# Cis-Trans Isomerization of Epoxides Catalyzed by Ruthenium(II) Porphyrins

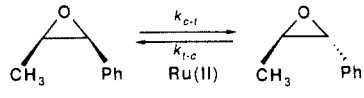
**John T. Groves,* Kwang-Hyun Ahn, and Robert Quinn**

*Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08544.* *Received June 29, 1987*

**Abstract:** Bis(tetrahydrofuran)(5,10,15,20-tetramesitylporphyrinato)ruthenium(II) [$Ru^{II}TMP(THF)_2$] and the corresponding *p*-tolylporphyrin [$Ru^{II}TTP(THF)_2$] have been found to catalyze the cis-trans isomerization of epoxides under mild conditions. For β-methylstyrene oxide an equilibrium ratio of 5.4:1 (trans/cis) was achieved with either isomer indicating a free energy difference of 1 kcal/mol. Inhibition of the isomerization by added olefins was observed and attributed to olefin coordination to ruthenium(II). *cis*-β-Methylstyrene oxide readily formed an adduct with $Ru^{II}TMP(CO)$, while the trans isomer did not. The isomerization of *trans*-(1*S*,2*S*)-β-methylstyrene oxide gave only *cis*-(1*R*,2*S*)-β-methylstyrene oxide. A mechanism for epoxide isomerization involving homolytic cleavage of the $C_1$-O bond to give carbon radical intermediate is proposed.

The isolation of a *trans*-dioxoruthenium(VI) porphyrin[1a] and the subsequent demonstration that such species are competent catalysts for the aerobic epoxidation of olefins[1b] has led us to investigate the interactions of ruthenium porphyrins with epoxides. We have discovered that a variety of ruthenium(II) porphyrin complexes catalyze the cis-trans isomerization of epoxides under mild conditions. We describe herein an investigation of the scope and mechanism of this unusual process.

**Isomerization of Epoxides by Ruthenium(II) Porphyrins.** In a typical reaction, bis(tetrahydrofuran)(5,10,15,20-tetramesitylporphyrinato)ruthenium(II) [$Ru^{II}TMP(THF)_2$] catalyzed the isomerization of *cis*-β-methylstyrene oxide in benzene over a 5-h period to an equilibrium mixture of *cis* and *trans*-epoxides. Trace amounts of phenylacetone and propiophenone were also observed. In several experiments direct confirmation of epoxide isomerization with $RuTMP(THF)_2$ was obtained by observation of the $^1H$ NMR spectrum of the reaction mixture containing *cis*-β-methylstyrene oxide as the substrate in $C_6D_6$. This result clearly showed growth in the amount of *trans*-epoxide and a corresponding decrease in the *cis*-epoxide to a final trans/cis ratio of 5.4. *trans*-β-Methylstyrene oxide was isomerized as well to the same mixture, indicating that the isomerization was reversible. Figure 1 shows the time course to achieve equilibrium from both directions. The rate of isomerization was found to be proportional to catalyst concentration. The apparent first-order rate constants $k_{c\to t}$ and $k_{t\to c}$ were determined from these data to be $2.16 \times 10^{-4}$ and $4.01 \times 10^{-5}$ $s^{-1}$, respectively (eq 1). The observed equilibrium constant




(1)

($K$ = 5.4) provides a direct technique for estimation of the free energy difference between the cis and trans isomers of an epoxide. For β-methylstyrene oxide the trans isomer is stabilized by 1 Kcal/mol relative to the cis isomer. The same value has been observed for the corresponding olefin.[2]

Other Ru(II) porphyrin complexes also catalyzed the isomerization of epoxides (Table I). $RuTTP(THF)_2$ (TTP = tetra-*p*-tolylporphyrin) catalyzed the isomerization of *cis*- or *trans*-β-methylstyrene oxide leading to the same cis-trans equilibrium ratio. Similar results were obtained for $(RuTTP)_2$.[3a] Accordingly, coordination of THF did not appreciably inhibit isomerization. By contrast, only partial equilibration was obtained with $RuTMP(MeCN)_2$. The greater stability of $RuTMP(MeCN)_2$ in air indicates that acetonitrile binds more strongly than THF

