on the styrene oxidation is unimportant as far as the enantioselectivity is concerned (see Table 5, entries 1–5), whereas the reaction temperature has a more profound influence on the enantioselectivity, for instance, oxidation of 4-chlorostyrene by **1d** can afford 4-chlorostyrene oxide in 56% ee at  $-15\text{ }^\circ\text{C}$  compared with 37% ee at  $25\text{ }^\circ\text{C}$  (entry 2).

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(23) (a) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1986**, *51*, 1110. (b) Creary, X.; Mehrsheikh-Mohammadi, M. E. *J. Org. Chem.* **1987**, *52*, 3254.

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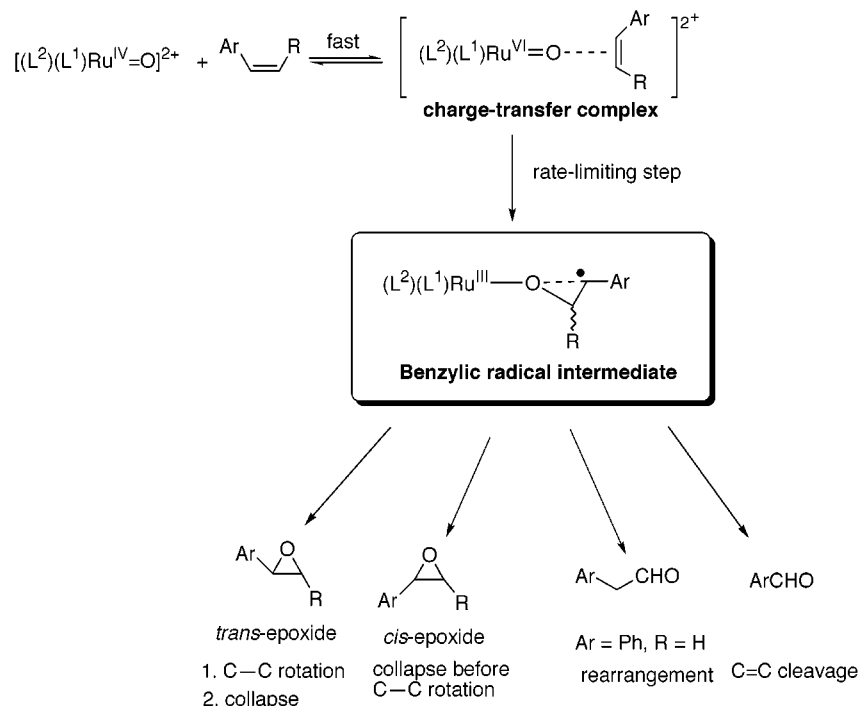
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## Scheme 5. Proposed Mechanism for the Oxidation of Aromatic Alkenes by Oxoruthenium(IV)

Table 5. Asymmetric Epoxidation of Aromatic Alkenes by  $[Ru^{IV}(PPz^*)(bpy)O](ClO_4)_2^a$ 

entry	alkenes	products	% yield <sup>b,c</sup>	% ee of epoxides (abs config) <sup>d,e</sup>	entry	alkenes	products	% yield <sup>b,c</sup>	% ee of epoxides (abs config) <sup>d,e</sup>
1			58	37 ( <i>R</i> )	5			63	37 ( <i>R</i> )
			10					9	
			10						
2			62	38 ( <i>R</i> )	6			72	35 ( <i>R</i> )
			58 (40 °C)	36 ( <i>R</i> ) (40 °C)				7	
			45 (0 °C)	45 ( <i>R</i> ) (0 °C)					
			25 (-15 °C)	56 ( <i>R</i> ) (-15 °C)	7			33	30 ( <i>1R,2S</i> )
			15					17	1 ( <i>1R,2R</i> )
			20 (40 °C)					31	
			22 (0 °C)		8			33	12 ( <i>1R,2R</i> )
			30 (-15 °C)					45	
3			60	36 ( <i>R</i> )					
			18						
4			39	36 ( <i>R</i> )					
			16						
			25						

<sup>a</sup> Reaction conditions: To an acetonitrile solution (5 mL) containing alkene (1–2 mmol) was added the chiral ruthenium oxidant (50  $\mu$ mol) under a  $N_2$  atmosphere. The homogeneous solution was stirred for 12 h at 25 °C. The reduced metal complex was removed by precipitation using diethyl ether. After addition of an internal standard, an aliquot was taken for analysis by GC or  $^1H$  NMR for product identification and quantification. <sup>b</sup> Yields were based on the amount of oxidants used. <sup>c</sup> Reactions were carried out at 25 °C unless otherwise noted. <sup>d</sup> Percent ee determined by either chiral GC or  $^1H$  NMR with  $Eu(hfc)_3$  shift reagent. <sup>e</sup> Absolute configuration was assigned by comparison with enantiopure authentic samples.

Previous studies revealed that electron-withdrawing and -donating substituents at the 4,4'-positions of the bipyridine ligand can affect the  $E^\circ(Ru^{VI/III})$  values of the

polypyridine-based oxoruthenium(IV) complexes.<sup>8c,30</sup> In this work, the  $E^\circ(Ru^{IV/III})$  of various  $[Ru^{IV}(PPz^*)(Y_2-bpy)O](ClO_4)_2$  complexes ( $Y_2 = 6,6'-Cl_2, 4,4'-Cl_2, 4,4'-Me_2$ , and



