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<td>Che, CM; Yu, WY</td>
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Ruthenium-oxo and -tosylimido porphyrin complexes for epoxidation and aziridination of alkenes*

Chi-Ming Che and Wing-Yiu Yu

Abstract: Dioxoruthenium(VI) porphyrins including those containing chiral porphyrinato ligands can be readily prepared by oxidation of [Ru II(Por)(CO)(MeOH)] with PhIO or meta-chloroperoxybenzoic acid. Similar reactions with PhINTs gave [Ru VI(Por)(NTs)2] isolated as air stable solids at room temperature. The [Ru VI(Por)O2] complexes are competent oxidants for epoxidation of alkenes with high selectivities. Enantioselective epoxidation of alkenes giving the corresponding organic epoxides with moderate to good enantioselectivities have also been achieved using chiral [Ru VI(D4-Por*)O2] [D4-Por* = 5,10,15,20-tetrakis-(1S,4R,5R,8S-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl)porphyrin] and [Ru VI(D2-Por*)O2] complexes. The mechanism of alkene epoxidation by [Ru VI(Por)O2] has been examined. Procedures for catalytic epoxidation of alkenes using ruthenium porphyrin catalysts has also been developed. [Ru VI(Por)(NTs)2] was found to undergo aziridination of alkenes and amidation of alkanes in organic solvents at room temperature.

INTRODUCTION

The formation of carbon—oxygen and carbon—nitrogen bonds with desirable selectivity remains one of the important challenges to synthetic chemists. A clue to this problem would be to develop new metal catalysts for these transformations. Despite the recent advances in metal catalyzed epoxidation [1] and aziridination of alkenes [2], the reactive intermediate(s) involved in these catalytic reactions remain poorly understood, and hence it is often difficult to improve the catalytic reactions in a rational manner. We conceive that by studying the stoichiometric reactions of reactive metal-oxo and -imido complexes having well-defined structures with alkenes should provide valuable knowledge on the structure-reactivity relationship [3], which would facilitate rational catalysts design. Extensive studies showed that high-valent ruthenium-oxo complexes in various oxidation states and with tunable physical and chemical properties can be isolated using a variety of macrocyclic ligands [4]. In particular, trans-dioxoruthenium(VI) complexes containing porphyrinato ligands are an important class of ruthenium oxidants [5]. This class of compounds are neutral and readily dissolve in nonpolar organic solvents, and yet are reactive toward alkene epoxidations and alkane hydroxylation. Furthermore, they can be modified by attaching chiral auxiliaries onto the porphyrinato ligands, thus providing an access to highly reactive chiral metal-oxo reagents [5d,6]. Recent studies by our research group revealed that a reactive bis(tosylimido)ruthenium(VI) complex, which is isoelectronic to a dioxoruthenium(VI), could also be prepared using porphyrins as supporting ligands [7]. Thus, the dioxo-and bis(tosylimido)-ruthenium(VI) porphyrins provide a unique opportunity to probe the mechanism of metal-mediated oxygen and nitrogen atom transfer reactions pertinent to the understanding of the asymmetric epoxidation and aziridination (Fig. 1).

SYNTHESIS OF DIOXO-AND BIS(TOSYLIMIDO)-RUTHENIUM(VI) PORPHYRINS

Dioxo-and bis(tosylimido)ruthenium(VI) porphyrin complexes are readily derived from carbonylruthenium(II) porphyrins using m-chloroperoxybenzoic acid (mcpba) and [N-(p-toluenesulfonyl)jimino]phenyliodinane

(PhINTs) as the source of oxygen and nitrogen, respectively. Carbonylruthenium(II) porphyrins, [(Por)RuII(CO)(MeOH)], are usually prepared by reacting [Ru3CO12] with the free-base porphyrins in refluxing toluene or other high boiling hydrocarbon solvents such as decalin and xylene. For some sterically bulky meso-tetraarylporphyrins, for instance tetrakis-(3,4,5-trimethoxyphenyl)porphyrin, tetrakis-(3,5-di-tert-butylphenyl)porphyrin and tetrakis-(2,4,6-trimethoxyphenyl)porphyrin, the metal insertion reactions should be carried out in either toluene or xylene at 120–175 °C under a sealed-tube condition for 5–24 h. However, metal insertion to meso-tetakis(2,6-dichlorophenyl)porphyrin (H2TDCPP) should employ molten naphthalene at 220 °C as reaction medium to obtain the best result. After purification of the crude ruthenium(II) complexes by chromatography on an alumina column, followed by recrystallization from a CH2Cl2/MeOH mixture, the carbonylruthenium(II) porphyrins were isolated in 50–90% yield as an adduct of methanol.

