

Ruthenium-oxo and -tosylimido porphyrin complexes for epoxidation and aziridination of alkenes*

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Abstract: Dioxoruthenium(vi) porphyrins including those containing chiral porphyrinato ligands can be readily prepared by oxidation of $[\text{Ru}^{\text{II}}(\text{Por})(\text{CO})(\text{MeOH})]$ with PhIO or meta-chloroperoxybenzoic acid. Similar reactions with PhINTs gave $[\text{Ru}^{\text{VI}}(\text{Por})(\text{NTs})_2]$ isolated as air stable solids at room temperature. The $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$ 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 $[\text{Ru}^{\text{VI}}(\text{D}_4\text{-Por}^*)\text{O}_2]$ [$\text{D}_4\text{-H}_2\text{Por}^* = 5,10,15,20\text{-tetrakis-(1S,4R,5R,8S-1,2,3,4,5,6,7,8\text{-octahydro-1,4:5,8\text{-dimethanoanthracen-9-yl)porphyrin}}$] and $[\text{Ru}^{\text{VI}}(\text{D}_2\text{-Por}^*)\text{O}_2]$ complexes. The mechanism of alkene epoxidation by $[\text{Ru}^{\text{VI}}(\text{Por})\text{O}_2]$ has been examined. Procedures for catalytic epoxidation of alkenes using ruthenium porphyrin catalysts has also been developed. $[\text{Ru}^{\text{VI}}(\text{Por})(\text{NTs})_2]$ 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 hydroxylations. 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)imino]phenyliodinane

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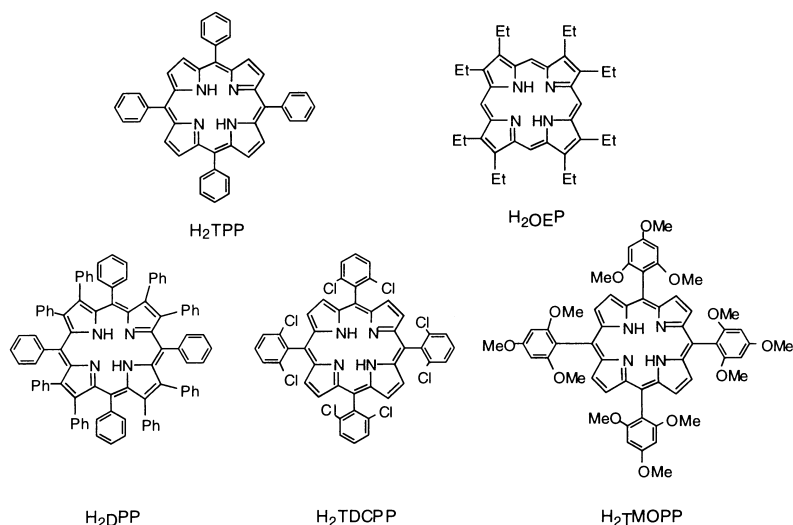
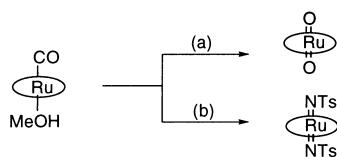


Fig. 1

(PhINTs) as the source of oxygen and nitrogen, respectively. Carbonylruthenium(II) porphyrins, $[(\text{Por})\text{Ru}^{\text{II}}(\text{CO})(\text{MeOH})]$, are usually prepared by reacting $[\text{Ru}_3\text{CO}_{12}]$ 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*-tetrakis(2,6-dichlorophenyl)porphyrin (H_2TDCPP) 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 $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture, the carbonylruthenium(II) porphyrins were isolated in 50–90% yield as an adduct of methanol.

