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Highly Efficient Asymmetric Epoxidation of Alkenes with a *D_4*-Symmetric Chiral Dichlororuthenium(IV) Porphyrin Catalyst

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A dichlororuthenium(IV) complex of 5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,2:5,8-dimethanoanthrance-9-yl]porphyrin, [$\mathrm{Ru^{IV}}(D_4\text{-Por*})\mathrm{Cl_2}$] (**1**), was prepared by heating [$\mathrm{Ru^{II}}$-(D_4-Por*)(CO)(MeOH)] (**2**) in refluxing $\mathrm{CCl_4}$. Complex **1** is characterized by ^{1}H NMR (paramagnetically shifted pyrrolic protons at $\delta_{\mathrm{H}} = -52.3$ ppm), FAB-mass spectroscopies, and magnetic susceptibility measurement ($\mu_{\mathrm{eff}} = 3.1\ \mu_{\mathrm{B}}$). The ruthenium complex exhibits remarkable catalytic activity toward enantioselective alkene epoxidation using 2,6-dichloropyridine *N*-oxide ($\mathrm{Cl_2pyNO}$) as terminal oxidant. The Ru(IV)-catalyzed styrene epoxidation is achieved within 2 h (versus 48 h for the **2**-catalyzed reaction), and optically active styrene oxide was obtained in 69% ee and 84% yield (875 turnovers). Likewise, substituted styrenes and some conjugated cis-disubstituted alkenes (e.g., *cis*-β-methylstyrene, *cis*-1-phenyl-3-penten-1-yne, 1,2-dihydronaphthalene, and 2,2-dimethylchromenes) are converted effectively to their organic epoxides in 50−80% ee under the Ru(IV)-catalyzed conditions, and more than 850 turnovers of epoxides have been attained. When subjecting **1** to four repetitive uses by recharging the reaction mixture with $\mathrm{Cl_2pyNO}$ and styrene, styrene oxide was obtained in a total of 2190 turnovers and 69% ee. UV−vis and ESI-mass spectral analysis of the final reaction mixture revealed that a ruthenium−carbonyl species could have been formed during the catalytic reaction, leading to the apparent catalyst deactivation. We prepared a heterogeneous chiral ruthenium porphyrin catalyst by immobilizing **1** into sol−gel matrix. The heterogeneous catalyst is highly active toward asymmetric styrene epoxidation producing styrene oxide in 69% ee with up to 10 800 turnovers being achieved. The loss of activity of the Ru/sol−gel catalyst is ascribed to catalyst leaching and/or deactivation. On the basis of Hammett correlation ($\rho^+ = -1.62$, $R = 0.99$) and product analysis, a dioxoruthenium(VI) porphyrin intermediate is not favored.

Introduction

Transition metal-catalyzed asymmetric epoxidation of simple alkenes remains a current interest in synthetic organic chemistry,[1−3] since chiral epoxides are versatile building blocks for construction of complex organic molecules.[4] Highly enantioselective alkene epoxidation has been achieved with the use of manganese Schiff base catalysts derived from C_2-symmetric chiral 1,2-diamines, and enantioselectivities >95% ee are attainable for the oxidation of conjugated cis-alkenes as well as some tri- and tetrasubstituted alkenes.[5] However, the Mn-catalyzed reactions often require 2.5−5 mol % catalyst with product turnovers seldom exceeding 100, and the instability of the chiral Mn(salen) catalysts remains to be addressed. In this connection, we are attracted to the oxidation chemistry of metalloporphyrins.[6] It is well-known that iron and manganese porphyrin complexes containing bulky/chiral auxiliaries can mediate alkene epoxidations[6] with excellent regio-[7] and enantioselectivi-

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(6) (a) Meunier, B. *Chem. Rev.* **1992**, *92*, 1411. (b) Mansuy, D. *Coord. Chem. Rev.* **1993**, *125*, 129. (c) *Metalloporphyrin in Catalytic Oxidations*; Sheldon, R. A., Ed.; M. Dekker: New York, 1994. (d) *Metalloporphyrin Catalyzed Oxidations*; Montanari, F., Casella, L., Eds.; Kluwer: Dordrecht, The Netherlands, 1994. (e) Dolphin, D.; Traylor, T. G.; Xie, L. Y. *Acc. Chem. Res.* **1997**, *30*, 251.

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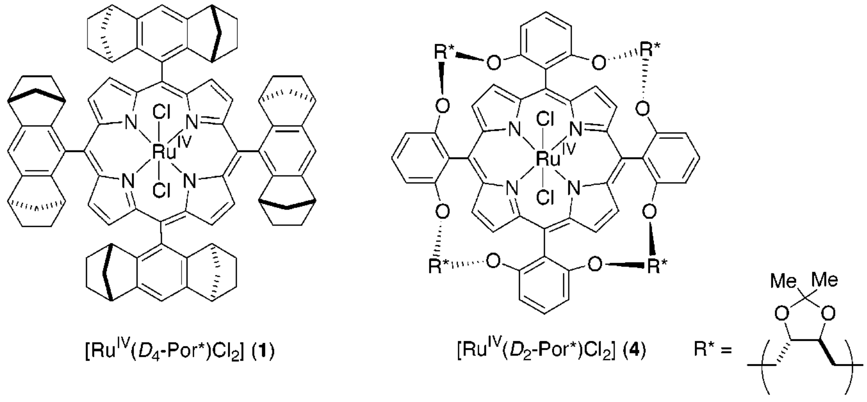

$[Ru^{IV}(D_4\text{-}Por^*)Cl_2]$ (**1**)

$[Ru^{IV}(D_2\text{-}Por^*)Cl_2]$ (**4**)

Figure 1.

ties.[8,9] Of particular note is that highly active and robust metalloporphyrin catalysts with thousands of turnovers can be obtained by introducing electron-withdrawing groups or nonplanar distortion to the porphyrin ligand.[6e] Recently, Collman and co-workers[8i] reported that a pseudo C_2-symmetric binaphthyl-strapped iron(III) porphyrin can effect enantioselective styrene oxidation with up to 5500 turnovers.