**Table I.** Isomerization of Epoxides by Various Ruthenium(II) Porphyrins

| catalyst | conc mM | epoxide, mM | | [*trans*-oxide]/[*cis*-oxide][a] |
|---|---|---|---|---|
| $RuTMP(THF)_2$ | 9.1 | *cis*-β-methylstyrene oxide | 0.42 | 5.2 |
| $RuTTP(THF)_2$ | 16.0 | *cis*-β-methylstyrene oxide | 0.75 | 5.4 |
| | 11.0 | *cis*-β-methylstyrene oxide | 0.75 | 5.4 |
| $(RuTPP)_2$ | ~5 | *cis*-β-methylstyrene oxide | 0.47 | 5.6 |
| $RuTMP(MeCN)_2$ | 10.0 | *cis*-β-methylstyrene oxide | 0.27 | 0.3 |
| $RuTMP(THF)_2$ | 8.2 | *cis*-2-heptene oxide | | 0.004 |
| | | *trans*-2-heptene oxide | | no *cis*-oxide |
| $RuTMP(THF)_2$[b] | 9.0 | *cis*-2-heptene oxide | 0.49 | 0.5 |
| | 8.8 | *cis*-2-heptene oxide | 0.63 | 0.3[c] |

[a] Except as noted, isomerizations were carried out in benzene at room temperature. Ratios were determined after 24 h. [b] Reactions run in mesitylene at 70 °C. [c] Ratio was determined after 48 h.

**Table II.** Inhibition of *cis*-β-Methylstyrene Oxide Isomerization by Olefins[a]

| nM [Ru] | olefin | mM | [epoxide] mM | [*trans*-oxide]/[*cis*-oxide] |
|---|---|---|---|---|
| 8.7 | styrene | 0.51 | 0.31 | 0.02 |
| 8.5 | *cis*-β-methylstyrene | 0.50 | 0.39 | 0.12 |
| 9.2 | norbornene | 0.53 | 0.42 | 0.03 |
| 8.6 | cyclooctene | 0.47 | 0.39 | 0.02 |
| 8.5 | *trans*-β-methylstyrene | 0.49 | 0.39 | 1.0 |

[a] All reactions were carried out in benzene at room temperature. Product ratios were determined after 24 h.

to ruthenium(II) porphyrin, inhibiting the coordination and subsequent isomerization of epoxide. $Ru^{II}TMP(CO)$ caused no isomerization under these conditions.

As shown in Table I, *cis*- and *trans*-2-heptene oxide were not appreciably isomerized at room temperature after 24 h. However, at 70 °C in mesitylene *cis*-2-heptene oxide was isomerized to the trans isomer to give a *trans*/*cis*-oxide ratio between 0.3 and 0.5, values considerably lower than that observed for *cis*-β-methylstyrene oxide.

The isomerization of *cis*-β-methylstyrene oxide was investigated in the presence of olefins to determine if epoxide metathesis reactions had occurred. Although no cross products were observed, a variety of olefins were shown to inhibit epoxide isomerization (Table II). Styrene, norbornene, cyclooctene, and *cis*-β-methylstyrene eliminated nearly all isomerization of *cis*-β-methylstyrene oxide. By contrast, *trans*-β-methylstyrene was found to be a significantly poorer inhibitor of isomerization than the other olefins. Ruthenium(II) porphyrins have been shown to be strongly coordinating; stable ethylene[3b] and dinitrogen[4a]

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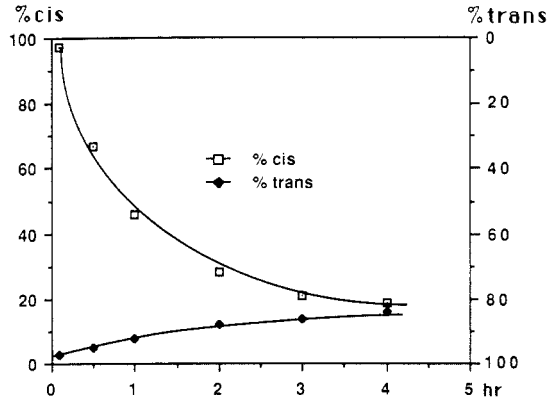



**Figure 1.** Reaction of *cis*-β-methylstyrene oxide with $Ru^{II}TMP(THF)_2$ (○), Reaction of *trans*-β-methylstyrene oxide with $Ru^{II}TMP(THF)_2$ (+).

