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Catalytic enantioselective oxidation of aromatic hydrocarbons with D_4-symmetric chiral ruthenium porphyrin catalysts

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Abstract—The [Ru^{II}(D_4-Por*)(CO)(MeOH)] (D_4-H_2Por* = 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) complex **1** is an effective catalyst for asymmetric hydroxylation of aromatic hydrocarbons with 2,6-dichloropyridine *N*-oxide (Cl_2pyNO) as terminal oxidant. Up to 76% ee was achieved for the catalytic hydroxylation of 4-ethyltoluene, 1,1-diethylindan and benzylcyclopropane. Both electron-donating and -withdrawing substituents were found to accelerate the catalytic oxidation reaction, and a large primary H/D kinetic isotope effect ($k_H/k_D = 11$ at 298 K) was observed for the catalytic ethylbenzene-d_{10} oxidation. A mechanism involving rate-limiting hydrogen atom abstraction by reactive oxoruthenium species is postulated.

1. Introduction

Selective oxidation of saturated hydrocarbons presents a major challenge in current chemical research.[1] In biological systems, alkanes are catalytically converted to alcohols by the cytochrome P-450 enzymes using dioxygen under physiological conditions, and considerable effort has been directed to the development of biomimetic transition metal catalysts for stereo- and regioselective organic oxidations.[2,3] While significant progress has been made in the transition metal-catalyzed enantioselective alkene epoxidations,[4] attempts to develop highly enantioselective alkane hydroxylations have been met with limited success.

In 1989, Groves et al. reported an asymmetric hydroxylation of ethylbenzene and derivatives using a chiral iron porphyrin complex as catalyst and iodosylbenzene (PhIO) as oxidant; the corresponding alcohols were obtained in 19–72% yield and 40–72% ee.[5] Later Jacobsen et al. reported that chiral [Mn^{III}(salen)] complexes derived from optically active diamines can effect catalytic diastereoselective hydroxylation of racemic 1,2-dihydronaphthalene oxide to afford optically active epoxyalcohols and epoxides in >90% ee through kinetic resolution.[6] By employing Mn(III)–salen complexes, which had chiral binaphthyl units as catalyst, Katsuki et al. reported the attainment of up to 90% ee for asymmetric hydroxylation of 1,1-dimethylindan by PhIO.[7] While Jacobsen's catalytic system produced only 14% ee for the same reaction, the atropochirality of the Katsuki's catalyst system was suggested to be important for the observed enantioselectivity.

In order to design effective chiral catalysts for enantioselective alkane hydroxylations, we decided to prepare structurally well-defined chiral oxo-metal complexes for stoichiometric asymmetric oxygen atom transfer reactions.[8] Previously, we showed that homochiral *trans*-dioxoruthenium(VI) porphyrins such as [Ru^{VI}(D_4-Por*)O_2]{D_4-H_2Por* = 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, Fig. 1} can undergo enantioselective oxygen atom transfer to alkenes.[8] Subsequently, we reported that [Ru^{VI}(D_4-Por*)O_2] is an effective catalyst for asymmetric hydroxylation of ethylbenzene with 2,6-dichloropyridine *N*-oxide (Cl_2pyNO) as oxidant, and (*S*)-1-phenylethanol was obtained in up to 76% ee.[9] The use of ruthenium porphyrins for catalytic organic oxidations is well documented.[10] We and others have reported catalytic systems based on ruthenium porphyrin catalyst for alkene epoxidations with Cl_2pyNO as oxidant.[8,10]

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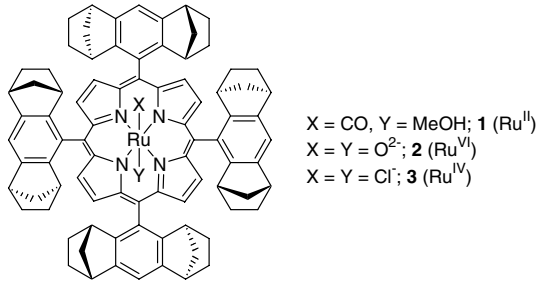


Figure 1.

Groves et al. recently described that a perfluorinated ruthenium porphyrin can catalyze alkane oxidation using aromatic *N*-oxides with high product turnovers.[10d] In conjunction to our earlier report,[9] we herein report a full account of the catalytic enantioselective alkane oxidations by homochiral ruthenium porphyrin complexes.