Previously we reported the preparation of a dioxoruthenium(VI) complex containing the D_4-symmetric tetrakis(dinorbornabenzene)-substituted porphyrin (D_4-H_2Por^* = 5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,2:5,8-dimethanoanthrance-9-yl]porphyrin, Figure 1) and its reactions with alkenes.[9e,f] This complex reacts preferentially with cis-disubstituted alkenes such as *cis*-*β*-methylstyrene under stoichiometric conditions to give cis-epoxide in up to 72% ee.[9f] Later we found that a series of D_2-symmetric threitol-strapped dioxoruthenium(VI) porphyrin complexes can undergo facile epoxidation of *trans*-*β*-methylstyrene with better enantioselectivity than the analogous reactions with the *cis*-alkene.[9j]

The effectiveness of *trans*-dioxoruthenium(VI) porphyrins for stoichiometric alkene epoxidation has led us to examine the application of ruthenium porphyrin for catalytic organic oxidations. Indeed, ruthenium porphyrins are known to exhibit promising catalytic activities toward organic oxidations using dioxygen,[9e,10] N_2O,[11] or 2,6-dichloropyridine *N*-oxide (Cl_2pyNO)[12] as terminal oxidant. Previously, Berkessal and co-workers[9d] communicated the use of the $[Ru^{II}(D_4\text{-}Por^*)(CO)(MeOH)]$ (**2**) catalyst for enantioselective styrene epoxidation by Cl_2-pyNO. We and Gross also reported the use of other chiral ruthenium(II) porphyrin derivatives for catalytic enantioselective oxidation of *trans*-alkenes[9h,j] and alkanes[13] by aromatic *N*-oxides. However, the catalytic reactions with these chiral ruthenium(II) porphyrin catalysts are slow and require long reaction time (ca. 48 h) for complete substrate consumption. In this regard, we were attracted to the work by Hirobe and co-workers[12d,e] that addition of mineral acids (HCl/HBr) was found to enhance the activities of the ruthenium porphyrin catalysts in the alkane oxidations by aromatic *N*-oxide. In this work, however, we found that addition of HBr to the "$[Ru^{II}(D_4\text{-}Por^*)(CO)] + Cl_2pyNO$" system in the styrene epoxidation led to unsatisfactory yield and enantioselectivity, albeit with complete substrate consumption within 3 h (see later sections). Here we describe a new and highly efficient enantioselective epoxidation of simple alkenes under ambient conditions using a chiral dichlororuthenium(IV) porphyrin, $[Ru^{IV}(D_4\text{-}Por^*)Cl_2]$ (**1**), as catalyst and Cl_2pyNO as terminal oxidant *without the need for an acid promoter.*

Results and Discussion

Preparation of the Dichlororuthenium(IV) Porphyrin Catalyst. Following the method reported by Gross and co-workers,[14a] $[Ru^{II}(D_4\text{-}Por^*)(CO)(MeOH)]$ (**2**)

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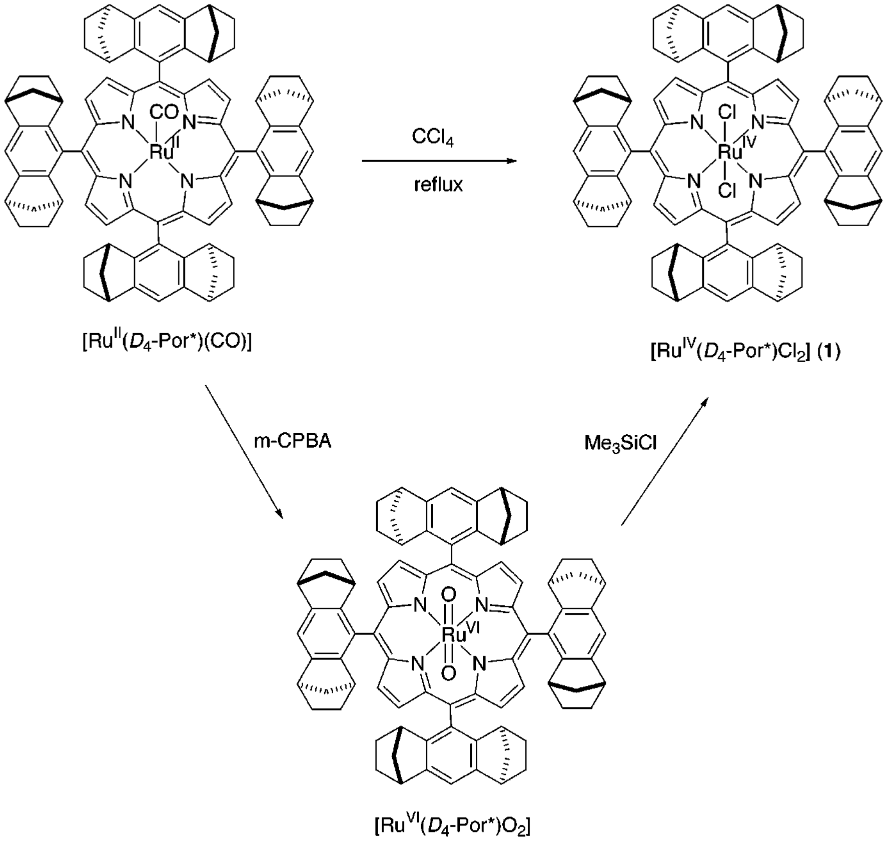
Scheme 1. Preparation of [Ru^{IV}(D_4-Por*)Cl$_2$]



was readily converted to [Ru^{IV}(D_4-Por*)Cl$_2$] (**1**) in 95% yield in refluxing CCl$_4$. The transformation is characterized by a distinct color change from orange to dark red-brown, accompanied by the shift of the Soret band from 414 to 411 nm (CH$_2$Cl$_2$). Compared with the ^{1}H NMR spectrum of the starting ruthenium(II) porphyrin, complex **1** shows considerably broadened resonance signals. A peak at δ_H -52.3 ppm (500 MHz in CDCl$_3$) was observed that we assign it to the paramagnetically shifted pyrrolic protons (see the Experimental Section). This chemical shift value is comparable to some reported data (δ_H -55.4 to -63.8 ppm) for the [Ru^{IV}(tetraarylporphyrin)Cl$_2$] complexes (Ar = Ph, C$_6$H$_4$Me-4, C$_6$H$_3$Me$_2$-2,6 and C$_6$H$_2$Me$_3$-2,4,6).[15] Magnetic susceptibility measurement (Evan's method) of **1** gave $\mu_{eff} = 3.1$ μ_B at 298 K, consistent with a Ru(+4) formulation and a triplet electronic ground state. The observed magnetic moment is comparable to those values for the [Ru^{IV}(DDP)(pz)$_2$] ($\mu_{eff} = 3.1$ μ_B; H$_2$DDP = 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin, Hpz = pyrazole)[16a] and [Ru^{IV}(D_4-Por*)(pz)$_2$] ($\mu_{eff} = 2.9$ μ_B) complexes.[9f] On the basis of the magnetic measurement and FAB-mass spectroscopy (see the Experimental Section), the compound is formulated as [Ru^{IV}(D_4-Por*)Cl$_2$]. Complex **1** can also be prepared by reacting [Ru^{VI}(D_4-Por*)O$_2$] (**3**) with excess Me$_3$SiCl in dichloromethane (Scheme 1).[17]