Treatment of $[\text{Ru}^{\text{II}}(\text{Por})(\text{CO})(\text{MeOH})]$ complexes with *mcpba* in $\text{CH}_2\text{Cl}_2/\text{EtOH}$ 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 (H_2OEP) and tetraphenylporphyrin (H_2TPP) [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, H_2DPP , H_2TDCPP and H_2TMOPP (Fig. 1), can be readily prepared by oxidation of the carbonylruthenium(II), $[(\text{Por})\text{Ru}^{\text{II}}(\text{CO})(\text{MeOH})]$, complexes with iodosylbenzene (*PhIO*) in CH_2Cl_2 . The analogous bis(tosylimido)ruthenium(VI) complexes were prepared by reacting $[(\text{Por})\text{Ru}^{\text{II}}(\text{CO})(\text{MeOH})]$ with PhINTs in CH_2Cl_2 [7]. The crude oxo- and bis(tosylimido)-ruthenium products could be purified by column chromatography on a dry alumina column using CH_2Cl_2 as the eluant, or by recrystallization from $\text{CH}_2\text{Cl}_2/\text{acetonitrile}$. 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.



(a) *m*-chloroperoxybenzoic acid or *PhIO* / CH_2Cl_2 , ROH

(b) PhINTs / CH_2Cl_2

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 [Ru^{VI}(*p*-X-TPP)O₂] (*p*-X = 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 [Ru^{VI}(Por)(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 [Ru^{II}(Por)(CO)(MeOH)] complexes lies within 1007–1009 cm⁻¹ range, whereas for [Ru^{VI}(Por)O₂] and [Ru^{VI}(Por)(NTs)₂] complexes the absorption bands are located in 1017–1020 cm⁻¹. An X-ray crystal structure has been obtained for a chiral [Ru^{VI}(D₄-Por*)O₂] complex [D₄-H₂Por* = 5,10,15,20-tetrakis-(1*S*,4*R*,5*R*,8*S*-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracen-9-yl)porphyrin] with Ru–O distances being 1.73 [1] and 1.75 [1] Å [6] (Table 1).

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

Complexes	Oxidation state marker band (cm ⁻¹)	$\nu_{\text{as}}(\text{RuO}_2)$ (cm ⁻¹)
[Ru ^{VI} (TPP)O ₂]	1017	819
[Ru ^{VI} (OEP)O ₂]	1018	822
[Ru ^{VI} (DPP)O ₂]	1012	818
[Ru ^{VI} (TDCPP)O ₂]	1017	824
[Ru ^{VI} (TMP)O ₂]	1021	820
[Ru ^{VI} (<i>p</i> -Cl-TPP)O ₂]		821
[Ru ^{VI} (<i>p</i> -Me-TPP)O ₂]		823
[Ru ^{VI} (<i>p</i> -MeO-TPP)O ₂]		821
[Ru ^{VI} (TPP)(NTs) ₂]	1016	914 (characteristic imido band)
[Ru ^{VI} (OEP)(NTs) ₂]	1018	900 (characteristic imido band)

Both the [Ru^{VI}(Por)O₂] and [Ru^{VI}(Por)(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 ¹H 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 carbonylruthenium(II) precursors; nevertheless, their values are rather insensitive to the *para*-substituents on the *meso*-phenyl groups. The ¹H NMR spectrum of the saddle-distorted [Ru^{VI}(DPP)O₂] complex (DPP = dodecaphenylporphyrin dianion) [10] showed a broad doublet at δ 7.44 ($J = 7.0$ Hz, 8H) assignable to the ortho protons at the *meso*-phenyl rings, and two sets of multiplets at δ 6.8 corresponding to the remaining 52 protons. The variable temperature NMR of the free H₂DPP 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 [Ru^{VI}(DPP)O₂]. 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 [Ru^{VI}(Por)O₂] 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 α and β 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 [Ru^{VI}(DPP)O₂] are red-shifted compared with those of [Ru^{VI}(TPP)O₂]. 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).

Table 2 UV-visible spectral data of selected dioxoruthenium(vi) porphyrins

Complexes	λ_{\max} ($\log - \epsilon$)/nm ($\text{dm}^3/\text{mol}/\text{cm}$)
[Ru ^{VI} (TPP)O ₂]	545 sh (3.89), 518 (4.24), 418 (5.29), 340 sh (4.19)
[Ru ^{VI} (OEP)O ₂]	540 (4.40), 508 (4.28), 396 (5.44), 335 sh (4.45)
[Ru ^{VI} (DPP)O ₂]	586 (3.59), 550 (3.85), 448 (4.78), 358 sh (3.98)
[Ru ^{VI} (TDCPP)O ₂]	420 (5.49), 510 (4.16), 566 sh (3.60)
[Ru ^{VI} (TMOPP)O ₂]	4.23 (5.38), 512 (4.40)
[Ru ^{VI} (TMP)O ₂]	4.22 (5.44), 526 (4.18)
[Ru ^{VI} (TPP)(NTs) ₂]	416 (5.14), 536 (4.18), 568 (3.77)
Ru ^{VI} (OEP)(NTs) ₂]	406 (5.07), 520 (4.21), 551 (4.16)

All the spectral data were recorded in CH₂Cl₂ at room temperature.