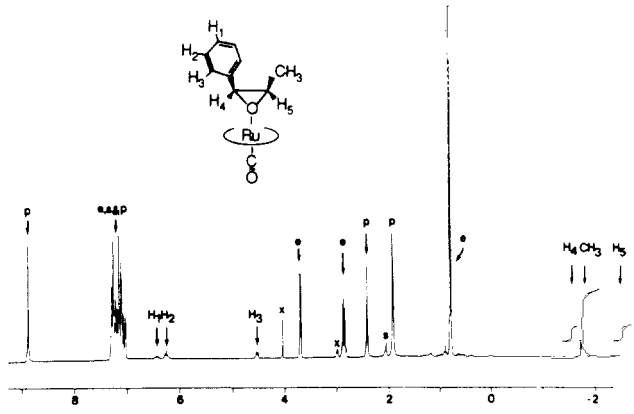
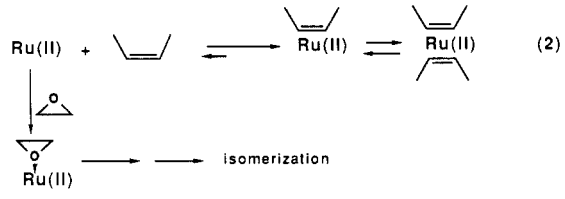


**Figure 2.** $^1H$ NMR (250 mHz) of a mixture of $Ru^{II}TMP(CO)(MeOH)$ (5.3 mM) with *cis*-β-methylstyrene oxide (61 mM) in toluene-$d_8$ at −50 °C. Resonance assigned to coordinated *cis*-β-methylstyrene oxide are indexed by number. Resonance due to the porphyrin (p), free *cis*-β-methylstyrene oxide (e), the solvents (s), and methanol (x) are also indicated.

adducts have been described recently. Accordingly, we attribute the inhibition of epoxide isomerization to competitive binding of ruthenium(II) by the added olefin (eq 2).[4b] One expects the affinity of a ruthenium(II) porphyrin for *trans*-β-methylstyrene to be lower than that of *cis*-β-methylstyrene on steric grounds.




**Coordination of Epoxides to Ruthenium(II) Porphyrins.** The coordination of *cis*-β-methylstyrene oxide to $Ru^{II}TMP(CO)(MeOH)$ was observed by $^1H$ NMR at −50 °C, although no isomerization was observed with this complex. Figure 2 shows the $^1H$ NMR spectrum observed for a solution of $Ru^{II}TMP(CO)(MeOH)$ (5.3 mM) and *cis*-β-methylstyrene oxide (61 mM) in toluene-$d_8$ at −50 °C. In addition to resonances for free *cis*-β-methylstyrene oxide, a clear set of resonances could be discerned for coordinated *cis*-β-methylstyrene oxide, all of which were shifted to high field positions by the diamagnetic anisotropy of the porphyrin ring. The fact that the upfield shifts of $H_4$ and $H_5$ are nearly identical and the unchanged cis vicinal coupling constant ($J_{4,5}$ = 4.2 Hz) is consistent with a symmetrically coordinated epoxide. Upon warming, the resonances of free and bound *cis*-

(4) (a) Camenzind, M. J.; James, B. R.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1137. (b) Direct evidence for olefin coordination to $Ru^{II}TMP(THF)_2$ has been discerned in benzene solutions containing *p*-methylstyrene.

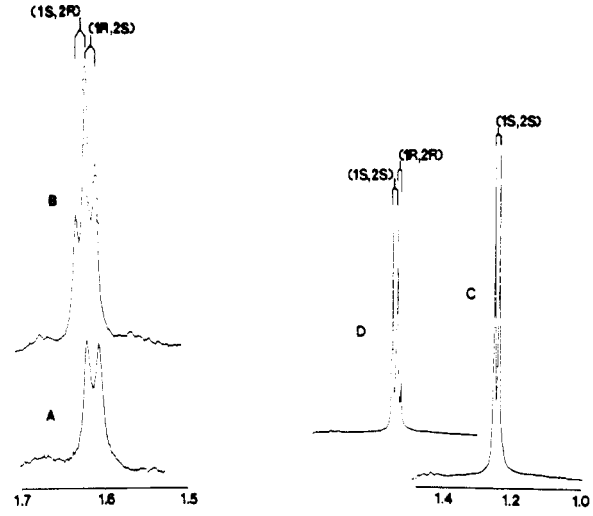



**Figure 3.** $^1H$ NMR of β-methylstyrene oxide in the presence of $Eu(tfc)_3$. (A) Methyl of *cis*-β-methylstyrene oxide after reaction with ruthenium(II). (B) After addition of racemic *cis*-β-methylstyrene oxide. (C) Methyl of *trans*-β-methylstyrene oxide after reaction with ruthenium(II). (D) After addition of racemic *trans*-β-methylstyrene oxide.