Catalytic Asymmetric Oxidation of Conjugated Alkenes. Treatment of styrene (0.5 mmol) with Cl$_2$pyNO (0.55 mmol) and **1** (0.5 μmol) in degassed benzene at room temperature afforded styrene oxide in 84% yield (i.e., 875 turnovers; Table 1, entry 1) within 1.5 h, and the enantioselectivity was found to be 69% ee. When **2** was used as catalyst for the same transformation under identical conditions, the reaction required 48 h for completion while giving comparable epoxide yield (80%) and enantioselectivity (70% ee).[9d] Previously Hirobe and co-workers showed that addition of trace amount of mineral acid such as HBr can promote alkane hydroxylations catalyzed by (carbonyl)ruthenium(II) porphyrin complexes.[12d,e] In this work, we attempted to accelerate the **2**-catalyzed alkene epoxidation by following a similar protocol and added 10 μL of HBr to the reaction mixture in the presence of 4 Å molecular sieves (50 mg). Indeed, we observed complete styrene consumption within 3 h after addition of mineral acid to the reaction mixture but the epoxide yield (52%) and enantioselectivity (58% ee) were considerably reduced. Berkessel and co-workers[9d] had reported that higher reaction temperature (125 °C) would promote the turnover frequency (100% conversion in 2 h) but lower enantioselectivity of 55% resulted. In this work, we employed benzene as solvent for all the catalytic reactions. When dichloromethane was used instead of benzene for the catalytic styrene epoxidation, slightly diminished enantioselectivity of 62% ee resulted.

Figure 2 depicts the time courses for the enantioselective styrene oxidation using **1**, **2**, and [Ru^{VI}(D_4-Por*)O$_2$] (**3**) as catalysts. With **2** as catalyst (curve A), a brief induction period was observed and the product evolution

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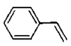
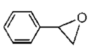
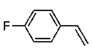
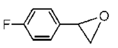
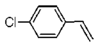
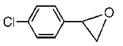
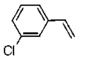
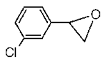
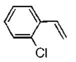
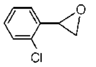
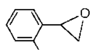
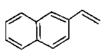
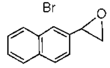
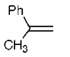
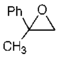
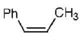
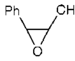
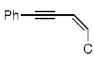
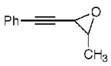
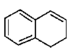
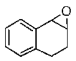
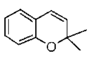
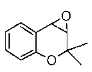
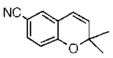
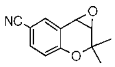
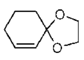
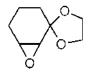
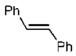
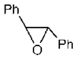
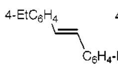
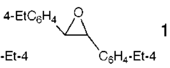
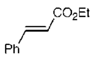
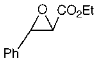
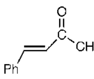
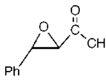
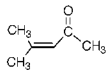
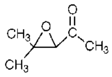
Table 1. [Ru^{IV}(D_4-Por*)Cl$_2$]-Catalyzed Asymmetric Epoxidations*

entry	substrate	product	time(h)	%conv.	epoxide yield% (TON)^a	%ee (abs. config.)^{b,c}
1			1.5	100	84(875)	69(*R*)
2			1.5	100	92(980)	71(*R*)
3			4	100	88(930)	65(*R*)
4			4	90	96(940)	72(*R*)
5			4	80	97(836)	52(*R*)
6			4	100	96(968)	50(*R*)
7			3	68	96(803)	72(*R*)
8			5	60	80(790)	24(n.d.)^d
9			3	100	98(990) (cis > 99%)	68(*1R2S*)
10			2	90	86(700)	70(n.d.)^{d,e}
11			3	100	78(890)	80(*1R2S*)^f
12			1	100	91(900)	65(n.d.)^d
13			2	90	85(860)	67(n.d.)^d
14			12	36	94(440)	35(*2R3S*)
15			16	21	98(270)	30(*1R2R*)
16			16	72	88(620)	14(n.d.)^{d,g}
17			16	18	95(220)	16(n.d.)^d
18			16	48	96(635)	14(n.d.)^d
19			16	30	95(360)	28(n.d.)^d

* Reaction conditions: a mixture containing alkene (0.5 mmol), Cl$_2$pyNO (0.55 mmol) and **1** (0.5 μmol) in degassed benzene (2−5 mL) was stirred at room temperature. Alkene conversion was determined by GLC analysis of the reaction mixture using the internal standard method (1,4-dichloro- or 1,4-bromochlorobenzene); error ±2% of the stated values; mass balance > 90% in most cases. [a] Yields are based on the amount of alkene consumed. TON = turnover numbers. [b] Ee's are determined by either chiral GC (Cyclodex-B or Chiraldex B-PM/GTA columns) or ^{1}H NMR with Eu(hfc)$_3$ as chiral shift reagent. [c] Absolute configurations are determined by comparison with enantiopure authentic samples. [d] n.d. = not determined. [e] Enantiomeric compositions are analyzed by chiral HPLC using a Chiralcel OD column [hexane/isopropanol = 9/1 (v/v), flow rate: 1 mLs^{-1}]. *trans*-Epoxide was formed in 12% yield (TON = 110) and 7% ee. [f] With [RuII(D_4-Por*)(CO)] as catalyst, the chiral epoxide was obtained in 81% yield and 71% ee after 48 h reaction in C$_6$H$_6$. [g] Temperature = 40 °C.

followed a slow reaction progress with < 40% alkene consumption in the first 1.5 h. When either **3** (curve B) or **1** (curve C) was employed as catalyst, there was no detectable induction period and the reaction proceeded to >97% conversion within 1 h.

The 4- and 3-substituted styrenes underwent facile epoxidation to give their epoxides in 65−72% ee (Table 1, entries 2−4) under the Ru(IV)-catalyzed conditions, and yet ca. 50% ee was observed for the analogous reaction with the 2-substituted derivatives (Table 1, entries 5 and 6). The oxidation of 2-vinylnaphthalene was equally effective, affording the epoxide in 96% yield and 72% ee (Table 1, entry 7). The Ru(IV)-catalyzed epoxidation of 1,1-disubstituted alkenes such as α-methylstyrene furnished the corresponding epoxide in 80% yield but with appreciably lower ee of 24% (Table 1, entry 8). Recently, Shi and co-workers[18] reported that optically active α-methylstyrene oxide (94% ee) can be prepared via the chiral ketone-catalyzed asymmetric epoxidation of vinylsilanes, followed by desilylation with TBAF.