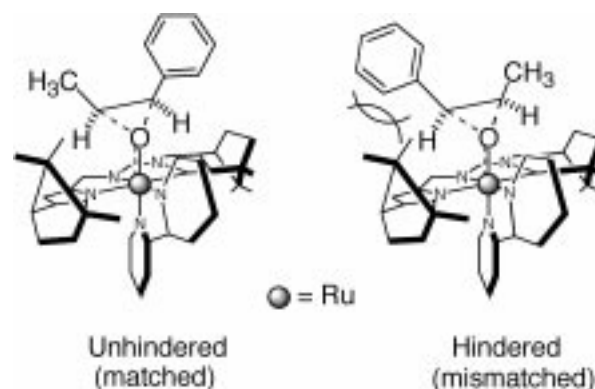
**Table 6. Asymmetric Alkene Epoxidation by Various Substituted Chiral Oxoruthenium(IV) Complexes at 25 °C<sup>a</sup>**

entry	oxidant + alkenes	products	% yield	% ee (abs config)
1	[Ru <sup>IV</sup> (PPz*)(bpy)(O)] <sup>2+</sup> + styrene	styrene oxide benzaldehyde phenylacetaldehyde	58 10 10	37 ( <i>R</i> )
2	[Ru <sup>IV</sup> (PPz*)(4,4'-Me <sub>2</sub> -bpy)(O)] <sup>2+</sup> + styrene	styrene oxide benzaldehyde phenylacetaldehyde	62 14 5	37 ( <i>R</i> )
3	[Ru <sup>IV</sup> (PPz*)(4,4'- <i>t</i> -Bu <sub>2</sub> -bpy)(O)] <sup>2+</sup> + styrene	styrene oxide benzaldehyde phenylacetaldehyde	67 10 5	38 ( <i>R</i> )
4	[Ru <sup>IV</sup> (PPz*)(4,4'-Cl <sub>2</sub> -bpy)(O)] <sup>2+</sup> + styrene	styrene oxide benzaldehyde phenylacetaldehyde	52 18 11	36 ( <i>R</i> )
5	[Ru <sup>IV</sup> (PPz*)(5,5'-Me <sub>2</sub> -bpy)(O)] <sup>2+</sup> + styrene	styrene oxide benzaldehyde phenylacetaldehyde	59 14 10	36 ( <i>R</i> )
6	[Ru <sup>IV</sup> (PPz*)(6,6'-Cl <sub>2</sub> -bpy)(O)] <sup>2+</sup> + styrene	styrene oxide benzaldehyde phenylacetaldehyde	68 11 4	45 ( <i>R</i> )
7	[Ru <sup>IV</sup> (PPz*)(6,6'-bpy)(O)] <sup>2+</sup> + <i>cis</i> - $\beta$ -methylstyrene	<i>cis</i> - $\beta$ -methylstyrene oxide benzaldehyde	58 25	59 (1 <i>R</i> ,2 <i>S</i> )

<sup>a</sup>  $E^\circ(\text{Ru}^{\text{III/IV}})$  of [Ru<sup>II</sup>(PPz\*)(Y<sub>2</sub>-bpy)Cl]ClO<sub>4</sub> (MeCN, room temperature): 0.46 V (Y<sub>2</sub> = 6,6'-Cl<sub>2</sub>-); 0.41 V (Y<sub>2</sub> = 4,4'-Cl<sub>2</sub>-); 0.35 V (Y<sub>2</sub> = H<sub>2</sub>); 0.30 V (Y<sub>2</sub> = 4,4'-Me<sub>2</sub>-); 0.29 V (Y<sub>2</sub> = 4,4'-*t*-Bu<sub>2</sub>-). All values are measured vs Cp<sub>2</sub>Fe<sup>+0</sup>.

4,4'-*t*-Bu<sub>2</sub>) in aqueous solution cannot be determined accurately because of their poor solubilities; however, the substituent electronic effect could be reflected qualitatively from the  $E^\circ(\text{Ru}^{\text{III/IV}})$  couples of the [Ru<sup>II</sup>(PPz\*)(Y<sub>2</sub>-bpy)Cl]ClO<sub>4</sub> derivatives (see caption of Table 6). The 4,4'-dichloro derivative has the highest  $E^\circ(\text{Ru}^{\text{III/IV}})$  value (0.41 V vs Cp<sub>2</sub>Fe<sup>+0</sup>), and the 4,4'-di-*tert*-butyl derivative has the lowest value (0.29 V vs Cp<sub>2</sub>Fe<sup>+0</sup>). For the oxidation of styrene by these chiral oxoruthenium(IV) complexes, the % ee values of the styrene oxide produced are invariant to these substituents on the 2,2'-bipyridine ligand (Table 6, entries 1–5). As mentioned earlier, the second-order rate constants for the styrene oxidation by the achiral oxoruthenium(IV) complexes are fairly insensitive to their  $E^\circ(\text{Ru}^{\text{IV/III}})$  values; hence, it is expected that the styrene epoxidation by the substituted chiral Ru<sup>IV</sup>=O complexes should result in similar product selectivities in accord with the Hammond postulate. Yet, [Ru<sup>IV</sup>(PPz\*)(6,6'-Cl<sub>2</sub>-bpy)O](ClO<sub>4</sub>)<sub>2</sub> (**1e**) bearing two chloro substituents at the 6,6'-positions of the bipyridine ligand notably improves the % ee of the epoxide products for its reactions with styrene (45% ee vs 37% ee for **1d**) and *cis*- $\beta$ -methylstyrene (59% ee vs 25% ee of *cis*-epoxide for **1d**) at room temperature (Table 6, entries 6 and 7).