Treatment of [RuII(Por)(CO)(MeOH)] complexes with mcpba in CH2Cl2/EtOH at room temperature afforded the corresponding dioxoruthenium(vi) porphyrin complexes in good yields (75–80%); the product complexes were isolated as air-stable solids. The presence of alcohol has proved crucial for the success of the synthesis, especially for those dioxoruthenium(vi) complexes containing nonsterically encumbered porphyrin ligands such as octaethylporphyrin (H2OEP) and tetraphenylporphyrin (H2TPP) [8]. No complication of μ-oxo formation via dimerization was observed. Presumably, the alcohol molecule coordinated to the putative Ru(IV) intermediate thus inhibiting the dimerization reaction (Scheme 1) [9]. Alternatively, trans-dioxoruthenium(vi) complexes of sterically encumbered porphyrins, such as, H2DPP, H2TDCPP and H2TMOPP (Fig. 1), can be readily prepared by oxidation of the carbonylruthenium(II), [(Por)RuII(CO)(MeOH)], complexes with iodosylbenzene (PhIO) in CH2Cl2. The analogous bis(tosylimido)ruthenium(vi) complexes were prepared by reacting [(Por)RuII(CO)(MeOH)] with PhINTs in CH2Cl2 [7]. The crude oxo- and bis(tosylimido)-ruthenium products could be purified by column chromatography on a dry alumina column using CH2Cl2 as the eluant, or by recrystallization from CH2Cl2/acetonitrile. Indeed, by employing the above synthetic method, trans-dioxo- and bis(tosylimido)-ruthenium(vi) containing a variety porphyrin ligands including those with chiral auxiliaries can be obtained.

![Scheme 1](image_url)

**Scheme 1** Synthesis of dioxo- and bis(tosylimido)ruthenium(vi) porphyrins.
The asymmetric O=Ru=O stretches for the trans-dioxoruthenium(vi) porphyrins occur at around 820 cm\(^{-1}\) (Table 1), and for \([\text{Ru}^{VI}(p-X\text{-TPP})\text{O}_2]\) \((p-X = \text{H, Cl, Me, OMe})\), the frequencies are invariant to the para-substituents on the meso-phenyl groups. The ‘characteristic imido bands’ for a series of \([\text{Ru}^{VI}(\text{Por})(\text{NTs})_2]\) were found to be within a 900–930 cm\(^{-1}\) range. The infra-red spectra of the ruthenium porphyrin complexes revealed a strong and sharp absorption near 1000 cm\(^{-1}\) which is assigned as the rocking vibrations of the porphyrin ring or the pyrrole units. The position of this band (here referred as oxidation marker band) is sensitive to the strength of the metal-nitrogen bond and can be related to the oxidation state of the ruthenium complexes. As shown in Table 1, the oxidation state marker band of the \([\text{Ru}^{VI}(\text{Por})(\text{CO})(\text{MeOH})]\) complexes lies within 1007–1009 cm \(^{-1}\) range, whereas for \([\text{Ru}^{VI}(\text{Por})\text{O}_2]\) and \([\text{Ru}^{VI}(\text{Por})(\text{NTs})_2]\) complexes the absorption bands are located in 1017–1020 cm\(^{-1}\). An X-ray crystal structure has been obtained for a chiral \([\text{Ru}^{VI}(D_4\text{-Por}*)\text{O}_2]\) complex \([D_4\text{-H}_2\text{Por}^* = 5,10,15,20\text{-tetraakis-(1S,4R,5R,8S-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl)porphyrin}]\) with Ru–O distances being 1.73 \(\pm 1\) and 1.75 \(\pm 1\) Å [6] (Table 1).