The cyclic voltammograms of [Ru^{VI}(Por)O₂] in 0.1 M Bu₄NPF₆-CH₂Cl₂ show one reversible oxidation couple and one irreversible reduction wave (Table 3). The oxidation couple is tentatively assigned as the ligand-centred oxidation [Ru^{VI}(Por)O₂]-e⁻ → [Ru^{VI}(Por^{o+})O₂], and the E° values for a series of dioxoruthenium(vi) tetraarylporphyrins (Ar = X-C₆H₄; X = 4-Cl, H, 4-Me and 4-MeO) being 0.86, 0.77, 0.72 and 0.64 V vs. Cp₂Fe⁺⁰, respectively. These values differ slightly with the variation of the para-substituents. As expected the ligand-centred oxidation of the saddle-shaped distorted [Ru^{VI}(DPP)O₂] occurs at 0.55 V vs. Cp₂Fe⁺⁰, which amounts to a 240-mV drop in the oxidation potential compared with E° value of 0.79 V for [Ru^{VI}(TPP)O₂]. The change in the E° value is again due to the destabilization of the HOMOs induced by conformational distortion of the porphyrin ring [10] (Table 3).

Table 3 E° values (V vs. Cp₂Fe⁺⁰) for selected dioxoruthenium(vi) porphyrins

Complexes	Oxidation	Reduction*
[Ru ^{VI} (OEP)O ₂]	0.60	-0.90
[Ru ^{VI} (TPP)O ₂]	0.79	-0.83
[Ru ^{VI} (<i>p</i> -Me-TPP)O ₂]	0.72	-0.85
[Ru ^{VI} (<i>p</i> -MeO-TPP)O ₂]	0.64	-0.88
[Ru ^{VI} (<i>p</i> -Cl-TPP)O ₂]	0.86	-0.76
[Ru ^{VI} (DPP)O ₂]	0.90*, 0.55	-1.00

Conditions: 0.1 mol/dm³ NBu₄PF₆ CH₂Cl₂, Ag/AgNO₃ in MeCN as the reference electrode and glassy carbon working electrode; scan rate = 100 mV/s.

*Irreversible.

STOICHIOMETRIC ALKENE EPOXIDATIONS AND AZIRIDINATIONS.

All the *trans*-dioxoruthenium(vi) porphyrins function as a competent two-electron oxidant for alkene oxidations in a CH₂Cl₂-EtOH or CH₂Cl₂-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 [Ru^{VI}(Por)O₂] afforded epoxides in good yields. When the oxidation reactions were carried out in the presence of pyrazole, [Ru^{IV}(Por)(pz)₂] were found as the reaction products. The [Ru^{IV}(Por)(pz)₂] products are paramagnetic ($\mu_{\text{eff}} \approx 2.8 \mu_{\text{B}}$) and the oxidation state marker bands are located around 1019 cm⁻¹, consistent with a Ru(IV) formulation.

The reactions of [Ru^{VI}(Por)O₂] with alkenes follow a second-order rate law, rate = k_2 [Ru][alkene], where k_2 = second-order rate constant. The k_2 values were determined from the linear plots of the pseudo-first-order rate constants (k_{obs}) vs. alkene concentrations, i.e. when [alkene] >> [Ru], then $k_{\text{obs}} = k_2$ [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

[Ru^{VI}(DPP)O₂] complex have a comparable k_2 value as those for the planar [Ru^{VI}(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).