Complex **1** was found to catalyze the *cis*-β-methylstyrene oxidation with complete stereoretention (>99% cis) and enantioselectivity of 68% ee was obtained (Table 1, entry 9). However, when *cis*-1-phenyl-3-penten-1-yne was treated with **1** and Cl$_2$pyNO under the standard conditions as denoted in Table 1, a significant amount of *trans*-epoxide was formed (cis/trans = 86:12; see Table 1, entry 10). The enantiopurity of the *cis*-epoxide was 70% ee versus 7% ee for the trans isomer. Up to 80% ee has been attained for the **1**-catalyzed enantioselective epoxidation of 1,2-dihydronaphthalene (Table 1, entry 11). Interestingly, when **2** was used as catalyst, the 1,2-dihydronaphthalene oxide was obtained in only 71% ee. It is noteworthy that over 850 turnovers of organic epoxides are readily attained for all the Ru(IV)-catalyzed enantioselective oxidations of styrenes and conjugated 1,2-disubstituted alkenes.

We have studied the catalytic epoxidation of some other planar cycloalkenes such as 2,2-dimethylchromene. By employing the reaction conditions that **1**/alkene/Cl$_2$pyNO = 1:1000:1100 in benzene at room temperature, epoxychromane was produced in 65% ee and 91% yield (Table 1, entry 12). Optically active 6-cyano-2,2-dimethyl-3,4-epoxychromane has been showed to be a useful intermediate for synthesis of cromakalin,[19] an anti-hypertensive drug. In this work, 6- cyano-2,2-dimethylchromene was converted to its epoxide in 67% ee and 85% yield (Table 1, entry 13) by the **1**-catalyzed asymmetric oxidation. Unlike the planar cycloalkenes, the catalytic oxidation of the nonplanar 3,3-ethylenedioxycyclohexene was less effective, and lower enantioselectivity (35% ee) and alkene conversion (36%) were observed after 12 h reaction (entry 14).

Catalytic Asymmetric Oxidation of *trans*-Alkenes and α,β-Unsaturated Ketones/Esters. When *trans*-stilbene was treated with **1** and Cl$_2$pyNO in benzene for 16 h at room temperature, *trans*-stilbene oxide in 30%

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(18) Warren, J. D.; Shi. Y. *J. Org. Chem.* **1999**, *64*, 7675.

(19) Jacobsen, E. N.; Zhang, W.; Deng, Li, US Patent 5,663,393, 1997.

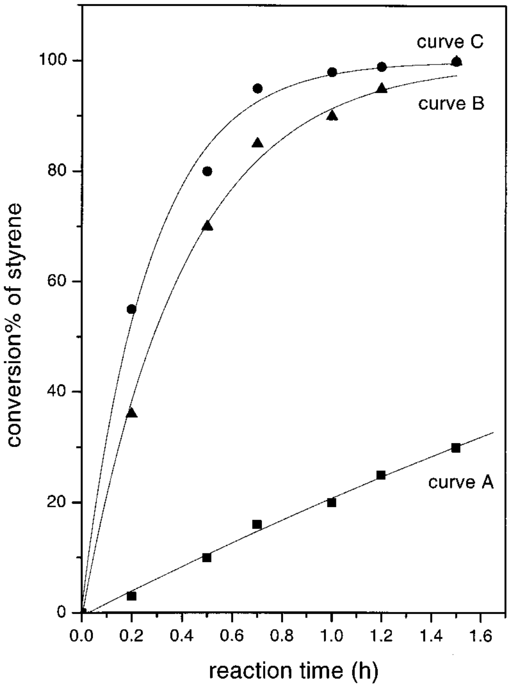

Figure 2. Time courses for the ruthenium-catalyzed styrene epoxidation in benzene (2 mL) at room temperature: styrene (0.5 mmol), Cl_2pyNO (0.55 mmol), Ru catalyst (0.5 μmol). Curve A: $[Ru^{II}(D_4\text{-Por*})(CO)(MeOH)]$ as catalyst. Curve B: $[Ru^{VI}(D_4\text{-Por*})O_2]$ as catalyst. Curve C: $[Ru^{IV}(D_4\text{-Por*})Cl_2]$ as catalyst.

ee was furnished in 98% yield with 21% substrate conversion (Table 1, entry 15). It is noteworthy that catalyst **2** is not effective in catalyzing *trans*-stilbene oxidation under similar conditions. With diethyl-substituted stilbene as substrate (entry 16), we observed higher epoxide yield (88%) and substrate consumption (72%) at higher reaction temperature (40 °C), despite that the substituted stilbene oxide was produced in only 16% ee.

We[9j] and Gross[9h] reported earlier that the D_2-symmetric threitol-substituted ruthenium porphyrin complexes can mediate stereoselective *trans*-alkene epoxidations. By adopting a similar synthetic procedure as that for complex **1**, we prepared the $[Ru^{IV}(D_2\text{-Por*})Cl_2]$ derivative (**4**, see Experimental Section for characterization data)[9k] and examined its catalytic activity for enantioselective trans-alkene epoxidations. Treatment of *trans*-β-methylstyrene (0.5 mmol) with Cl_2pyNO (0.55 mmol) and **4** (0.5 μmol) in degassed benzene at room temperature for 24 h produced *trans*-β-methylstyrene oxide in 56% ee and 98% yield based on 24% substrate consumption (Table 2, entry 5). This ee value is below the 67% ee value for the related stoichiometric epoxidation of *trans*-β-methylstyrene by $[Ru^{VI}(D_2\text{-Por*})O_2]$.[9j] Similarly, the stoichiometric epoxidation of 2-chloro- and 2-bromostyrenes by $[Ru^{VI}(D_2\text{-Por*})O_2]$ gave the corresponding epoxides in 88 and 80% ee, respectively.[20] However, the **4**-catalyzed epoxidations were found to produce the 2-chloro- and 2-bromostyrene oxides in only 52 and 41% ee, respectively (Table 2, entries 2 and 3). Indeed, compared with **1**, complex **4** exhibits much lower catalytic activity for alkene epoxidation by Cl_2pyNO as reflected by the lower substrate conversions (<50%) and long reaction time (24 h). Attempt to improve the enantioselectivity for the 2-chlorostyrene epoxidation was futile. For instance, when the reaction was performed at −30 °C in toluene, we obtained even lower enantioselectivity (23% ee) accompanied with 16% substrate consumption after 24 h reaction. Compared to catalyst **1**, $[Ru^{IV}(D_2\text{-Por*})Cl_2]$ (**4**) exhibits negligible activity toward catalytic *trans*-stilbene epoxidation.

The catalytic epoxidation of some electron-deficient alkenes[3a−c,e] such as α,β-unsaturated ketones/esters with catalyst **1** has also been attempted. With *trans*-ethyl cinnamate, the corresponding epoxide was formed in 95% yield with 7% alkene conversion as determined by GLC analysis and the enantiopurity of the organic epoxide was found to be 18% ee (Table 1, entry 17). Likewise, the related catalytic oxidation of the α,β-unsaturated ketones are achieved in low enantioselectivities (14−28% ee), irrespective of the excellent chemoselectivities (ca. 95%; see Table 1, entries 18 and 19). Indeed, to our knowledge, there are limited precedent for metalloporphyrin-catalyzed asymmetric epoxidation of α,β-unsaturated ketones/esters.