### Table 1 Positions of characteristic infra-red absorption bands of selected dioxo-and bis(tosylimido)-ruthenium(vi) porphyrins

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Oxidation state marker band (cm (^{-1}))</th>
<th>(\nu_{\text{ao}}(\text{RuO}_2)) (cm (^{-1}))</th>
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<tr>
<td>([\text{Ru}^{VI}(\text{TPP})\text{O}_2])</td>
<td>1017</td>
<td>819</td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(\text{OEP})\text{O}_2])</td>
<td>1018</td>
<td>822</td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(\text{DPP})\text{O}_2])</td>
<td>1012</td>
<td>818</td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(\text{TDCPP})\text{O}_2])</td>
<td>1017</td>
<td>824</td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(\text{TMP})\text{O}_2])</td>
<td>1021</td>
<td>820</td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(p-\text{Cl-TPP})\text{O}_2])</td>
<td>821</td>
<td></td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(p-\text{Me-TPP})\text{O}_2])</td>
<td>823</td>
<td></td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(p-\text{MeO-TPP})\text{O}_2])</td>
<td>821</td>
<td></td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(\text{TPP})(\text{NTs})_2])</td>
<td>1016</td>
<td>914 (characteristic imido band)</td>
</tr>
<tr>
<td>([\text{Ru}^{VI}(\text{OEP})(\text{NTs})_2])</td>
<td>1018</td>
<td>900 (characteristic imido band)</td>
</tr>
</tbody>
</table>

Both the \([\text{Ru}^{VI}(\text{Por})\text{O}_2]\) and \([\text{Ru}^{VI}(\text{Por})(\text{NTs})_2]\) complexes are diamagnetic solids in accordance with a \((d_{xy})^2\) ground state. The symmetric and planar dioxo-and bis(tosylimido)-ruthenium(vi) complexes of tetraarylporphyrins display well-resolved \(^1\)H NMR spectra which reveal a pseudo \(D_{4h}\) symmetry. In general, the pyrrolic proton signals of the oxo-and imido-ruthenium(vi) porphyrins are about 0.4 p.p.m. down-field shifted from those of the carboxylruthenium(II) precursors; nevertheless, their values are rather insensitive to the para-substituents on the meso-phenyl groups. The \(^1\)H NMR spectrum of the saddle-distorted \([\text{Ru}^{VI}(\text{DPP})\text{O}_2]\) complex (DPP = dodecaphenylporphyrin dianion) [10] showed a broad doublet at \(\delta 7.44\) \((J = 7.0\) Hz, 8H) assignable to the ortho protons at the meso-phenyl rings, and two sets of multiplets at \(\delta 6.8\) corresponding to the remaining 52 protons. The variable temperature NMR of the free \(\text{H}_2\text{DPP}\) revealed that the ligand can undergo NH tautomerism and macrocyclic inversion, and the free energy of activation for the latter was estimated to be 10.9 kcal/mol. However, no dynamic processes were observed for the saddle-distorted \([\text{Ru}^{VI}(\text{DPP})\text{O}_2]\). Since the nonplanar distorted structure of the metalloporphyrin had been established by X-ray crystallography, the free energy of activation for the ring inversion of the dioxoruthenium(vi) complex should be probably small (\(<7\) kcal/mol) [10].