**Facial Selectivity versus Diastereoselectivity of Epoxide Ring Closure.** The [Ru<sup>IV</sup>(terpy)(cxhn)O](ClO<sub>4</sub>)<sub>2</sub> complex [cxhn = (-)-(1*R*,2*R*)-*N,N,N,N*-tetramethyl-1,2-diaminocyclohexane] was our earliest attempt to bring about enantioselective aromatic alkene epoxidations using chiral oxoruthenium(IV) complexes.<sup>7g</sup> However, this complex failed to effect asymmetric induction because of the undesirable disposition of the dissymmetric diamine and the terpyridine ligands, resulting in a lack of enantiotopic face discrimination. We had envisioned and it was established by crystal structure analysis of [Ru<sup>II</sup>(PPz\*)(bpy)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub><sup>7f</sup> that the O=Ru axis should be orthogonal to the molecular plane of the PPz\* ligand but collinear to that of the 2,2'-bipyridine ligand; the oxo moiety is thus sterically encumbered with the camphor auxiliaries and the bipyridine, and only one face of the O=Ru site is exposed for interaction with the

**Scheme 6. Diagrammatic Representation of the Side-On Approach of *cis*- $\beta$ -Methylstyrene to the Chiral Oxoruthenium(IV)**

incoming alkene molecule. The facial selection can be explained by the "side-on approach" model,<sup>31</sup> in which the unhindered facial approach leads to the major enantiomeric epoxide (Scheme 6). For instance, when (+)-PPz\* is the chiral auxiliary, *cis*-(1*R*,2*S*)- $\beta$ -methylstyrene oxide is preferentially produced, and the selection for the opposite prochiral face is disfavored due to steric interaction.

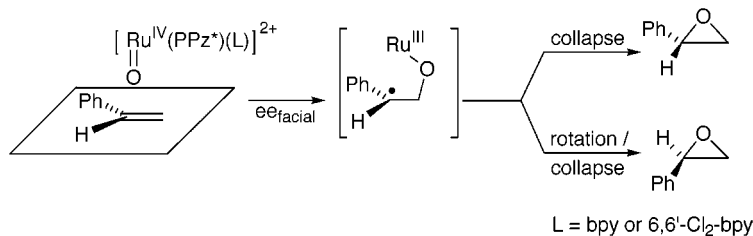
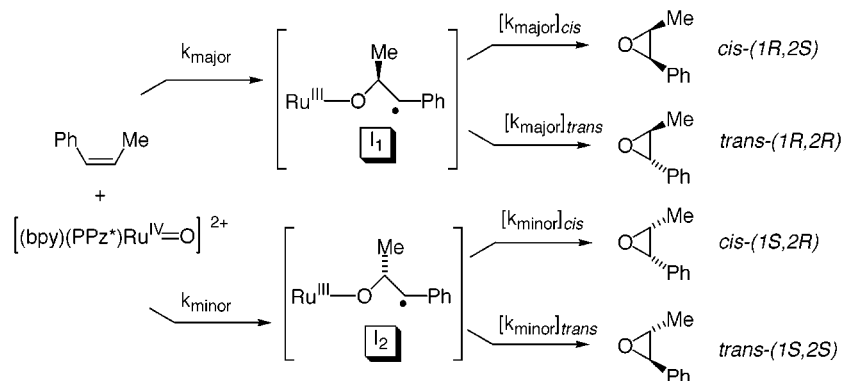
Because aromatic alkene epoxidations by oxoruthenium(IV) complexes proceed via two sequential C–O bond-formation steps, the addition of a Ru=O to a C=C bond generates a benzylic radical intermediate which undergoes the collapse (*cis*) and rotation/collapse (*trans*) processes, affording the observed mixture of *cis*- and *trans*-epoxides. Moreover, the *cis*-epoxide production is more enantioselective than that of the *trans*-epoxide; therefore, the observed % ee of the epoxide cannot be dependent solely on the facial selectivity of the initial irreversible C–O bond formation step. It must also be dependent on the extent of *cis*–*trans* isomerization before the second C–O bond formation. In the case of styrene oxidation, the  $\alpha$  carbon (i.e., the only asymmetric center to be created) remains epimeric; the rotation/collapse pathway tends to reduce the enantioselectivity by generating the opposite enantiomeric epoxide (Scheme 7).

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(31) (a) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791. (b) Groves, J. T.; Han, Y.; Van Engen, D. V. *J. Chem. Soc., Chem. Commun.* **1990**, 436.



## Scheme 7. Nonstereospecific Oxidation of Styrene by Chiral Oxoruthenium(IV)

Scheme 8. Nonstereospecific Oxidation of *cis*- $\beta$ -Methylstyrene by Chiral Oxoruthenium(IV)

The damaging effect of the rotation/collapse pathway can be evaluated by using *cis*- $\beta$ -deuteriostyrene as a probe substrate. The oxidation of *cis*- $\beta$ -deuteriostyrene by **1d** under typical reaction conditions (acetonitrile at 25 °C and [alkene]:[Ru]  $\approx$  20:1) resulted in a mixture of *cis*- and *trans*- $\beta$ -deuteriostyrene oxides (*cis*:*trans* = 84:16). <sup>1</sup>H NMR analysis in the presence of a chiral shift reagent [Eu(hfc)<sub>3</sub>] revealed the enantiomeric composition of both the *cis*- (43% ee) and *trans*-epoxides (<1% ee). As discussed in earlier sections, all the steps shown in Scheme 7 can be considered irreversible. Thus, the observed enantioselectivity (*ee*<sub>obs</sub>) for styrene oxidation by **1d** can be correlated to the *ee* values of *cis*- and *trans*- $\beta$ -deuteriostyrene oxides as such: *ee*<sub>obs</sub> = [(*ee*<sub>cis</sub>)(% *cis*-oxide) - (*ee*<sub>trans</sub>)(% *trans*-oxide)] according to related works by Jacobsen and co-workers.<sup>32</sup> The substitution of the stereochemical data for the *cis*- $\beta$ -deuteriostyrene oxidation into the equation gives a calculated *ee*<sub>obs</sub> = 36% ee, which closely matches the experimental value of 37% ee. Because the  $\alpha$  carbon of styrene is the only epimeric/asymmetric center, the facial selectivity (*ee*<sub>facial</sub>) at the initial C–O bond formation step would, therefore, approach the *ee*<sub>cis</sub> value when the styrene epoxidation became fully stereospecific, and the rotation/collapse pathway should account for approximately a 6% ee reduction.