Table 4 Second-order rate constants (k_2) for the reaction of styrene and norbornene with selected dioxo- and bis(tosylimido)-ruthenium(vi) porphyrins

complexes	$\times 10^3 k_2$ (dm ³ /mol/s) at 298 K	
	styrene	norbornene
[Ru ^{VI} (TPP)O ₂]	4.30 ± 0.3	3.01 ± 0.09
[Ru ^{VI} (OEP)O ₂]	1.55 ± 0.09	0.39 ± 0.02
[Ru ^{VI} (DPP)O ₂]	4.78 ± 0.01	3.76 ± 0.04
[Ru ^{VI} (TDCPP)O ₂]	3.90 ± 0.04	12.68 ± 0.16
[Ru ^{VI} (TMOPP)O ₂]	0.61 ± 0.03	0.87 ± 0.03
[Ru ^{VI} (TPP)(NTs) ₂]	9.0 ± 0.1	1.1 ± 0.1

Reaction conditions: in CH₂Cl₂ containing 2% (w/w) pyrazole.

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 [Ru^{VI}(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 [Ru^{VI}(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, [Ru^{VI}(TDCPP)O₂] and [Ru^{VI}(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 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 [Ru^{VI}(TDCPP)O₂] was the oxidant, whereas the respective *cis*- and *trans*-epoxide yields of 58% and 50% were attained for [Ru^{VI}(TMOPP)O₂]. It is also noteworthy that the ΔS^\ddagger values for the oxidations of styrene (-21.9 e.u. for [Ru^{VI}(TDCPP)O₂] and -27.3 e.u. for [Ru^{VI}(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: [Ru^{VI}(DPP)O₂], [Ru^{VI}(TDCPP)O₂] and [Ru^{VI}(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 \approx 9–5-fold for

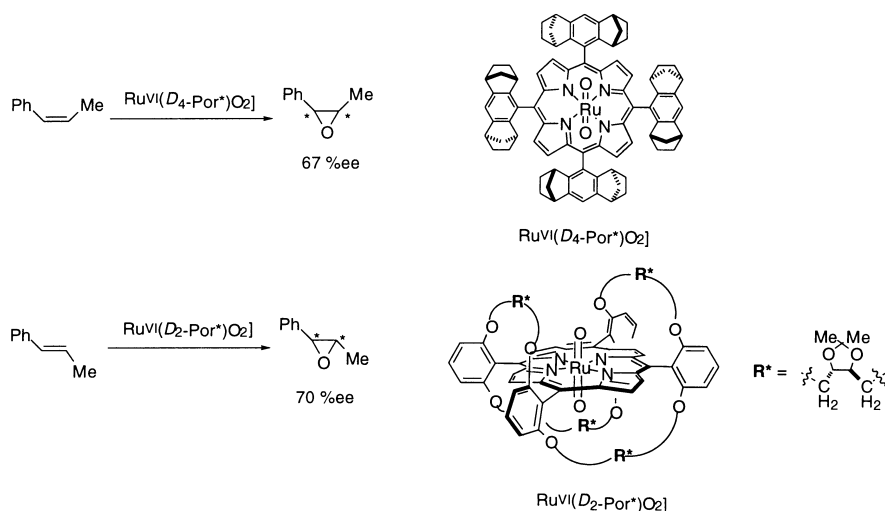
4-methoxystyrene and 2–1.1-fold for 3-nitrostyrene). Correlations of $\log k_{\text{rel}}$ [$k_{\text{rel}} = k_2(\text{para-substituted styrene})/k_2(\text{styrene})$] vs. σ^+ resulted in concave Hammett curves [8b]. This finding is contrary to the styrene oxidations by $[\text{Fe}^{\text{IV}}(\text{TMP}^{\text{O}^+})\text{O}]$ [14], $[\text{Cr}^{\text{V}}(\text{Br}_8\text{TPP})(\text{O})\text{X}]$ [15] and $[\text{Ru}^{\text{VI}}(\text{N}_4)\text{O}_2]^{2+}$ ($\text{N}_4 =$ macrocyclic tertiary amines) [16] complexes wherein linear Hammett correlation of $\log k_{\text{rel}}$ vs. σ^+ ($\rho^+ = -1.9 - -2.1$) were obtained. However, we have found that the kinetic data have been successfully correlated with a series of carboradical ($\sigma_{\text{JJ}}^{\text{O}}$) and polar effect (σ_{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_2Cl_2 (containing 2% w/w Hpz) $[\text{Ru}^{\text{VI}}(\text{TPP})(\text{NTs})_2]$ 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 $[\text{Ru}^{\text{VI}}(\text{TPP})(\text{NTs})_2]$ vs. Hammett σ^+ substituent constants resulted a straight line with slope = $\rho^+ = -1.1$. The negative ρ^+ 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 enantio-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, $[\text{Ru}^{\text{VI}}(\text{D}_4\text{-Por}^*)\text{O}_2]$ had also been prepared and characterized, and it reacted with prochiral alkenes such as styrene and *cis*- β -methylstyrene under stoichiometric conditions ($\text{CH}_2\text{Cl}_2/2\%$ 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 $[\text{Ru}^{\text{VI}}(\text{D}_4\text{-Por}^*)\text{O}_2]$ was poorly enantioselective, for example, the *trans*- β -methylstyrene oxidation produced the *trans*-epoxide in only 20% ee.