The UV-vis spectra of \([\text{Ru}^{VI}(\text{Por})\text{O}_2]\) are featured mainly by the B band (Soret band) and a less intense Q band typical of a normal porphyrin, the Q band is split to \(\alpha\) and \(\beta\) bands in the OEP system. The analogous imidoruthenium(vi) porphyrins also exhibit similar UV-vis spectral feature. UV-vis spectral data of some selected dioxoruthenium(vi) porphyrins are listed in Table 2. It is noteworthy that both the Soret and Q bands of \([\text{Ru}^{VI}(\text{DPP})\text{O}_2]\) are red-shifted compared with those of \([\text{Ru}^{VI}(\text{TPP})\text{O}_2]\). Theoretical calculations [11] performed by other workers have indeed suggested that the steric-induced macrocyclic distortion would lead to a larger destabilization of the ligand’s HOMOs than its LUMOs, hence the smaller HOMO-LUMO gap results in the red-shift of the optical spectrum (Table 2).
The cyclic voltammograms of \([\text{Ru VI}(\text{Por})\text{O}_2]\) in 0.1 M \(\text{Bu}_4\text{NPF}_6\)-CH\(_2\)Cl\(_2\) show one reversible oxidation couple and one irreversible reduction wave (Table 3). The oxidation couple is tentatively assigned as the ligand-centred oxidation \([\text{Ru VI}(\text{Por})\text{O}_2]\)–e \(\rightarrow\) \([\text{Ru VI}(\text{Por}^+\text{)}\text{O}_2]\), and the \(E^\circ/H_11034\) values for a series of dioxoruthenium(VI) tetraarylporphyrins (Ar = X-C\(_6\)H\(_4\); X = 4-Cl, H, 4-Me and 4-MeO) being 0.86, 0.77, 0.72 and 0.64 V vs. \(\text{Cp}_2\text{Fe}^+/0\), respectively. These values differ slightly with the variation of the para-substituents. As expected the ligand-centred oxidation of the saddle-shaped distorted \([\text{Ru VI}(\text{DPP})\text{O}_2]\) occurs at 0.55 V vs. \(\text{Cp}_2\text{Fe}^+/0\), which amounts to a 240-mV drop in the oxidation potential compared with \(E^\circ/H_11034\) value of 0.79 V for \([\text{Ru VI}(\text{TPP})\text{O}_2]\). The change in the \(E^\circ\) value is again due to the destabilization of the HOMOs induced by conformational distortion of the porphyrin ring [10] (Table 3).

**STOICHIOMETRIC ALKENE EPOXIDATIONS AND AZIRIDINATIONS.**

All the trans-dioxoruthenium(vi) porphyrins function as a competent two-electron oxidant for alkene oxidations in a CH\(_2\)Cl\(_2\)-EtOH or CH\(_2\)Cl\(_2\)-Hpz mixture (Hpz = pyrazole) under ambient conditions. Unlike the analogous cationic macrocyclic dioxoruthenium(VI) complexes that gave substantial C=C cleavage products upon reactions with alkenes, the oxidation of alkenes by \([\text{Ru VI}(\text{Por})\text{O}_2]\) afforded epoxides in good yields. When the oxidation reactions were carried out in the presence of pyrazole, \([\text{Ru VI}(\text{Por})(\text{pz})_2]\) were found as the reaction products. The \([\text{Ru VI}(\text{Por})(\text{pz})_2]\) products are paramagnetic (\(\mu_{\text{eff}} = 2.8 \mu_\text{B}\)) and the oxidation state marker bands are located around 1019 cm \(^{-1}\), consistent with a Ru(IV) formulation.

The reactions of \([\text{Ru VI}(\text{Por})\text{O}_2]\) with alkenes follow a second-order rate law, rate \(= k_2[\text{Ru}][\text{alkene}]\), where \(k_2 = \text{second-order rate constant}\). The \(k_2\) values were determined from the linear plots of the pseudo-first-order rate constants \((k_{\text{obs}})\) vs. alkene concentrations, i.e. when [alkene] \(>>\) [Ru], then \(k_{\text{obs}} = k_2[\text{alkene}]\). Second-order rate constants obtained with some dioxoruthenium(vi) porphyrins are listed in Table 4. It is interesting to note that the styrene and norbornene oxidations by the saddle-distorted
[RuVI(DPP)O2] complex have a comparable \( k_2 \) value as those for the planar [RuVI(TPP)O2] analogue [10], although nonplanar distorted metalloporphyrin catalysts were reported to display enhanced catalytic activities toward hydrocarbon oxidations. To account for the similar reactivities of the planar and the saddle-distorted dioxoruthenium(VI) complexes, we proposed that the macrocyclic distortion should mainly destabilize the ligand’s HOMO energies, however, the LUMOs related to the O=Ru=O moiety are relatively less perturbed (Table 4).