With regards to the higher enantioselectivity for the styrene epoxidation (45% ee vs 37% ee for **1d**) by the 6,6'-dichloro-substituted derivative **1e**, *cis*- $\beta$ -deuteriostyrene oxidation was also carried out using this complex as the oxidant, and an enantiomeric composition of *cis*- (49% ee) and *trans*-epoxides (<1% ee) with an improved stereoselectivity of *cis*:*trans* = 91:9 was observed. Therefore, the ee enhancement should be the result of better facial selectivity (49% ee vs 43% ee for **1d**), as well as higher stereoselectivity of epoxide ring closure, i.e., less *cis*–*trans* isomerization.

To rationalize the moderate ee enhancement observed at lower reaction temperature for the 4-chlorostyrene epoxidation (37% ee at 25 °C, 45% ee at 0 °C, 56% ee at

–15 °C, see Table 5, entry 2), we performed the *cis*- $\beta$ -deuteriostyrene oxidation by complex **1d** at –15 °C; a *cis*–*trans*-epoxide selectivity of 88:12, which is close to that of 84:16 obtained at 25 °C, was achieved. We, therefore, reason that the improved enantioselectivity at lower reaction temperatures should arise from the increase in facial selectivity alone.

For the oxidation of *cis*-1,2-disubstituted alkenes such as *cis*- $\beta$ -methylstyrene and *trans*- $\beta$ -methylstyrene oxides were formed. As depicted in Scheme 8, the *cis*- and *trans*-epoxides mixture should be produced by the two diastereomeric benzylic radical intermediates *I*<sub>1</sub> and *I*<sub>2</sub> generated at the first C–O bond formation step while creating an asymmetric center at the  $\beta$  carbon. On the basis of the ligand dissymmetry, *I*<sub>1</sub> and *I*<sub>2</sub> will undergo different degrees of collapse (*cis*) and rotation/collapse (*trans*) processes leading to their own *cis*–*trans*-oxide compositions. Therefore, the % ee for the *cis*- $\beta$ -methylstyrene oxidation would be influenced by (1) the facial selectivity of the first step (*ee*<sub>facial</sub>, determined by *k*<sub>major</sub> vs *k*<sub>minor</sub>) and (2) the relative diastereoselectivity of ring closure ([*k*<sub>major</sub>]<sub>cis</sub>/[*k*<sub>major</sub>]<sub>trans</sub> vs [*k*<sub>minor</sub>]<sub>cis</sub>/[*k*<sub>minor</sub>]<sub>trans</sub>) for the two diastereomeric carboradical intermediates. This situation has been analyzed meticulously by Jacobsen and co-workers in their mechanistic investigation of the asymmetric addition reactions to alkenes.<sup>33</sup> The diastereoselectivity of ring closure, again, can be assessed based on the *cis*–*trans*-epoxide ratio. Because the products are epimeric at the  $\alpha$  carbon, the values of *ee*<sub>facial</sub> and relative diastereoselectivity of ring closure can be calculated by the following equations:<sup>33</sup>

The epoxidation of *cis*- $\beta$ -methylstyrene has afforded *cis*-(1*R*,2*S*)- $\beta$ -methylstyrene oxide (33% yield, 30% ee) preferentially and *trans*-(1*R*,2*R*)- $\beta$ -methylstyrene oxide (17% yield, 1% ee) as a minor product. Using the above equations, we obtain the calculated *ee*<sub>facial</sub> and relative

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$$ee_{\text{facial}} = \frac{I_1 - I_2}{I_1 + I_2} = (ee_{\text{cis}} \times \% \text{cis}) + (ee_{\text{trans}} \times \% \text{trans}) \quad (1)$$

relative diastereoselectivity of ring closure =

$$\frac{[\text{cis}]_{\text{major}} / [\text{trans}]_{\text{major}}}{[\text{cis}]_{\text{minor}} / [\text{trans}]_{\text{minor}}} = \frac{(1 + ee_{\text{cis}}) / (1 - ee_{\text{cis}})}{(1 + ee_{\text{trans}}) / (1 - ee_{\text{trans}})} \quad (2)$$

diastereoselectivity of ring closure to be 20% ee and 1.8, respectively. A relative diastereoselectivity > 1 (i.e.,  $[k_{\text{major}}]_{\text{cis}} / [k_{\text{major}}]_{\text{trans}} > [k_{\text{minor}}]_{\text{cis}} / [k_{\text{minor}}]_{\text{trans}}$ ) would imply that the production of the minor *cis*-epoxide from  $I_2$  is relatively disfavored, or that of the major *cis*-epoxide from  $I_1$  is favored, by the ligand dissymmetry. Therefore, the different degrees to which the diastereomeric  $I_1$  and  $I_2$  to undergo *cis*–*trans* isomerization would lead to an ee enhancement of the major *cis*-epoxide by 10% ee (compare  $ee_{\text{obs}} = 30\%$  ee with  $ee_{\text{facial}} = 20\%$  ee). This finding indeed coincides with the previous findings by Jacobsen.<sup>34</sup> When complex **1e** bearing the sterically bulky 6,6'-dichloro-2,2'-bipyridine ligand was used as the oxidant, the reaction with *cis*- $\beta$ -methylstyrene attained an enantioselectivity of 59% ee and >99% *cis* retention. In this case, the ee improvement should only arise from better facial selectivity as  $ee_{\text{obs}} = ee_{\text{facial}} = 59\%$  ee.