Effect of Oxidants. Using *cis*-β-methylstyrene as substrate, we have studied the effect of other 2,6-disubstituted pyridine *N*-oxides as oxidant on the $[Ru^{IV}(D_4\text{-Por*})Cl_2]$-catalyzed alkene epoxidation. As depicted in Scheme 2, the best ee (68% ee) and stereoselectivity (cis−trans ratio > 99%) were obtained when using Cl_2pyNO or F_2pyNO as oxidant. When Br_2pyNO was employed, we observed slightly reduced enantioselectivity of 63% ee and formation of the *trans*-epoxide (cis/trans = 19:1). Using unsubstituted pyridine *N*-oxide or *N*-methylmorpholine *N*-oxide (NMO) as terminal oxidant, low substrate conversions (25% for pyNO; 16% for NMO) as well as reduced ee's (35% for pyNO; 55% for NMO) and stereoselectivities (cis/trans = 4:1 for pyNO; cis/trans = 8:1 for NMO) of the organic epoxides were obtained.

Catalyst Deactivation. With styrene as substrate, the activity of catalyst **1** has been further evaluated through a sequence of four successive reactions. The reaction mixture was continuously recharged with fresh Cl_2pyNO and alkene at a regular interval for over 22 h, and the results are depicted in Scheme 3. Under reaction conditions (**1** (0.7 μmol), Cl_2pyNO (0.5 mmol), and styrene (0.5 mmol) in benzene at room temperature), all the reaction runs exhibited mass balance >90%, and the overall enantioselectivity was found to be 69%, which is identical with that observed in a single reaction run. More importantly, a total of 2190 turnovers of styrene oxide was attained after the four-reaction sequence. However, the alkene conversion decreased steadily over the first three consecutive reactions: first run, 100% conversion; second run, 80% conversion and third run, 50% conversion. Upon proceeding further to the fourth reaction run, the activity of **1** was low and that only 36% styrene consumption was registered after 16 h of reaction. On the other hand, we found that similar catalytic turnovers (2600) and 69% ee of styrene oxide can be achieved by using 0.01 mol % Ru catalyst (i.e., **1** = 0.05 μmol, styrene = 0.5 mmol, and Cl_2pyNO = 0.55 mmol) after 28 h of reaction.

As noted earlier, the catalytic activity of **1** decreases with successive uses. When the reaction mixture obtained after four consecutive reactions was analyzed by UV−vis spectroscopy, we observed distinct absorption bands at λ_{max} = 414 (Soret band) and 529 nm (Q-band) (see the

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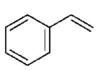
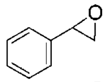
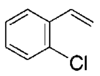
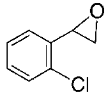
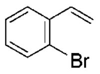
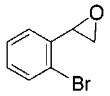
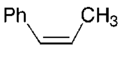
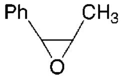
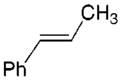
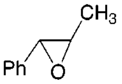
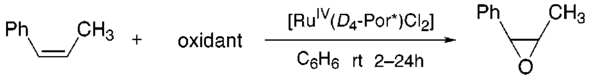
[20] Zhang, R.; Che, C.-M. Manuscript in preparation.

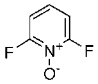
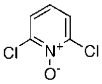
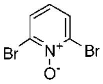
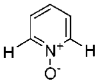
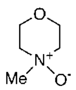
Table 2. [Ru^{IV}(D_2-Por*)Cl$_2$]-Catalyzed Asymmetric Alkene Epoxidations*

entry	alkene	product	t/h	conv.%	yield%	ee% (abs.config.)
1			24	50	82	32 (*R*)
2			24	48	94	52 (*R*)
3			24	50	92	41 (*R*)
4			24	15	80 (cis:trans = 5:1)	10 (*1R2S*)
5			24	24	98	56 (*1R2R*)

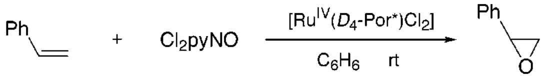
* Reaction conditions: A mixture containing [Ru^{IV}(D_2-Por*)Cl$_2$] (0.5 μmol), alkene (0.5 mmol), and Cl$_2$pyNO (0.55 mmol) was stirred at room temperature in degassed benzene (2–5 mL) for ca. 24 h. Alkene conversion was determined by GLC analysis of the crude reaction mixture using the internal standard method (1,4-dichloro- or 1,4-bromochlorobenzene); error ±2% of the stated values; the mass balance >90% in most cases. Chemical yields are based on the amount of alkene consumed. Ee values were determined by chiral GC equipped with either the Cyclodex-B or Chiraldex B-PM/G-TA columns. The absolute configurations were assigned by comparison with the enantiopure authentic samples.

Scheme 2. Effect of Amine *N*-Oxides on the Ru(IV)-Catalyzed Alkene Epoxidation



oxidant	conv%	epoxide yield%	ee%
	65	96 cis>99%	68
	100	98 cis>99%	68
	64	92 cis:trans = 19	63
	25	76 cis:trans = 4	35
	16	96 cis:trans = 8:1	55

Scheme 3. Results of Four Consecutive Homogeneous Ru(IV)-Catalyzed Epoxidations



run	reaction time (h)	conv.%	TON
1	2	100	560
2	2	80	1060
3	2	50	1360
4	16	36	2190

See text for detailed description

Supporting Information), which corresponds to the characteristic spectral profile of the [Ru^{II}(D_4-Por*)(CO)(MeOH)] complex. The mixture was further analyzed by electrospray ionization mass spectroscopy; several prominent ion clusters with maximum intensities at m/z = 1257, 1274, 1287, 1301, and 1315 were observed (see the Supporting Information). We are not able to identify all the ionic species, and yet the most abundant ionic species with m/z = 1287 could be assigned to "[Ru^{II}(D_4-Por*)(CO)] + OH", in which case the ligand could be oxidatively modified during the reaction. On the basis of these findings, we suggest that the gradual deactivation of **1** may arise from the formation of a ruthenium(II)-carbonyl species that is considerably less active than the dichlororuthenium(IV) complex. Previous work by Groves and co-workers[10] also revealed the formation of [Ru^{II}(TMP)(CO)] (H$_2$TMP = *meso*-tetramesitylporphyrin) in the [Ru^{VI}(TMP)O$_2$]-catalyzed aerobic epoxidation of alkenes.