Stereoselective oxidation of cis-alkenes as compared to trans-alkenes are well documented for the metalloporphyrin-catalyzed epoxidation of alkenes, and a ‘side-on approach’ model was first proposed by Groves and co-workers [12] to rationalize the cis- vs. trans-alkenes selectivity. In our studies, all the [RuVI(Por)O2] complexes did not react with trans-stilbene but readily acted on cis-stilbene to afford cis-stilbene oxide in good yield, and >99% stereoretention has often been attained for most of the oxoruthenium complexes, except for [RuVI(OEP)O2] which generated mainly trans-stilbene oxide (44%) plus the cis-oxide (16%).

To test the generality of the ‘side-on approach’ as a transition state model for the metalloporphyrin-catalyzed epoxidations, we studied the reactions of two sterically congested dioxoruthenium(VI) porphyrins, [RuVI(TDCPP)O2] and [RuVI(TMOPP)O2] [TMOPP = meso-tetrakis-(2,4,6-trimethoxyphenyl)porphyrin dianion], with cis- and trans-β-methylstyrenes. The eight bulky ortho substituents will prevent a side-on approach of the trans-alkene to the O=Ru=O moiety; therefore, these encumbered dioxoruthenium(VI) porphyrins are expected to be inactive toward trans-β-methylstyrene oxidation if the ‘side-on approach’ is an obligatory route for epoxidation. And yet, both alkenes were found to be readily epoxidized by both ruthenium oxidants to produce the corresponding epoxides stereospecifically, and the cis- and trans-epoxides were produced in 84% and 81% yield, respectively, when [RuVI(TDCPP)O2] was the oxidant, whereas the respective cis- and trans-epoxide yields of 58% and 50% were attained for [RuVI(TMOPP)O2]. It is also noteworthy that the \( \Delta S^\ddagger \) values for the oxidations of styrene (~21.9 e.u. for [RuVI(TDCPP)O2] and ~27.3 e.u. for [RuVI(TMOPP)O2]) and trans-β-methylstyrene (~23.7 e.u. for both ruthenium oxidants) do not differ significantly. This reveals that both trans-β-methylstyrene and styrene can associate with the Ru=O in a similar degree in the transition states despite that a side-on approach of the trans-alkene is not favored by the bulky ligands. Apparently, our findings do not reconcile with the ‘side-on approach’ model (manuscript submitted).

The concertedness of the epoxidation reactions has been examined by using cis-β-deuteriostyrene as a mechanistic probe. The epoxidation reactions of the cis-alkene with the sterically congested dioxoruthenium(VI) porphyrins: [RuVI(DPP)O2], [RuVI(TDCPP)O2] and [RuVI(TMOPP)O2], were found to give a mixture of the cis- and trans-epoxides in ratio of 61:39, 87:13 and 62:14, respectively. The nonstereospecificity for the alkene oxidations discounts a concerted oxene insertion mechanism [13].

The effect of para-substituents on the styrene oxidations by dioxoruthenium(VI) porphyrins had been examined. It is interesting to note that both electron-releasing and -withdrawing substituents can accelerate the reactions, and the variation of the \( k_2 \) values is small (typically ~9–5-fold for