The poor enantioselectivity (1% ee) of the *trans*-(1*R*,2*R*)-epoxide produced from the *cis*- $\beta$ -methylstyrene oxidation by complex **1d** is striking because the same ruthenium oxidant was found to react with *trans*- $\beta$ -methylstyrene to give the *trans*-(1*R*,2*R*)-epoxide in 12% ee. Unlike the *cis*-alkene oxidations, the  $ee_{\text{obs}}$  for the oxidation of the *trans*-alkene should be determined only by the facial selectivity, i.e.,  $ee_{\text{facial}}$ . Thus, the ee discrepancy of the *trans*-epoxides obtained from the *cis*- and *trans*- $\beta$ -methylstyrene oxidations suggests that the difference of the diastereoselectivities of ring closure of the diastereomeric benzylic radical intermediates  $I_1$  and  $I_2$  has caused an 11% ee reduction (cf. 10% ee enhancement for the *cis*-epoxide) for the *trans*-(1*R*,2*R*)- $\beta$ -methylstyrene oxide production.

### Conclusion

With regards to the mechanism of aromatic alkene oxidations by oxoruthenium(IV) complexes, the following findings can be concluded:

(i) The stereoselectivity for the epoxide formation varies with both the alkenes and the ruthenium oxidants; it decreases in the order *cis*-stilbene > *cis*- $\beta$ -methylstyrene > *cis*- $\beta$ -deuteriostyrene. The sterically bulky  $[\text{Ru}^{\text{IV}}(\text{PPz}^*)(6,6'\text{-Cl}_2\text{-bpy})\text{O}](\text{ClO}_4)_2$  complex can afford a better stereoselectivity than the other ruthenium oxidants.

(ii) The observation of inverse secondary KIE for the oxidation of  $\beta$ -*d*<sub>2</sub>-styrene [ $k_{\text{H}}/k_{\text{D}} = 0.87$  for **1b** and  $k_{\text{H}}/k_{\text{D}} = 0.86$  for **1d**] and its absence in the  $\alpha$ -deuteriostyrene oxidations are incompatible with either a rate-limiting formation of a metallaoxetane or a concerted oxene insertion mechanism.

(iii) The second-order rate constants for the styrene oxidations are insensitive to the variation of the  $E^\circ(\text{Ru}^{\text{IV/III}})$  of the ruthenium oxidants and para substituents of styrene.

(iv) A linear free-energy correlation between the  $\log(k_{\text{rel}})$  and the TE for the ruthenium oxidation of para substituted styrenes is established. Thus, aromatic alkene oxidations by oxoruthenium(IV) complexes should proceed via the rate-limiting formation of a benzylic

radical intermediate. The stability of the benzylic radical is dependent on the spin delocalization (major) and charge (minor) effects exerted by the para substituents.

Complex **1d** can induce moderate enantioselectivities for the oxidation of styrene (37% ee), *cis*- $\beta$ -methylstyrene (30% ee for the *cis*-epoxide, 1% ee for the *trans*-epoxide), and *trans*- $\beta$ -methylstyrene (12% ee for the *trans*-epoxide). Because of the nonconcerted nature of the epoxidation reaction, the product enantioselectivity (%  $ee_{\text{obs}}$ ) is not established at the first irreversible C–O bond formation step, that is,  $ee_{\text{obs}} \neq ee_{\text{facial}}$ . Because the acyclic carbonyl radical intermediate undergoes collapse (*cis*) and rotation/collapse (*trans*) processes before the epoxide ring closure, the stereoselectivity of epoxide ring closure is also important in controlling the product enantioselectivity. In this study, we found that a 6,6'-dichloro-substituted 2,2'-bipyridine ligand could improve the enantioselectivities of styrene/*cis*- $\beta$ -methylstyrene epoxidations by promoting the facial selectivity and the stereoselectivity of ring closure.

### Experimental Section

Solvents were of analytical grade and were purified by the standard procedures. Acetonitrile (AR, LabScan) for stoichiometric oxidations and kinetic experiments was first distilled from alkaline potassium permanganate and then over calcium hydride under a nitrogen atmosphere. Deionized water was distilled from alkaline potassium permanganate prior to use. Silver trifluoromethanesulfonate (99+%, Aldrich) was dried in a vacuum oven and stored in a desiccator. The alkene substrates were purified by either vacuum distillation or recrystallization, and their purities were checked by GC or <sup>1</sup>H NMR analysis. *cis*- $\beta$ -Methylstyrene,<sup>34</sup> *cis*- $\beta$ -deuteriostyrene,<sup>34</sup>  $\beta$ -*d*<sub>2</sub>-styrene,<sup>35a,b</sup> and  $\alpha$ -deuteriostyrene<sup>35a,c</sup> were prepared according to the literature procedures. The ruthenium complexes  $[\text{Ru}^{\text{IV}}(\text{terpy})(6,6'\text{-Cl}_2\text{bpy})\text{O}](\text{ClO}_4)_2$  (**1a**),<sup>9b</sup>  $[\text{Ru}^{\text{IV}}(\text{terpy})(\text{tmeda})\text{O}](\text{ClO}_4)_2$  (**1b**),<sup>12</sup> and  $[\text{Ru}^{\text{IV}}(\text{Cn})(\text{bpy})\text{O}](\text{ClO}_4)_2$  (**1c**)<sup>13</sup> were prepared by Ce(IV) oxidation of the aquaruthenium(II) complexes according to the reported procedures.

A modified procedure for the preparation of  $[\text{Ru}^{\text{IV}}(\text{PPz}^*)(\text{bpy})\text{O}](\text{ClO}_4)_2$  (**1d**)<sup>7f</sup> is described following those for the  $\text{Ru}^{\text{II}}$  complexes.