2. Results and discussion

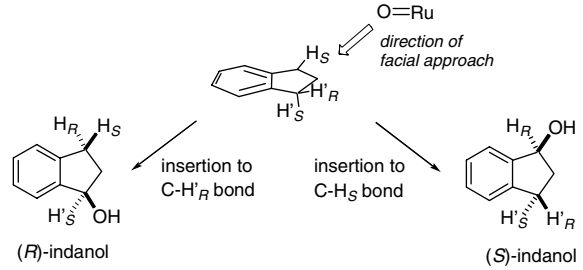
Treatment of ethylbenzene (0.5 mmol) with Cl_2pyNO (0.55 mmol) and a catalytic quantity (0.5 μmol) of either [Ru^{II}(D_4-Por*)(CO)(MeOH)] **1** or [Ru^{VI}(D_4-Por*)O_2] **2** in dry degassed benzene (5 mL) at room temperature for 12 h afforded a mixture of (*S*)-1-phenylethanol (62%) and acetophenone (37%) (Table 1, entry 1). The enantiopurity of the phenylethanol was determined to be 72% ee by chiral capillary GC analysis. However, when the ethylbenzene oxidation was performed under stoichiometric conditions: **2** (30 μmol), ethylbenzene (1 mmol) in CH_2Cl_2 (containing 2% pyrazole as additive), (*S*)-1-phenylethanol was obtained in 32% yield and 45% ee. Similar results [30% yield and 37% ee for (*S*)-1-phenylethanol formation] were obtained with benzene as solvent for the same transformation.

Previously we reported that [Ru^{IV}(D_4-Por*)Cl_2] **3** is a highly effective catalyst for enantioselective alkene epoxidation using Cl_2pyNO as oxidant.[8f] In this work, we found that **3** is equally effective as **1** and **2** for asymmetric ethylbenzene oxidation, and comparable results were obtained. Unless otherwise noted, **1** was chosen hereafter as the catalyst for the rest of our study because of sample availability.

At higher temperature (40 °C), the **1**-catalyzed ethylbenzene oxidation proceeded faster without compromising the enantioselectivity (70% ee), albeit with a lower alcohol yield (45%). Benzene was found to be the solvent of choice; polar solvents such as CH_2Cl_2 gave a lower enantioselectivity of 62% for the asymmetric ethylbenzene oxidation.

As shown in Table 1, *para*-substituted ethylbenzenes (Y = H, F, Cl, Br, Me and MeO) are also effective substrates for the **1**-catalyzed asymmetric hydroxylation, and the corresponding 1-arylethanols were produced in comparable ee of 62–76% (entries 2–6). However, the analogous catalytic oxidation of 2- and 3-ethyltoluenes furnished their corresponding alcohols in 38% and 48% ee, respectively, (entries 7 and 8). When 2-ethylnaphthalene was employed as a substrate, (*S*)-1-(2-naphthyl)ethanol was obtained in 62% yield and 75% ee (entry 9). This level of enantioselectivity is comparable to the best results for the reported metal-catalyzed asymmetric hydroxylation of ethylbenzenes.[5–7]

Cyclic alkanes such as indane and tetrahydronaphthalene are poor substrates, and enantioselectivities of ca. 12% ee were obtained (entries 10 and 11). Assuming a reactive O=Ru species as an intermediate, functionalization of the two enantiotopic benzylic C–H bonds of the cycloalkanes would generate two enantiomeric alcohols, thereby accounting for the observed low ee for the indane and tetrahydronaphthalene oxidation (Scheme 1). However, with 1,1-diethylindane as substrate, the **1**-catalyzed oxidation reaction gave the (*S*)-alcohol in 76% ee (entry 12).



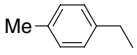
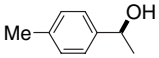
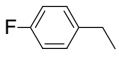
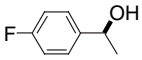
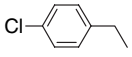
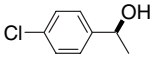
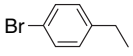
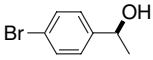
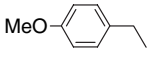
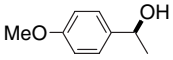
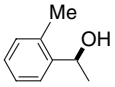
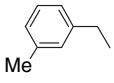
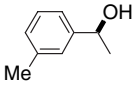
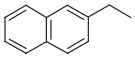
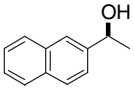
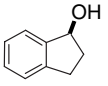
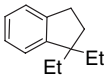
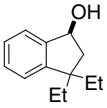
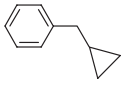
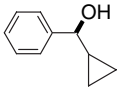
Scheme 1.

Subjecting benzylcyclopropane to the **1**-catalyzed oxidation, the corresponding benzyl alcohol and ketone were formed in 28% and 70% yield, respectively (entry 13). No ring opened products were detected by NMR or GLC techniques. Using chiral capillary GC analysis, the enantiopurity of the product alcohol was determined to be 76% ee.