<table>
<thead>
<tr>
<th>complexes</th>
<th>( \times 10^3 ) ( k_2 ) (dm³/mol/s) at 298 K</th>
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<tr>
<td></td>
<td>styrene</td>
</tr>
<tr>
<td>[RuVI(TPP)O2]</td>
<td>4.30 ± 0.3</td>
</tr>
<tr>
<td>[RuVI(OEP)O2]</td>
<td>1.55 ± 0.09</td>
</tr>
<tr>
<td>[RuVI(DPP)O2]</td>
<td>4.78 ± 0.01</td>
</tr>
<tr>
<td>[RuVI(TDCPP)O2]</td>
<td>3.90 ± 0.04</td>
</tr>
<tr>
<td>[RuVI(TMOPP)O2]</td>
<td>0.61 ± 0.03</td>
</tr>
<tr>
<td>[RuVI(TPP)(NTs)2]</td>
<td>9.0 ± 0.1</td>
</tr>
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Reaction conditions: in CH₂Cl₂ containing 2% (w/w) pyrazole.
4-methoxystyrene and 2–1.1-fold for 3-nitrostyrene). Correlations of log $k_{\text{rel}}$ [$k_{\text{rel}} = k_{2}$ (para-substituted styrene)/$k_{2}$ (styrene)] vs. $\sigma^+$. resulted in concave Hammett curves [8b]. This finding is contrary to the styrene oxidations by [Fe$^{IV}$(TMP$^{+}$)O] [14], [Cr$^{IV}$(Br$_3$TPP)(O)X] [15] and [Ru$^{VI}$($N_4$)O$_2$]$^{2+}$ ($N_4$ = macrocyclic tertiary amines) [16] complexes wherein linear Hammett correlation of log $k_{\text{rel}}$ vs. $\sigma^+$ ($\rho^+ = -1.9 - -2.1$) were obtained. However, we have found that the kinetic data have been successfully correlated with a series of carboradical ($\sigma_{JJ}^*$) and polar effect ($\sigma_{mb}$) parameters developed by Jiang & Ji ([17], manuscript submitted for publication).

Analogous to the alkene epoxidations, bis(tosylimido)ruthenium($vi$) porphyrins react with alkenes to give aziridines. For example, in CH$_2$Cl$_2$ (containing 2% w/w Hpz) [Ru$^{VI}$(TPP)(NTs)$_2$] reacted with styrene and norbornene to give their aziridines in 75% and 68% yield, respectively. The reactions of the imidoruthenium complex with cis-stilbene and cis-β-methylstyrene afforded mixtures of trans-aziridines as the major products: trans:cis ratios = 86:14 (cis-stilbene) and 66:34 (cis-β-methylstyrene). The plot of log $k_{\text{rel}}$ values for the stoichiometric aziridination of a series of para-substituted styrenes with [Ru$^{VI}$(TPP)(NTs)$_2$] vs. Hammett $\sigma^+$ substituent constants resulted a straight line with slope $\rho^+ = -1.1$. The negative $\rho^+$ value is indicative of electrophilic nature of the bis(tosylimido)ruthenium($vi$) complex [7].

**ASYMMETRIC EPOXIDATION OF UNFUNCTIONALIZED ALKENES**

Enantioselective epoxidation of unfunctionalized alkenes is an attractive method for preparing enanti-enriched organic epoxides directly. It has already been demonstrated by various groups that metalloporphyrin catalysts modified with chiral auxiliaries can produce nonracemic epoxides in moderate to good enantiomeric excess (ee). Although oxo-metal species have often been invoked as a reactive intermediate, their isolation and characterization remain somewhat elusive. Recently, we were gratified that a well-characterized cationic oxoruthenium($iv$) complex containing a chiral $C_2$-symmetric bispyrazolylpyridine ligand can effect enantiomeric epoxidation of simple alkenes in up to 60%ee [13]. Similarly, [Ru$^{VI}$(D$_4$-Por*)O$_2$] had also been prepared and characterized, and it reacted with prochiral alkenes such as styrene and cis-β-methylstyrene under stoichiometric conditions (CH$_2$Cl$_2$/2%w/w Hpz) to afford enantio-enriched epoxides: 65%ee for styrene oxide; 67%ee for cis-β-methylstyrene oxide (Scheme 2) [6a,b]. Like other reported chiral metalloporphyrin catalyst systems [2b], the oxidation of trans-alkenes by [Ru$^{VI}$(D$_4$-Por*)O$_2$] was poorly enantioselective, for example, the trans-β-methylstyrene oxidation produced the trans-epoxide in only 20%ee.

Importantly, a dioxoruthenium($vi$) complex of a $D_2$-symmetric porphyrin facially encumbered by four thrietyl units can effect enantioselective epoxidation of trans-β-methylstyrene in up to 70%ee, whereas the cis-β-methylstyrene oxidation afforded only 40%ee under identical reaction conditions (Scheme 2) [6c]. The apparent trans-preference can be understood by adopting a ‘head-on approach’ of trans-β-methylstyrene as a transition state model.