**$[\text{Ru}^{\text{II}}(\text{PPz}^*)(\text{bpy})\text{Cl}]\text{ClO}_4$ .** A mixture of  $[\text{Ru}^{\text{III}}(\text{PPz}^*)\text{Cl}_3]$  (0.31 mmol, 200 mg), 2,2'-bipyridine (0.31 mmol, 50 mg), LiCl (0.4 g), and triethylamine (0.5 mL) in ethanol (150 mL) was refluxed for 2 h. After being cooled to room temperature, the red solution was filtered, and solvent was removed to ca. 10 mL by rotary evaporation. A brown-red solid was precipitated upon addition of a saturated sodium perchlorate solution (20 mL). The crude product was collected by filtration, washed with water followed by diethyl ether, and dried in vacuo. The titled complex was recrystallized from dichloromethane/diethyl ether. Yield: 75%. Anal. Calcd for  $\text{C}_{37}\text{H}_{41}\text{N}_7\text{Cl}_2\text{O}_4\text{Ru}$ : C, 54.21; H, 5.04; N, 11.96. Found: C, 53.94; H, 5.18; N, 11.71. FAB-MS *m/z*: 721 ( $\text{M} - \text{ClO}_4$ )<sup>+</sup>.  $E^\circ(\text{Ru}^{\text{III/II}}) = 0.35$  V versus  $\text{Cp}_2\text{Fe}^{+/0}$  in a 0.1M *n*-Bu<sub>4</sub>NPF<sub>6</sub>/acetonitrile solution. UV–vis (MeOH)  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon_{\text{max}}/\text{cm}^{-1} \text{M}^{-1}$ ): 287 (47 200), 324 (29 500), 394 (4670), 463 (5480).

**$[\text{Ru}^{\text{II}}(\text{PPz}^*)(6,6'\text{-Cl}_2\text{-bpy})\text{Cl}]\text{ClO}_4$ .** A mixture of  $[\text{Ru}^{\text{III}}(\text{PPz}^*)\text{Cl}_3]$  (0.31 mmol, 200 mg), 6,6'-dichloro-2,2'-bipyridine (0.31 mmol, 80 mg), and LiCl (0.4 g) in ethylene glycol (10 mL) was heated to 140 °C for 4 h under a nitrogen atmosphere. After being cooled, the red solution was added to a saturated sodium perchlorate solution. The resulting red solid was

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collected on a frit, washed with ice-cold water followed by diethyl ether, and dried in vacuo. Yield: 65%. Anal. Calcd for  $C_{37}H_{39}N_7Cl_4O_4Ru$ : C, 50.01; H, 4.42; N, 11.03. Found: C, 49.75; H, 4.66; N, 10.98. FAB-MS  $m/z$ : 790 ( $M - ClO_4$ )<sup>+</sup>.  $E^{\circ}(Ru^{III/II}) = 0.46$  V versus  $Cp_2Fe^{+/0}$  in 0.1M *n*-Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution. UV-vis (in MeOH)  $\lambda_{max}/nm$  ( $\epsilon_{max}/cm^{-1} M^{-1}$ ): 285 (43 300), 317 (42 600), 482 (5300).

**[Ru<sup>II</sup>(PPz\*)(bpy)(H<sub>2</sub>O)](OTf)<sub>2</sub>.** A mixture of [Ru<sup>II</sup>(PPz\*)(bpy)Cl]ClO<sub>4</sub> (0.12 mmol, 100 mg) and silver trifluoromethanesulfonate (1.1 equiv) in an acetone/water mixture (25 mL, 1:1 v/v) was heated at reflux for 30 min. After being cooled to room temperature, the red solution was filtered to remove the insoluble silver chloride. The complex was isolated by precipitation with an aqueous ammonium trifluoromethanesulfonate solution. Recrystallization was performed by dissolving the crude product in a minimum amount of hot water; the red solution was kept in a refrigerator (5 °C) overnight. The red microcrystalline solids deposited were collected by filtration and dried in vacuo. Yield: 80%. Anal. Calcd for  $C_{39}H_{43}N_7O_7F_6S_2Ru$ : C, 46.80; H, 4.33; N, 9.79. Found: C, 45.86; H, 4.50; N, 9.69. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  -0.07 (s, 3H), 0.08 (s, 3H), 0.13 (s, 3H), 0.22 (m, 1H), 0.60 (s, 3H), 0.75 (s, 3H), 0.81 (s, 3H), 0.87 (m, 1H), 1.19 (m, 1H), 1.29 (m, 1H), 1.50 (m, 1H), 1.75 (m, 1H), 1.90 (m, 1H), 2.08 (m, 1H), 2.83 (d, 2H,  $J = 3.6$  Hz), 7.17 (m, 1H), 7.43 (d, 1H,  $J = 5.3$  Hz), 7.75 (d, 1H,  $J = 4.2$  Hz), 7.77 (d, 1H,  $J = 4.1$  Hz), 7.85 (m, 2H), 8.25 (m, 4H), 8.41 (d, 1H,  $J = 8.1$  Hz), 8.61 (d, 1H,  $J = 8.1$  Hz), 9.77 (d, 1H,  $J = 5.5$  Hz). UV-vis (in H<sub>2</sub>O/MeOH, 1:1 v/v)  $\lambda_{max}/nm$  ( $\epsilon_{max}/cm^{-1} M^{-1}$ ): 286 (46 500), 324 (26 800), 375 (3870), 446 (5140).