Heterogeneous Ru/Sol–Gel Catalyst. We reported earlier that ruthenium porphyrin catalysts can be immobilized on surfaces of mesoporous MCM-41 by coordinative grafting,[21a,b] and Merrifield's resin through covalent attachment.[21c] These supported ruthenium complexes exhibit versatile and robust catalytic activities and can be reused with little deterioration of activity and selectivity. In this work, we have prepared a new heterogeneous catalyst by encapsulating complex **1** within the sol–gel silica. Compared to other solid support materials for catalyst immobilization, inorganic sol–gel supports are superior in their thermal stability, inertness toward the entrapped molecules, high porosity (20—100 Å) and large surface areas (>100 m^2 g^{-1}).[22] The sol–gel catalyst was prepared by hydrolysis and condensation of tetraethyl

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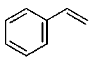
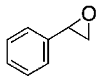
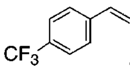
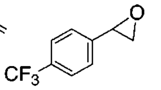
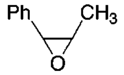
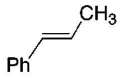
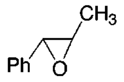
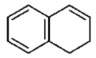
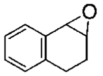
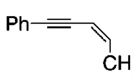
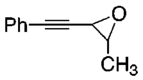
[21] (a) Liu, C.-J.; Li, S.-G.; Pang, W.-Q.; Che, C.-M. *J. Chem. Soc., Chem. Commun.* **1997**, 65. (b) Liu, C.-J.; Yu, W.-Y.; Li, S.-G.; Che, C.-M. *J. Org. Chem.* **1998**, *63*, 7364. (c) Yu, X.-Q.; Huang, J.-S.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2000**, *122*, 5337.

[22] Avnir, D. *Acc. Chem. Res.* **1995**, *28*, 328.

Table 3. Heterogeneous Catalytic Asymmetric Alkene Epoxidations by [Ru^{IV}(D_4-Por*)Cl_2]-Entrapped in Sol–Gel Silica*

entry	alkene	product	t/h	conv.%	yield% (TON)	ee% (abs.config.)
1			48	60	75 (10,800)	70 (*R*)
2			48	23	96 (6100)	71 (*R*)
3			48	32	98 (8480)	66 (*1R2S*)
4			48	20	96 (5580)	26 (*1R2R*)
5			48	52	65 (4300)	72 (*1R2S*)
6			48	24	85 (6300)[a]	72 (n.d.)[b]

* Reaction conditions: A mixture containing Ru/sol–gel catalyst (0.5%w/w) (5 mg), alkene (0.5 mmol), and Cl_2pyNO (0.55 mmol) was stirred at room temperature in degassed benzene (2–5 mL) for ca. 48 h. Alkene conversion was determined by GLC analysis of the crude reaction mixture using the internal standard method (1,4-dichloro- or 1,4-bromochlorobenzene); error ±2% of the stated values; the mass balance >90% in most cases. Chemical yields are based on the amount of alkene consumed. Ee values were determined by chiral GC equipped with either the Cyclodex-B or Chiraldex B-PM/G-TA columns. The absolute configurations were assigned by comparison with the enantiopure authentic samples. [a] *trans*-Epoxide was formed in 13% yield and 2% ee. [b] n.d. = not determined. Ee values determined by chiarl HPLC as depicted in Table 1.

orthosilicate (TEOS) in the presence of **1** in an aqueous ethanol mixture (see the Experimental Section for details), and the ruthenium content entrapped within the silica matrix was determined to be ca. 0.5% w/w.

When styrene (0.5 mmol) was treated with Cl_2pyNO (0.55 mmol) and the Ru/sol–gel catalyst (5 mg) in degassed benzene for 48 h at room temperature, styrene oxide was produced in 75% yield (based on 60% substrate conversion) and 70% ee (Table 3, entry 1) with up to 10,800 turnovers being achieved. The observed enantioselectivity is close to that attained by the homogeneous reaction (see Table 1, entry 1). Apparently the heterogeneous styrene oxidation requires much longer reaction time for completion (cf. 100% conversion in 1.5 h for the homogeneous reaction). It is presumably due to diffusional hindrance for the substrate to approach the active site and the lower catalyst loading (0.02 μmol) (cf. 0.5 μmol of Ru in the homogeneous conditions) employed in the heterogeneous reactions. The oxidation of *cis*-β-methylstyrene was attained with >99% stereoretention and 66% ee; these values are comparable to those of the homogeneous Ru-catalyzed reaction (Table 3, entry 2).

The reusability of the Ru/sol–gel catalyst has been studied by subjecting the catalyst for four repetitive uses under the conditions: styrene (0.5 mmol), Cl_2pyNO (0.55 mmol), and 30 mg of Ru/sol–gel catalyst (0.5%w/w) in benzene at room temperature for 24 h. The solid catalyst was recycled by filtration and washed thoroughly with benzene before reuse. We observed a gradual decrease in catalyst activity over four successive reactions: first run, epoxide yield = 82% (conversion = 90%), 70% ee, turnover 3360 (TOF = 140 h^{-1}); second run, epoxide yield = 82% (conversion = 51%), 69% ee, turnovers = 2180 (TOF = 91 h^{-1}); and third run, epoxide yield = 80% (conversion = 12%), 69% ee, turnovers = 600 (TOF = 25 h^{-1}). The sol–gel catalyst had become largely inactive at the fourth run, and only a trace amount of epoxide was detected. It is important to note that the enantio- and chemoselectivities are retained throughout these consecutive reactions, and a total of over 6000 turnovers of the organic epoxide has been attained. Indeed, when the Ru/sol–gel catalyst was suspended with stirring in benzene at room temperature over 24 h, about 30% of the entrapped ruthenium catalyst was found to have leached into the solvent based on UV–vis spectroscopic analysis of the filtrate. Therefore, the diminishing activity of the sol–gel catalyst can be ascribed to catalyst leaching and/or deactivation.