β-methylstyrene oxide were observed to broaden due to chemical exchange. That the RuTMP(CO)-*cis*-β-methylstyrene oxide adduct was completely formed under these conditions allows an estimation of the binding constant for this complex. If one assumes that the concentration of uncoordinated RuTMP(CO)(MeOH) was $\leq 10^{-4}$ M, the binding constant must be $>10^3$. By contrast, *trans*-β-methylstyrene oxide was not appreciably coordinated with RuTMP(CO)(MeOH) or RuTTP(CO)(MeOH) under these conditions.

Evidence of epoxide coordination was also observed with $Ru^{II}TMP(THF)_2$ in the course of catalytic isomerization. Shortly after the addition of 16 equiv of *cis*-β-methylstyrene oxide to a solution of $Ru^{II}TMP(THF)_2$, the $^1H$ NMR spectrum indicated resonances due to the cis epoxide and those of an adduct RuTMP(*cis*-β-methylstyrene oxide)(THF) with characteristic high field resonances similar to those described above for the $Ru^{II}$-(CO)–epoxide adduct. Only small amounts of the trans epoxide were observed at this time (5 min).

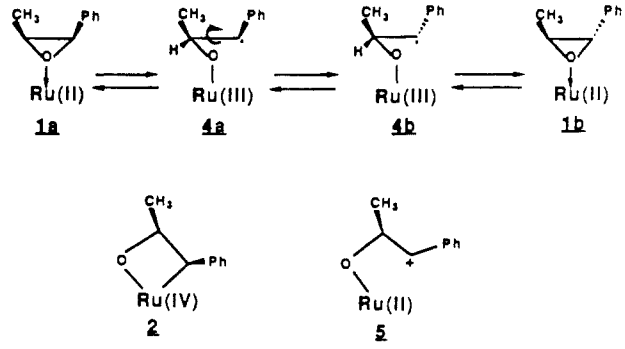
The position of the resonances for $H_4$ and $H_5$ in the *cis*-β-methylstyrene oxide complex of $RuTMP(THF)_2$, δ−1.18 ($J$ = 4.73) and −2.01 (m), respectively, were separated by nearly the same amount as those of the corresponding complex of RuTMP(CO)(MeOH). Further, the coupling constant, $J_{H_4-H_5}$, is the same in both complexes and in free *cis*-β-methylstyrene oxide. These similarities support a symmetrical coordination of the epoxide oxygen to ruthenium(II) as in **1** and are counterindicative of an alternative oxametallacyclic formulation (**2**).

**Isomerization of Chiral Epoxides.** To probe the mechanism of this unusual isomerization, we have explored the effect of ruthenium(II) porphyrins on a chiral epoxide. A sample of *trans*-β-methylstyrene oxide enriched in the (1*S*,2*S*)-enantiomer was prepared and exposed to $RuTTP(THF)_2$. The products obtained from the reaction with *trans*-(1*S*,2*S*)-β-methylstyrene oxide were identified from the $^1H$ NMR spectrum taken in the presence of the chiral shift reagent [Eu(tfc)$_3$] (Figure 3). As can be seen, only *trans*-(1*S*,2*S*)-β-methylstyrene oxide and *cis*-(1*R*,2*S*)-β-methylstyrene oxide were present in the reaction mixture. Thus, *the cis–trans isomerization had occurred by disturbing the stereochemistry only at* $C_1$.

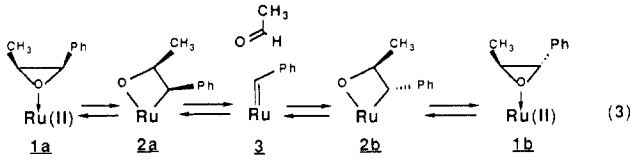
## Discussion

Eliminated by these results are any metathetical processes which result in complete disassembly of the starting epoxides. The direct observation of a ruthenium(II) epoxide adduct under the conditions of this isomerization strongly suggests such a coordination as the initial step. Oxidative addition of the epoxide to ruthenium(II) to give an oxametallacycle (**2**) is a conceivable second step for this isomerization.[5] Subsequent dissociation of **2** to give a me-

**Scheme I**




tallocarbene[3b] **3** and acetaldehyde would provide an opportunity for cis–trans isomerization (eq 3). However, this process would

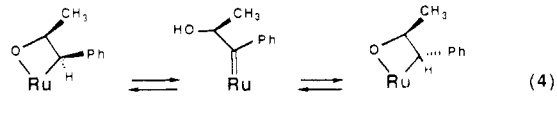



(3)

require simultaneous loss of stereochemistry at both oxirane carbons and is, thus, inconsistent with the results. Another counterindication of the intermediacy of a ruthenium(II) carbene **3** was the failure to observe epoxide formation upon reaction of the carbethoxycarbene complex[3b] of $Ru^{II}TTP$ with benzaldehyde.