**[Ru<sup>II</sup>(PPz\*)(6,6'-Cl<sub>2</sub>-bpy)(H<sub>2</sub>O)](OTf)<sub>2</sub>.** The same procedure as for the preparation of [Ru<sup>II</sup>(PPz\*)(bpy)(H<sub>2</sub>O)](OTf)<sub>2</sub> was adopted here. Anal. Calcd for  $C_{39}H_{41}N_7O_7Cl_2F_6S_2Ru$ : C, 43.78; H, 3.87; N, 9.17. Found: C, 43.33; H, 3.99; N, 8.94. <sup>1</sup>H NMR (270 MHz, CD<sub>3</sub>CN):  $\delta$  0.14 (s, 3H), 0.15 (s, 3H), 0.34 (s, 3H), 0.51 (s, 3H), 0.68 (m, 1H), 0.84 (s, 3H), 0.85 (s, 3H), 0.97 (m, 1H), 1.32 (m, 1H), 1.69 (m, 2H), 2.81 (d, 1H,  $J = 3.9$  Hz), 2.96 (d, 1H,  $J = 4.1$  Hz), 7.30 (m, 1H), 7.61 (d, 1H,  $J = 8.3$  Hz), 7.68 (d, 1H,  $J = 7.8$  Hz), 7.84 (m, 1H), 8.06 (m, 1H), 8.17 (s, 1H), 8.24 (m, 2H), 8.33 (m, 1H), 8.39 (s, 1H), 8.51 (m, 1H). UV-vis (in H<sub>2</sub>O/MeOH, 1:1 v/v)  $\lambda_{max}/nm$  ( $\epsilon_{max}/cm^{-1} M^{-1}$ ): 286 (44 500), 317 (42 900), 469 (5400).

**[Ru<sup>IV</sup>(PPz\*)(bpy)O](ClO<sub>4</sub>)<sub>2</sub> (1d).** To an ice-cooled solution of [Ru<sup>II</sup>(PPz\*)(bpy)(H<sub>2</sub>O)](OTf)<sub>2</sub> (0.10 mmol, 100 mg) in deionized water (50 mL) was added an ammonium cerium(IV) nitrate solution (200 mg in 5 mL of water), causing an immediate color change from red to yellow. The titled complex was isolated as a yellow solid by adding a saturated sodium perchlorate solution. The product was collected on a frit, washed with a small amount of cold water, and then dried in vacuo. Yield: 70%. Anal. Calcd for  $C_{37}H_{39}N_7O_9Cl_2Ru$ : C, 49.39; H, 4.59; N, 10.90. Found: C, 49.18; H, 4.68; N, 10.73. Magnetic moment  $\mu_{eff}$  (room temperature) = 2.91  $\mu_B$ . UV-vis (in MeCN)  $\lambda_{max}/nm$  ( $\epsilon_{max}/cm^{-1} M^{-1}$ ): 287 (45 100). IR (Nujol mull): 788  $cm^{-1}$  ( $\nu_{Ru=O}$ ).

**[Ru<sup>IV</sup>(PPz\*)(6,6'-Cl<sub>2</sub>-bpy)O](ClO<sub>4</sub>)<sub>2</sub> (1e).** The same procedure as for the preparation of [Ru<sup>IV</sup>(PPz\*)(bpy)O](ClO<sub>4</sub>)<sub>2</sub> was adopted here. Yield: 45%. Anal. Calcd for  $C_{37}H_{39}N_7O_9Cl_2Ru$ : C, 45.88; H, 4.06; N, 10.12. Found: C, 45.75; H, 3.98; N, 9.82. Magnetic moment  $\mu_{eff}$  (room temperature) = 2.89  $\mu_B$ . UV-vis (in MeCN)  $\lambda_{max}/nm$  ( $\epsilon_{max}/cm^{-1} M^{-1}$ ): 287 (44 900). IR (Nujol mull): 792  $cm^{-1}$  ( $\nu_{Ru=O}$ ). *Caution: Metal perchlorate salts are potentially explosive and must be handled in small quantities with proper safety precautions.*

**General Procedures for the Stoichiometric Oxidation of Alkenes by Oxoruthenium(IV) Complexes and the Isolation of [Ru<sup>II</sup>(L<sup>1</sup>)(L<sup>2</sup>)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> Complexes.** The ruthenium oxidant (50  $\mu$ mol) was added to an acetonitrile solution (4 mL) containing alkene (1–2 mmol) in a 25-mL round-bottom flask under a nitrogen atmosphere. The solution mixture was stirred for 12 h at room temperature. [Ru<sup>II</sup>(L<sup>1</sup>)(L<sup>2</sup>)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> was isolated by precipitation using diethyl ether (>95% yield) and recrystallized by the slow diffusion of diethyl ether into an acetonitrile solution. An internal stan-

dard was added to the organic filtrate, and an aliquot was taken for analysis by GC or <sup>1</sup>H NMR for product identification and quantification. The ee of chiral epoxides was determined either by GC analysis using chiral columns [Cyclodex-B (J&W Scientific, 30 m  $\times$  0.25 mm i.d., 0.25- $\mu$ m thickness), Chiraldex G-TA (Astec, 30 m  $\times$  0.32 mm i.d., 0.125- $\mu$ m thickness)], or by <sup>1</sup>H NMR analysis using the chiral shift reagent (–)-tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III), Eu(hfc)<sub>3</sub>. The *cis*–*trans*-epoxide ratios for the *cis*- $\beta$ -deuteriostyrene oxidations were evaluated from the integration ratio of the appropriate proton resonance: *cis*- $\beta$ -deuteriostyrene oxide ( $\delta$ H = 3.18 ppm) and *trans*- $\beta$ -deuteriostyrene oxide ( $\delta$ H = 2.80 ppm).

Characterizations of complexes **2a**,<sup>19b</sup> **2b**,<sup>12</sup> and **2c**<sup>13</sup> have already been reported elsewhere.