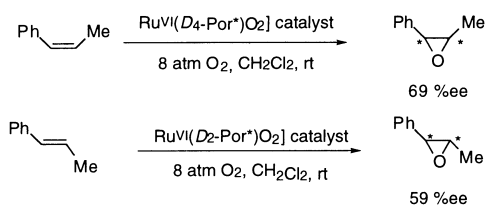
Importantly, a dioxoruthenium(vi) complex of a D_2 -symmetric porphyrin facially encumbered by four thriol units can effect enantioselective epoxidation of *trans*- β -methylstyrene in up to 70% ee, whereas the *cis*- β -methylstyrene oxidation afforded only 40% ee under identical reaction conditions (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

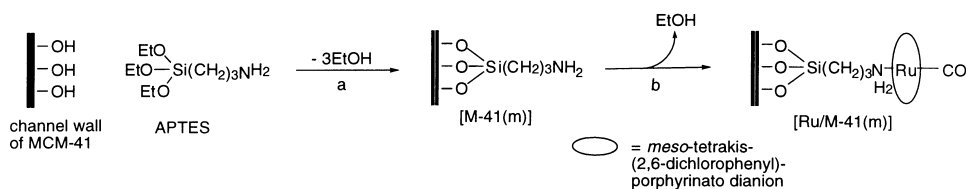
Among various terminal oxidants used for metalloporphyrin catalyzed oxidations, dioxygen is the most appealing since it is abundant and water generated as a side-product is safe for disposal. In the literature, few catalytic systems are known to utilize dioxygen for hydrocarbon oxidations without the 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 $[\text{Ru}^{\text{VI}}(\text{D}_4\text{-Por}^*)\text{O}_2]$ 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_2Cl_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].



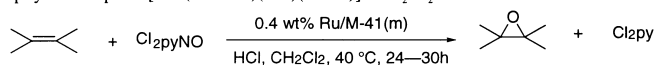
Scheme 3 Aerobic asymmetric epoxidation of *cis*- and *trans*- β -methylstyrenes.

Apart from dioxygen, ruthenium porphyrins also display promising selectivities and activities toward hydrocarbon oxidations using other mild oxidizing agents such as N_2O [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 heterogeneous catalysts are able to attain high catalytic turnovers (> 1000) and product selectivities.

In this regard, we have developed a supported Ru catalyst by grafting $[\text{Ru}^{\text{II}}(\text{TDCPP})(\text{CO})(\text{EtOH})]$ 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 heterogeneous Ru-catalyzed reactions; however, these alkenes are unreactive in the zeolite-based titanium silicate (TS-1)-catalyzed epoxidation reactions



(a) modification of MCM-41 channel wall: APTES / CHCl_3 ; (b) encapsulation of a ruthenium porphyrin complex: $[\text{Ru}^{\text{II}}(\text{TDCPP})(\text{CO})(\text{EtOH})]$ / CH_2Cl_2



Scheme 4 Encapsulation of *meso*-tetrakis(2,6-dichlorophenyl)porphyrinoruthenium(II) carbonyl complex into mesoporous MCM-41 and the use of $[\text{Ru}/\text{m-41}(\text{m})]$ for heterogeneous alkene epoxidation.

because of the small pore diameter ($< 7 \text{ \AA}$) 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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