Hammett Correlation Studies. The effect of para and meta substituents on the homogeneous Ru(IV)-catalyzed styrene oxidation has been investigated. The relative rates (k_{rel}) for the catalytic oxidation of several substituted styrenes (Y-styrene, Y = 4-MeO, 4-Me, 4-F, H, 4-Cl, and 3-NO_2) were evaluated by monitoring the alkene consumption using gas chromatography (see the Experimental Section). In this work, all the catalytic epoxidation proceeded with good epoxide yields (>80%) and mass balance (>95%), and in all cases no traces of polymers or oligomers were detected. Thus, the rate of alkene disappearance should reasonably reflect the alkene reactivity toward the ruthenium-catalyzed epoxidation. Figure 3 depicts a linear correlation (R = 0.998) of log k_{rel} [k_{rel} = k(Y-styrene)/k(styrene)] versus Hammett σ^+ substituent constant. The slope (ρ^+) of the plot is −1.62, which is about 2-fold larger in magnitude than the previously reported value (−0.72) for a related reaction using [Ru^{II}(TDCPP)(CO)(MeOH)] [H_2TDCPP = *meso*-tetrakis(2,6-dichlorophenyl)porphyrin] as catalyst.[21b] Indeed, this observed ρ^+ value is close to those ($\rho^+ = -1.2$ to −2.0) reported for the styrene oxidations by peracids,[23]

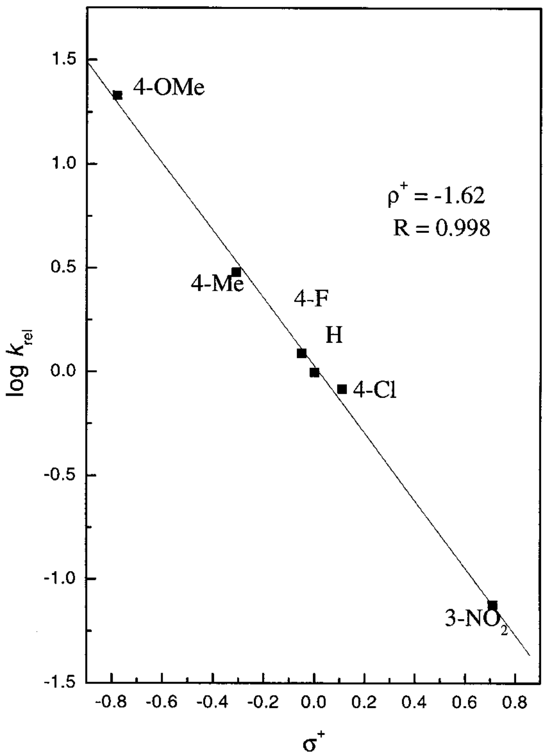


Figure 3. Hammett correlation studies (log k_{rel} vs σ^+) for the Ru(IV)-catalyzed epoxidation of substituted styrenes by Cl_2pyNO.

$[Fe^{IV}(TMP^{\bullet +})O]$ (H_2TMP = tetramesitylporphyrin),[24] $[(Br_8TPP)Cr^V(O)(X)]$ (H_2TPPBr_8 = octabromotetraphenylporphyrin)[25] and $[Ru^{VI}(N_4)O_2]^{2+}$ (N_4 = macrocyclic tertiary tetramine) complexes.[26]

Previously, we showed that the stoichiometric styrene oxidation by dioxoruthenium(VI) porphyrins exhibits a nonlinear (log k_{rel} vs σ^+) Hammett relationship, in which case both electron-donating and -withdrawing substituents moderately promote the reaction.[27] This is in contrast to the linear Hammett relationship observed in this work. The stoichiometric styrene oxidation by $[Ru^{VI}(D_4\text{-Por*})O_2]$ produced styrene oxide in 65% ee comparable to 69% ee observed in the $[Ru^{IV}(D_4\text{-Por*})Cl_2]$-catalyzed styrene oxidation.[9f] However, it should be noted that while the Ru(IV)-catalyzed epoxidation of *cis*-β-methylstyrene exhibits complete stereoretention, partial loss of stereoretention (cis/trans = 10:1) was observed in the related stoichiometric reaction by $[Ru^{VI}(D_4\text{-Por*})O_2]$.[9f] Apparently, based on the product analysis and Hammett correlation studies, involvement of dioxoruthenium(VI) species as the premier reactive intermediate is implausible.

An oxoruthenium(V) complex has been implicated as the active species for the alkane oxidation using the "$[Ru^{II}(TPFPP)(CO)]$ + Cl_2pyNO" system (H_2TPFPP = *meso*-tetrakis(pentafluorophenyl)porphyrin).[28] Previously, we reported a ρ^+ value of −0.72 in our related study on the $[Ru^{II}(TDCPP)(CO)]$-catalyzed epoxidation of substituted styrenes.[21b] In this work, a significantly larger ρ^+ value of −1.62 found for the **1**-catalyzed alkene epoxidation is indicative of a more reactive and oxidizing intermediate compared to the one involved in the Ru(II) system. Indeed, the apparent effectiveness of the Ru(IV)-catalyzed system for *trans*-stilbene epoxidation is indicative of the higher reactivity of the reactive intermediate than the one generated in the Ru(II)-catalyzed reaction. However, we are not able to isolate or detect the reactive species by reacting **1** with excess Cl_2pyNO in either benzene or dichloromethane. Analysis of the reaction mixture by electrospray ionization mass spectroscopy revealed a complicated spectrum, which does not warrant any definitive assignment.

Experimental Section

Materials. All solvents and organic substrates were purified by the standard procedures. The heteroaromatic *N*-oxides (2,6-dichloropyridine *N*-oxide, 2,6-dibromopyridine *N*-oxide, and 2,6-difluoropyridine *N*-oxide) were prepared by oxidation of the corresponding pyridine precursors by H_2O_2 (50%) according to the literature.[29] *trans*-Ethyl cinnamate and 3,3-ethylenedioxycyclohexene were prepared by the literature methods.[19] $[Ru^{II}(Por^*)(CO)(MeOH)]$ and $[Ru^{VI}(Por^*)O_2]$ were prepared by the reported procedures.

Preparation of (Carbonyl)ruthenium(II) Porphyrin $[Ru^{II}(Por^*)(CO)(MeOH)]$. A mixture of $Ru_3(CO)_{12}$ (100 mg) and free chiral porphyrin (H_2Por^*, 100 mg) was heated at reflux in decalin (for D_4-H_2Por^*; see ref 9f) or 1,2,4-trichorobenzene (for D_2-H_2Por^*; see ref 9j) under an argon atmosphere for 14−36 h. After the mixture was cooled to room temperature, the trichlorobezene was removed by distillation and the residue was loaded onto an alumina column. In the case of decalin as solvent, the reaction mixture was directly loaded on an alumina column. For $[Ru^{II}(D_4\text{-Por*})(CO)]$ complex, the column was first eluted with hexanes to remove the decalin and unreacted $Ru_3(CO)_{12}$, followed by elution with dichoromethane. A dark red band containing the desired ruthenium complex was collected. For $[Ru^{II}(D_2\text{-Por*})(CO)]$ complex, the alumina column was first eluted with dichloromethane followed by a dichloromethane−acetone mixture (1:1 v/v), and the ruthenium product was isolated as a brick red compound. The crude complexes were recrystallized from a dichloromethane-hexane mixture and isolated as a dark purple solid. Isolated yield = 87% for $[Ru^{II}(D_4\text{-Por*})(CO)]$; 90% for $[Ru^{II}(D_2\text{-Por*})(CO)]$.