By *classical* analysis (vide infra) there are four mechanisms which are consistent with the observed single-site stereoisomerization. (1) Homolytic $C_1$–O cleavage: Cleavage of the $C_1$–O bond to give a benzylic radical species coordinated to Ru(III) **4**; single bond rotation and subsequent reclosure to a coordinated epoxide accommodates the stereochemical results (Scheme I). (2) Heterolytic $C_1$–O bond cleavage to afford a cationic intermediate **5** has been suggested for the observed cis–trans isomerization of β-deuterio-*p*-methoxystyrene oxide.[6] Such a process is considered unlikely for the ruthenium(II)-catalyzed reaction since negligible rearrangement to ketones was observed. (3) Ru–$C_1$ bond cleavage of an oxametallacycle: The same radical intermediate **4** could result from oxidative addition of the coordinated epoxide in **1** to give **2** and subsequent cleavage of the carbon–metal bond. In the absence of definitive evidence for a metallacycle **2**, however, there is no clear distinction between mechanisms (1) and (3).

(4) Stereoisomerization by $C_1$–H bond cleavage: Deprotonation of an oxametallacycle **2** to give a ruthenium(II) carbene adduct **6** would also provide an opportunity for single-site stereoisomerization. Such a mechanism finds precedent in the well-known base-catalyzed isomerization of oxaphosphatanes[7] and may provide a rationale for the unusual hydrogen–deuterium exchange we have observed during the epoxidation of propylene by cytochrome P-450.[8] However, when the isomerization of *cis*-β-methylstyrene oxide was carried out in moist ($D_2O$) benzene, *no* incorporation of deuterium could be detected in the mass spectrum of the product *trans*-β-methylstyrene oxide.




(4)

Stereoisomerization by rupture of the $C_1$–O bond in a ruthenium–epoxide adduct such as **1** (mechanism 1) accommodates all the results. The rate of epoxide isomerization observed here indicates a substantial weakening of the $C_1$–O bond due to ruthenium binding. A coordinated epoxide is expected to be a π-acid in a manner similar to coordinated CO due to the strain inherent to the oxirane ring. Thus, ligation of the epoxide to ruthenium(II) must involve an interaction of the oxygen lone pair with the vacant $d_{z^2}$ orbital on the metal. The filled metal d-orbitals, $d_{xz}$ and $d_{yz}$, have the correct symmetry to back bond with the vacant and low-lying σ* orbital of the $C_1$–O bond (Figure 4, **7**). Estimates of the C–O bond dissociation energy for propylene oxide are in the range of 50 kcal/mol.[2b] That the isomerization of *cis*-2-heptene oxide was observed at 70 °C indicates a substantial stabilization of the ring-opened form by ruthenium. It is not clear that an intermediate diradical such as **4**, which can be regarded either as an alkoxy radical coordinated to ruthenium(II) or a ruthenium(III) alkoxide, is sufficiently stabilized relative to the ruthenium(II)–epoxide adduct to explain this facile ring opening.

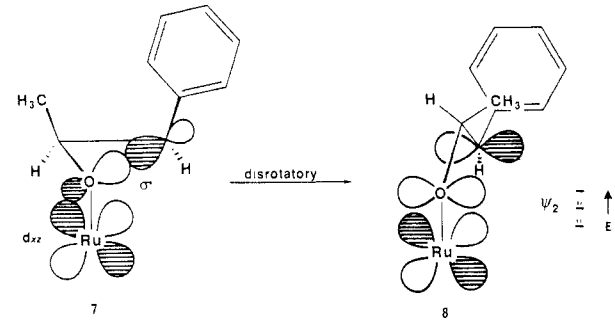



**Figure 4.** Idealized orbital diagram for the disrotatory ring opening of a ruthenium(II)–epoxide adduct **7** to a homoallylic conformation **8**. The $d_{xz}$ ($d_{yz}$) → σ* interaction in **7** transforms adiabatically to $\Psi_2$ of the homoallylic array. The oxygen p-orbital has been drawn without indications of phase to emphasize the nodal character at this position.