**[Ru<sup>II</sup>(PPz\*)(bpy)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> (2d).** Anal. Calcd for  $C_{39}H_{44}N_8O_8Cl_2Ru$ : C, 50.65; H, 4.80; N, 12.12. Found: C, 49.64; H, 4.75; N, 11.76. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  -0.06 (s, 3H), 0.09 (s, 3H), 0.13 (s, 3H), 0.25 (m, 1H), 0.59 (s, 3H), 0.75 (s, 3H), 0.81 (s, 3H), 0.85 (m, 1H), 1.19 (m, 1H), 1.30 (m, 1H), 1.50 (m, 1H), 1.75 (m, 1H), 1.90 (m, 1H), 2.06 (m, 1H), 2.82 (d, 2H,  $J = 3.4$  Hz), 7.18 (m, 1H), 7.43 (d, 1H,  $J = 4.9$  Hz), 7.93 (m, 4H), 8.28 (m, 2H), 8.48 (s, 1H), 8.51 (s, 1H), 8.53 (d, 1H,  $J = 7.9$  Hz), 8.76 (d,  $J = 8.1$  Hz), 9.82 (d, 1H,  $J = 5.4$  Hz). IR (Nujol): 2256  $cm^{-1}$  ( $\nu_{C=N}$ ). UV-vis (in MeCN)  $\lambda_{max}/nm$  ( $\epsilon_{max}/cm^{-1} M^{-1}$ ): 285 (44 700), 317 (28 400), 424 (5730). FAB-MS  $m/z$ : 826 ( $M - ClO_4$ )<sup>+</sup>.

**[Ru<sup>II</sup>(PPz\*)(6,6'-Cl<sub>2</sub>-bpy)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> (2e).** Anal. Calcd for  $C_{39}H_{42}N_8O_8Cl_2Ru$ : C, 47.14; H, 4.26; N, 11.28. Found: C, 48.16; H, 4.34; N, 11.62. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN):  $\delta$  0.13 (s, 3H), 0.15 (s, 3H), 0.35 (s, 3H), 0.52 (s, 3H), 0.69 (m, 1H), 0.83 (s, 3H), 0.84 (s, 3H), 0.97 (m, 1H), 1.30 (m, 1H), 1.70 (m, 2H), 2.82 (d, 1H,  $J = 4.0$  Hz), 2.95 (d, 1H,  $J = 4.1$  Hz), 7.32 (m, 1H), 7.59 (d, 1H,  $J = 8.1$  Hz), 7.67 (d, 1H,  $J = 7.9$  Hz), 7.85 (m, 1H), 8.05 (m, 1H), 8.15 (s, 1H), 8.25 (m, 2H), 8.34 (m, 1H), 8.37 (s, 1H), 8.52 (m, 1H). UV-vis (in MeCN)  $\lambda_{max}/nm$  ( $\epsilon_{max}/cm^{-1} M^{-1}$ ): 284 (40 900), 311 (41 200), 446 (5980). FAB-MS  $m/z$ : 895 ( $M - ClO_4$ )<sup>+</sup>.

**Kinetic Studies for Alkene Oxidations by Oxoruthenium(IV) Complexes.** Kinetic experiments were performed on a diode array UV-vis spectrophotometer interfaced with an IBM-compatible PC. The measurements were made in standard 1.0 cm quartz cuvettes. The solution temperature during kinetic experiments was maintained to within  $\pm 0.2$  °C using a circulating water bath. The oxidation of alkenes by the oxoruthenium(IV) complexes was followed by monitoring the growth of the MLCT band of [Ru<sup>II</sup>(L<sup>1</sup>)(L<sup>2</sup>)(MeCN)](ClO<sub>4</sub>)<sub>2</sub> (**2**) under the condition that the concentration of alkenes was at least 100-fold in excess of the ruthenium oxidants. Pseudo-first-order rate constants,  $k_{obs}$ , were obtained by nonlinear least-squares fits of  $(A_f - A_t)$  to time ( $t$ ) according to the equation:

$$(A_f - A_t) = (A_f - A_i) \exp(-k_{obs} t)$$

where  $A_i$  and  $A_f$  are the initial and final absorbances, respectively, and  $A_t$  is the absorbance at time  $t$ . Kinetic data over 4 half-lives ( $t_{1/2}$ ) were used for the least-squares fitting. Second-order rate constants,  $k_2$ , were obtained from the linear fit of the  $k_{obs}$  values to the alkene concentrations.

Activation enthalpy ( $\Delta H^\ddagger$ ) and activation entropy ( $\Delta S^\ddagger$ ) were calculated from the linear plot of  $\ln(k_2/T)$  versus  $(1/T)$  according to the Eyring equation:

$$\ln(k_2/T) = \ln(R/N_A h) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT$$

where  $T$  is the temperature in Kelvin scale (K),  $N_A$  is Avogadro's number,  $R$  is the universal gas constant, and  $h$  is Planck's constant.

**Acknowledgment.** We acknowledge support by The University of Hong Kong and the Hong Kong Research Grants Council. We are also thankful to Dr. Wing-Chi Cheng for his contribution at the early stage of this work



and to Dr. Kung-Kai Cheung for X-ray structure determination of  $[\text{Ru}^{\text{II}}(\text{PPz}^*)(6,6'\text{-Cl}_2\text{-bpy})(\text{MeCN})](\text{ClO}_4)_2$ .

**Supporting Information Available:** This material contains characterization data of the ruthenium complexes, X-ray structure of  $[\text{Ru}^{\text{II}}(\text{PPz}^*)(6,6'\text{-Cl}_2\text{-bpy})(\text{MeCN})](\text{ClO}_4)_2$  including

tables of crystal data, atom coordinates, and structure refinement (25 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO980755C