Preparation of Dichlororuthenium(IV) Porphyrin $[Ru^{IV}(Por^*)Cl_2]$. A CCl_4 solution (20 mL) of $[Ru^{II}(Por^*)(CO)(MeOH)]$ (10 mg, 8 μmol) was refluxed overnight under an inert atmosphere. The reaction was characterized by a color change from orange to dark red-brown, and a shift of the Soret band (λ_{max} from 414 to 411 nm for **1**, 426 to 438 nm for **4** in CH_2Cl_2) was observed. After the mixture was cooled to room temperature, the solvent was removed by vacuum evaporation to afford a dark solid, which was collected on a frit and washed with MeOH (for **1**) or hexane (for **4**).

1. Yield: 95%. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ_H 5.93 (s, 4H, phenyl-H), 5.71 (s, 8H), 4.62 (s, 8H), 2.52 (d, 8H), 2.15 (br, 8H), 1.99 (br, 8H), 1.88 (br, 8H), 1.72 (br, 16), −52.3 (s, 8H, pyrrole-H). IR (KBr, cm^{-1}): 1010 (oxidation state marker band). FAB-MS *m*/*z*: 1280 (M^+ − Cl). UV−vis (CH_2Cl_2) λ_{max}/nm (logϵ): 411(5.12), 517 (4.03). μ_{eff} (Evans method) = 3.14 μ_B (solid, room temperature). Anal. Calcd for $C_{84}H_{76}N_4Cl_2Ru \cdot 2.5CH_3OH$: C, 74.54; H, 6.18; N, 4.02; Cl, 5.10. Found: C, 74.45; H, 6.35; N, 3.82; Cl, 4.97.

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4. Yield: 86% (ref 9k). ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ_H −53.3 (s, 4H, pyrrole-H) and −55.4 (s, 4H, pyrrole). IR (KBr, cm^{-1}): 1012 (oxidation state marker band). FAB-MS *m/z*: 1418 (M$^+$). UV−vis (CH$_2$Cl$_2$) λ_{max}/nm (logϵ): 436 (5.10), 532 (4.00). μ_{eff} (Evans method) = 3.14 μ_B (solid, room temperature).

Preparation of the Sol−Gel Encapsulated Dichlororuthenium(IV) Porphyrin [Ru^{IV}(D_4-Por*)Cl$_2$] Catalyst (Ru/Sol−Gel). The sol−gel entrapped catalyst was prepared by hydrolysis and condensation of tetraethyl orthosilicate (TEOS). To a premixed solution containing TEOS (0.69 g), ethanol (0.6 g) and H$_2$O (0.24 g, containing 0.03M HCl) complex **1** (1.25 mg) dissolved in CHCl$_3$ (0.15 mL) was added. The mixture was left to stand at room temperature for 2 weeks and the resultant solid was dried at 90 °C until a constant weight was achieved. The Ru/sol−gel obtained was washed with CHCl$_3$ (5 mL) every 2 h until the filtrate became colorless, and the solid was dried in vacuum for 2 days. The content of ruthenium porphyrin complex in sol−gel matrix was determined to be 0.5% w/w by dissolving the sample into HF, followed by atomic absorption analysis.

General Procedure for the Chiral Ruthenium Porphyrin Catalyzed Alkenes Epoxidations. A mixture of alkene (0.5 mmol), aromatic *N*-oxide (0.55 mmol), and ruthenium catalyst (0.5 μmol) in degassed benzene (2 mL) was stirred under an inert atmosphere at room temperature for 1.5−48 h. After addition of internal standard, the aliquot was taken for GLC or ^{1}H NMR analysis. The yields were based on the amount of alkene consumed.

Determination of Enantiomeric Excess. The enatiopurities of styrene oxide, 4-fluoro-/4-chlorostyrene oxides, *cis*-β-methylstyrene oxide, and 1,2-dihydronaphthalene oxide were determined by chiral GLC using J&W Scientific Cyclodex B column (30 m × 0.25 mm i.d.; 0.125 μm thickness). The enantiopurities of 2-chloro-/2-bromostyrene oxide and α-methylstyrene oxide were determined by chiral GLC using Chiraldex B-PM column (30 m × 0.32 mm, i.d.; 0.125 μm thickness). For those epoxides from the α,β-unsaturated ketones/esters and *trans*-β-methylstyrene oxidations, their enantiomeric purities were analyzed by chiral GLC using Chiraldex G-TA column (30 m × 0.32 mm, id.; 0.125 μm thickness). A HPLC method was employed to determine the enantiopurity of the epoxy vinyl phenylacetylene using a Chiralcel OD column [eluant: hexane/isoproyl alcohol (90:10 v/v); flow rate 1 mL s^{-1}; UV detector monitored at 254 and 230 nm].

The enantiomeric purities of the organic epoxides other than those state above were determined by ^{1}H NMR spectroscopy in the presence of [Eu(hfc)$_3$] as chiral shift reagent. A CDCl$_3$ solution (3 mL) of [Eu(hfc)$_3$] (150 mg) was added in a 10 μL portion to a NMR tube containing the chiral epoxide (∼5 mg) in CDCl$_3$, and a ^{1}H NMR spectrum was acquired after each addition of the shift reagent. The shift reagent was added continuously until baseline resolution of the absorption peak(s) was achieved. Enantiomeric excess was determined based on the integral ratio of the resolved peaks due to enantiomers.

In all cases, the conditions for chiral resolution employing either the chiral GLC or ^{1}H NMR technique were set up and optimized with baseline resolution of racemic epoxides.

Procedure for the Heterogeneous Alkene Epoxidations Catalyzed by Ru/Sol−Gel. The procedure is the same as the general procedure for the ruthenium porphyrin catalyzed alkene epoxidations, except that the sol−gel encapsulated Ru catalyst (5 mg) was used. At the end of the reaction, the catalyst was removed by the centrifugation-filtration procedure. The filtrate was taken for GLC analysis for product characterization and quantification.

Determination of Relative Reactivities (k_{rel}) for the Catalytic Oxidation of substituted Styrenes. A CH$_2$Cl$_2$ solution containing styrene (0.5 mmol), substituted styrene (0.5 mmol) and Cl$_2$pyNO (0.55 mmol) was prepared and complex **1** (0.5 μmol) was added. The reaction mixture was stirred for 2 h at room temperature. The amount of styrenes before and after the reactions were determined by GLC. The relative reactivities were determined by the following equation:

$$k_{rel} = k_Y/k_H = \log (Y_f/Y_i)/\log (H_f/H_i)$$

where Y_f and Y_i are the final and initial quantities of the substituted styrenes; H_f and H_i are the final and initial quantities of styrene.

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Supporting Information Available: UV−vis and electrospray ionization mass spectra of the Ru(IV)-catalyzed styrene oxidations (Figures S1−4). This material is available free of charge via the Internet at http://pubs.acs.org.

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