An attractive alternative which allows $C_1$–O bonding throughout the course of the stereoisomerization at $C_1$ is shown in Figure 4. A disrotatory disconnection of the $C_1$–O bond of the coordinated epoxide **7** to afford **8** is analogous to a cyclopropylcarbinyl → homoallyl rearrangement. Inspection of the coefficients of the highest occupied molecular orbital ($\Psi_2$) indicates that the charge density in **8** will be distributed antisymmetrically between $C_1$ and ruthenium and that the epoxide oxygen will occupy a nodal position. In this light there can be no difference between a singlet diradical species derived from a formal homolytic cleavage of the carbon–oxygen bond (mechanism 1) and the intermediate derived from heterolytic cleavage (mechanism 2) since the two electrons donated by ruthenium(II) into σ* of the epoxide $C_1$–O bond occupy the same orbital. This analysis is analogous to the description of a diamagnetic Fe(II)–$O_2$ adduct described by Goddard.[9] The much faster isomerization of β-methylstyrene oxides as compared to 2-heptene oxide is consistent with resonance stabilization of the homoallyl intermediate **8**.

We have suggested a similar $d_{xz}$ → σ* interaction to explain the facile O–O bond cleavage of (acylperoxo)metalloporphyrins.[10] A diradical intermediate has been postulated for the CoTPP-catalyzed rearrangement of endoperoxides to bis epoxides[11] and for the deoxygenation of epoxides with various reducing metal complexes.[12,13] The formation of stereoisomeric mixtures of olefins in some cases can be accommodated by single bond rotation prior to the second C–O bond cleavage (eq 5). Consideration of the

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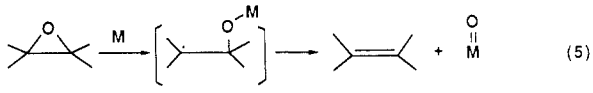
homoallylic orbital interactions in **8** suggests that the rotational barrier in such intermediates will be a sensitive function of the d-orbital electronic configuration of the deoxygenating metal.



(5)

No epoxide deoxygenation has been observed for the reaction of ruthenium(II) porphyrins with epoxides. This must reflect a relatively low oxophilicity for oxoruthenium(IV) porphyrins. By inference, then, oxoruthenium(IV) porphyrins may be able to transfer the oxo ligand to olefins, but this process cannot be rapid.[14] We have recently described the characterization of an oxoruthenium(IV) porphyrin formed either via the oxygenation of ruthenium(II) or the deoxygenation of dioxoruthenium(VI). It is apparent from this work that the epoxidation of olefins by oxoruthenium(IV) porphyrins must be very slow. Accordingly, deoxygenation of epoxides as a preliminary step in the epoxide isomerization reported here is unlikely.[15] This and other aspects of the oxygen-transfer reaction of ruthenium porphyrins are under continued investigation.

## Experimental Section

**Syntheses of Ruthenium(II) Porphyrins. Preparation of Bis(tetrahydrofuran)(5,10,15,20-tetramesitylporphyrinato)ruthenium(II) [RuTMP(THF)$_2$].** RuTMP(THF)$_2$ was synthesized by one of two methods, the second being preferred.

Method (1): *trans*-dioxo(5,10,19,20-tetramesitylporphyrinato)ruthenium(VI) [Ru$^{VI}$TMP(O)$_2$] prepared according to ref 1a was dissolved in THF stirred over solid $KBH_4$ for 48 h. The solution was passed down a short neutral alumina column in an inert atmosphere chamber. The solid was isolated by removing the solvent under vacuum.

Method (2): Solid RuTMP(CH$_3$CN)$_2$ was dissolved in THF and stirred for 48 h. Following chromatography on neutral alumina/THF, solid RuTMP(THF)$_2$ was isolated under vacuum.

NMR ($C_6D_6$) $\delta$ 8.44 (s, pyr-H), 7.22 (s, *m*-H), 2.47 (s, *p*-$CH_3$), 2.20 (s, *o*-$CH_3$), −0.99, −1.41 (THF); vis (THF) ($\lambda_{max}$, log $\epsilon$) 405.6 (5.18), 503.2 (4.17) nm.

**Preparation of Bis(acetonitrile)(5,10,15,20-tetramesitylporphyrinato)ruthenium(II) [RuTMP(CH$_3$CN)$_2$].** In an inert atmosphere chamber, RuTMP(O)$_2$ in 70:30 benzene/acetonitrile was stirred over Zn dust or Zn amalgam for 48 h. Following removal of solvent under vacuum, the solid was dissolved in benzene and chromatographed on a short neutral alumina column. The desired product, which eluted with benzene, was then isolated under vacuum: NMR ($C_6D_6$) 8.60 (s, pyr-H), 7.22 (s, m-H), 2.49 (s, p-Me), 2.16 (s, o-Me), −1.34 (s, $CH_3CN$); vis (1:3 benzene/acetonitrile) ($\lambda_{max}$, log $\epsilon$) 418.8 (5.44), 511.2 (4.08) nm; IR (KBr) C≡N 2251 cm$^{-1}$.