Scheme 2 Asymmetric epoxidation of cis- and trans-β-methylstyrenes.
TOWARD THE DEVELOPMENT OF ECONOMICAL AND ENVIRONMENTALLY FRIENDLY OXIDATION REACTIONS

Among various terminal oxidants used for metalloporphyrin catalyzed oxidations, dioxygen is the most appealing since it is abundant and water generated as a side-product is safe for disposal. In the literature, few catalytic systems are known to utilize dioxygen for hydrocarbon oxidations without the use of a sacrificial reducing agent such as aldehydes [18]. In 1985, Groves & Quinn pioneered in using the dioxoruthenium(vi) complex of tetramesitylporphyrin (TMP) as a catalyst to mediate aerobic alkene epoxidation, and aldehyde was not required for this reaction [19]. Recently, we reported that the [RuVI(D$_4$-Por*)O$_2$] complex can effect the first example of aerobic enantioselective epoxidation [6a]. The optimum results were obtained when the catalytic reaction was carried out in CH$_2$Cl$_2$ solution under 8 atmospheres of dioxygen (Scheme 3). Under such conditions, styrene oxide was obtained in 10 turnovers and 70%ee. With cis-β-methylstyrene as the substrate, its cis-epoxide was produced in 20 turnovers and 69%ee, and 73%ee was attained if toluene was the solvent for the reaction. Likewise, the related D$_2$-symmetric chiral dioxoruthenium(vi) porphyrin could also mediate enantioselective aerobic epoxidation of trans-β-methylstyrene, and the trans-epoxide was furnished in 59%ee (turnover = 7) [6c].

Apart from dioxygen, ruthenium porphyrins also display promising selectivities and activities toward hydrocarbon oxidations using other mild oxidizing agents such as N$_2$O [20] and substituted pyridine N-oxides [21] under homogeneous conditions. Apparently, heterogeneous catalysis can offer additional advantages over its homogeneous counterpart for easy catalyst recycling and product isolation; however, few heterogenous catalysts are able to attain high catalytic turnovers (>1000) and product selectivities.

In this regards, we have developed a supported Ru catalyst by grafting [RuII(TDCPP)(CO)(EtOH)] into mesoporous MCM-41 molecular sieves [22]. The MCM-41 solid support consists of an ordered array of hexagonal channels with an average pore diameter of 36 Å, which permits a low diffusional resistance for the reactant molecules to access the metal active sites located within the channels [23]. The immobilized Ru catalyst exhibits enhanced stability and good catalytic activity toward alkene oxidations using tert-butyl hydroperoxide (TBHP). It is noteworthy that this supported Ru catalyst can effect highly selective heterogeneous alkene epoxidation using 2,6-dichloropyridine N-oxide as terminal oxidant (Scheme 4). Aromatic and aliphatic alkenes can be efficiently converted to their corresponding epoxides stereospecifically in good to excellent yields. Oxidation of cycloalkenes such as norbornene and cyclooctene can be carried out effectively using the heterogenous Ru-catalyzed reactions; however, these alkenes are unreactive in the zeolite-based titanium silicate (TS-1)-catalyzed epoxidation reactions.

Scheme 3 Aerobic asymmetric epoxidation of cis- and trans-β-methylstyrenes.

Scheme 4 Encapsulation of meso-tetrakis(2,6-dichlorophenyl)porphyrinoruthenium(II) carbonyl complex into mesoporous MCM-41 and the use of [Ru/m-41(m)] for heterogeneous alkene epoxidation.
because of the small pore diameter (<7 Å) of the zeolite support [24]. On the other hand, the Ru-MCM-41 catalyst displays size selectivity in the (+)-limonene oxidation where the terminal C=C bond (vs. internal trisubstituted C=C bond) was more readily oxidized. The Ru/MCM-41 catalyst can be repeatedly used, and 67% of its initial activity is retained after 11 691 turnovers (three runs) [21b].

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REFERENCES