**Preparation of Bis((5,10,15,20-tetra-*p*-tolylporphyrinato)ruthenium(II) [(RuTPP)$_2$].** Solid RuTTP(CH$_3$CN)$_2$ was heated to 190 °C under vacuum for 24 h according to the related procedure of Collman.[3a] The resulting black solid was only slightly soluble in benzene giving a brownish solution. Exposure of such a solution to air instantaneously produced [RuTTP(OH)]$_2$O.

**Preparation of Bis(acetonitrile)(5,10,15,20-tetra-*p*-tolylporphyrinato)ruthenium(II) [RuTPP(CHCN)$_2$].** RuTTP(CO) (257 mg 0.32 mmol) in $CH_2Cl_2$ was stirred with 100 mg (0.58 mmol) was mCPBA at room temperture for 2 h. *m*-Chlorobenzoic acid was added, and the mixture was stirred overnight. The crude product was purified by chromatography on alumina. A green band eluted with $CH_2Cl_2$ was bis(*m*-chlorobenzoato)($\mu$-oxo)(5,10,19,20-tetra-*p*-tolylporphyrinato)ruthenium(IV) [RuTPP(mCB)]$_2$O (200 mg, 0.11 mmol): vis ($CH_2Cl_2$) $\lambda_{max}$ 393 (Soret), 592 nm; NMR ($CDCl_3$) $\delta$ 8.65 (s, pyr), 8.83 (d), 7.80 (d), 7.31 (d), 7.13 (d), 2.78 (s, p-Me), mCBA 6.12 (d), 3.48 (d), 5.64 (t), 2.74 (s).

[RuTTP(mCB)]$_2$O and Zn dust were stirred in 1:1 $CH_3CN$/benzene at room temperature for 2 h. The solid product was isolated under vacuum and eluted with benzene down a short neutral alumina column. The product, RuTPP(CH$_3$CN)$_2$, was isolated under vacuum: vis (1:3 benzene/$CH_3CN$) ($\lambda_{max}$, log $\epsilon$) 419.2 (5.32), 509.2 (3.95) nm; NMR ($CD_2Cl_2$) 8.33 (s, pyr-H), 8.00 (d, m-H), 7.49 (d, o-H), 2.64 (s, p-Me), −0.02 (s, $CH_3CN$).

**Synthesis of (*S*,2*S*)-*trans*-$\beta$-Methylstyrene Oxide and (1*S*,2*R*)-*cis*-$\beta$-Methylstyrene Oxide.** Epoxides were prepared from ephedrine and $\psi$-ephedrine, respectively, by the method of Witkop and Foltz.[16] Crude epoxides were purified by column chromatography on alumina. After elution with pentane, pure epoxides were obtained by elution with $CH_2Cl_2$: (1*S*,2*S*)-*trans*-$\beta$-methylstyrene oxide, $[\alpha]^{23}D$ = −46.9; (1*S*,2*R*)-*cis*-$\beta$-methylstyrene oxide, $[\alpha]^{23}D$ = +41.

**Catalytic Isomerization of Epoxides.** All reactions were carried out in an inert atmosphere (He) chamber with degassed solvents. Typically, a 30–50-fold excess of epoxide was added to an 8–12 mM solution of an appropriate ruthenium(II) porphyrin in benzene. Following stirring at room temperature, typically for 24 h, the volatile components of the reaction mixture were isolated by vacuum distillation and analyzed by GC (OV-17 column), $^1$H NMR, or GC–MS.

The isomerization of *cis*-2-heptene oxide in mesitylene at 70 °C was carried out in an evacuated, sealed glass container. The reaction products were isolated and analyzed as described above.

**Reaction of (1*S*,2*S*)-*trans*-$\beta$-Methylstyrene Oxide with Ru$^{II}$TTP(THF)$_2$.** A solution of RuTTP(THF)$_2$ (2 mg) and (1*S*,2*S*)-*trans*-$\beta$-methylstyrene oxide (10 $\mu$L) in degassed benzene-$d_6$ was stirred for 43 h in a drybox. The solution was transferred to a round-bottomed flask and distilled under vacuum. The $^1$H NMR of the distillate showed that *trans*- and *cis*-$\beta$-methylstyrene oxide were the major products (trans/cis = 5.4 ± 0.2). Addition of the chiral shift reagent [Eu(tfc)$_3$] showed no separation of the methyl peaks of either of the isomeric epoxides. Accordingly, only one enantiomer was obtained for each stereoisomer. From the addition of authentic samples to these solutions, the product epoxides were identified as *trans*-(1*S*,2*S*)-$\beta$-methylstyrene oxide and *cis*-(1*R*,2*S*)-$\beta$-methylstyrene oxide.

**Kinetics of the Isomerization of *cis*- and *trans*-$\beta$-Methylstyrene Oxide.** *cis*-$\beta$-Methylstyrene oxide (38.5 mM) was added to a solution of RuTMP(THF)$_2$ (1.76 mM) in 1 mL of benzene. Aliquots of the reaction mixture were removed at intervals and quenched by the addition of 4,4′-bipyridyl. The relative amounts of *cis*- and *trans*-epoxide were determined by GC. Similarly, *trans*-$\beta$-methylstyrene oxide (38.5 mM) in benzene was treated with Ru$^{II}$TMP(THF)$_2$ (1.76 mM), and the ratio of epoxide stereoisomers was determined at intervals as described above.

The apparent first-order rate constants, $k_1$ and $k_2$, were determined to be $2.16 \times 10^{-4}$ s$^{-1}$ and $4.01 \times 10^{-5}$ s$^{-1}$, respectively, from a plot of $\ln(\Delta cis/\Delta cis_0)$ versus time, where $\Delta cis = [cis]_t - [cis]_{eq}$ and $\Delta cis_0 = [cis]_{init} - [cis]_{eq}$.

**Direct Observation of Epoxide Isomerization by NMR.** *cis*-$\beta$-Methylstyrene oxide (ca. 48 mM) was added to the solution of Ru$^{II}$TMP(THF)$_2$ (ca. 3 mM) and Ru$^{II}$TMP(CH$_3$CN)$_2$ (ca. 10% of THF adduct) in benzene-$d_6$. This solution was prepared in a drybox and sealed in an NMR tube. The reaction was followed by $^1$H NMR. Resonance corresponding to *cis*-$\beta$-methylstyrene oxide decreased with time, whereas the resonance due to the *trans*-epoxide increased: $^1$H NMR (benzene-$d_6$) (room temperature) porphyrin 8.50 (s, pyr), 7–7.2 (m-H), 2.42 (s, *p*-Me), 2.12 and 2.07 (s, *o*-Me), epoxide 6.42 (1 H, t, $J$ = 7.35), 6.28 (2 H, t, $J$ = 7.67), 4.70 (2 H, d, $J$ = 7.63), −1.18 (1 H, d, $J$ = 4.73), −1.55 (3 H, d, $J$ = 5.6), −2.01 (1 H, m), THF −0.94 (m), −1.40 (m). Free THF was observed at $\delta$ 1.36 and 3.50.

A solution of RuTMP(CO)(MeOH) (5.3 mM) and *cis*-$\beta$-methylstyrene oxide (61 mM) was dissolved in toluene-$d_8$. No attempt was made to protect the solution from air: $^1$H NMR toluene-$d_8$, −50 °C; porphyrin 8.92 (s, pyr), 7.0–7.2 (m-H), 2.41 (s, *p*-Me), 1.88 and 1.87 (s, *o*-Me), epoxide 6.45 (1 H, t, $J$ = 7.0), 6.25 (2 H, t, $J$ = 7.7), 4.54 (2 H, d, $J$ = 7.7), −1.50 (1 H, d, $J$ = 4.2), −1.73 (3 H, d, $J$ = 5.3), −2.44 (1 H, m).

**Reaction of Ru(TTP)(CHCO$_2$CH$_2$CH$_3$) with Benzaldehyde.** (Carbethoxymethyleno)(5,10,15,20-tetra-*p*-tolylporphyrinato)ruthenium(IV) [Ru(TTP)(CHCO$_2$CH$_3$CH$_3$)] was prepared by the addition of a slight excess of ethyl diazoacetate to a solution of RuTTP(THF)$_2$ (1.88 mM) in benzene under helium. The $^1$H NMR spectrum of the carbene adduct was identical with reported values.[6a] Excess benzaldehyde was added to the benzene solution of the carbene complex at room temperature. No change was observed in the NMR spectrum, and after 2 h no other organic products were detected.

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