Previously, we reported that homochiral D_2-symmetric [Ru^{VI}(D_2-Por*)O_2] can effect asymmetric epoxidation of *trans*-alkenes in up to 80% ee.[8e] Herein, we found that neither [Ru^{VI}(D_2-Por*)O_2] nor [Ru^{II}(D_2-Por*)(CO)(MeOH)] exhibited comparable enantioselectivity for catalytic ethylbenzene oxidation. For example, treatment of ethylbenzene (0.5 mmol) with Cl_2pyNO (0.55 mmol) and [Ru^{VI}(D_2-Por*)O_2] (0.5 mmol) in degassed benzene afforded (*S*)-1-phenylethanol in only 13% ee with only 4% substrate conversion. Recently, Gross et al. reported that an isostructural chiral D_2-symmetric ruthenium porphyrin complex containing four diaryl-substituted threitol units catalyzed oxidation of tertiary alkanes with 38% ee.[8d]

By competitive experiments, a primary kinetic isotope effect (k_H/k_D) = 11.2 (298 K) was established for the **1**-catalyzed oxidation of ethylbenzene-d_{10}. This indicates that the rate-limiting step involves substantial C–H bond cleavage.[11] Similarly, the electronic effect on the catalytic oxidation of *para*-substituted ethylbenzenes

Table 1. Ruthenium-catalyzed asymmetric alkane oxidation

Entry	Substrate	Product	Time (h)	% Conv	Alcohol yield %[a]	% ee (abs. config.)	Ketone yield %[a]
1			12 12[b]	13 10[b]	62 67[b]	72 (*S*) 62 (*S*)[b]	37 32
2			30	20	72	76 (*S*)	24
3			10	11	60	72 (*S*)	38
4			18	23	28	74 (*S*)	70
5			8	14	63	74 (*S*)	36
6			8	15	65	62 (*S*)	32
7			16	5	90	38 (*S*)	10
8			22	12	60	48 (*S*)	40
9			20	15	62	75 (*S*)	38
10			6	54	65	12 (*S*)	34
11			2	42	60	12 (*S*)	40
12			3	36	70	76 (*S*)	30
13			18	30	28	76 (*S*)	70

Reaction conditions: A mixture of alkane (0.5 mmol), [Ru^{II}(D_4-Por*)(CO)(MeOH)] (0.5 μmol) and Cl_2pyNO (0.55 mmol) was stirred in dry C_6H_6 (5 mL) for 12 h at room temperature. Aliquots were analyzed by chiral capillary GC equipped with either J & W scientific Cyclodex B or B-PM chiral column for quantification and ee determination.

[a] % Yield were based on the amount of alkane consumed.

[b] In CH_2Cl_2.

(Y = H, F, Cl, Br, Me and MeO) was also examined. Both electron-donating and -withdrawing substituents were found to accelerate the catalytic reactions. This result is incompatible with a mechanism involving either rate-limiting carbocation or cation radical formation. Figure 2 depicts a dual Hammett correlation analysis of the relative rate constants ($\log k_{rel}$) using the substituent constants σ_p^+ and $\sigma_{JJ}^\bullet$, a linear correlation ($R = 0.99$) was established: $\log k_{rel} = 0.78\sigma_{JJ}^\bullet - 0.71\sigma_p^+$. The term $\sigma_{JJ}^\bullet$ is a carboradical substituent constant developed by Jiang and Ji to measure the spin delocalization effect of the benzylic radical transition state.[12] The $\rho_{JJ}^\bullet/\rho_p^+ = 1.1$ reflects that both spin delocalization and polar effects are equally important with respect to their influence to the transition state energy.

It is well documented that dioxoruthenium(VI) porphyrins are potent oxidants for alkenes and alkanes.[13] Herein, we have examined the stoichiometric reactions of **2** with a series of substituted ethylbenzenes and related compounds for a better understanding of the nature of the active species involved in the catalytic ethylbenzene oxidation. As noted in earlier sections, the stoichiometric ethylbenzene oxidation by **2** produced 1-phenylethanol in only 45% ee, which is appreciably lower than the 72% ee value observed for the catalytic reactions. Likewise, the stoichiometric oxidation of other substituted ethylbenzenes also gave <60% ee.

Using UV–vis spectrophotometry, we have undertaken a kinetic study on the stoichiometric oxidation of ethyl-

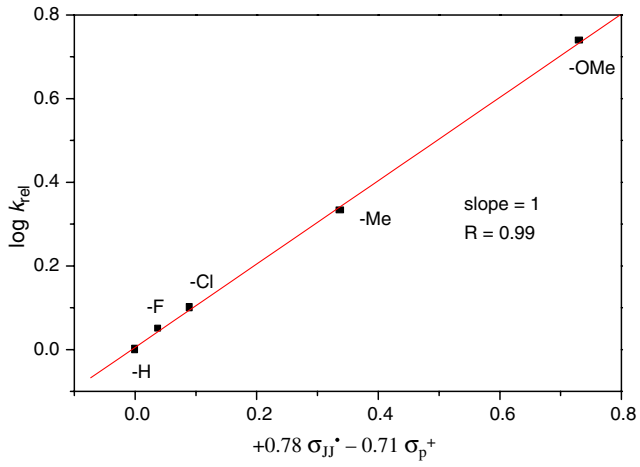


Figure 2. Dual parameter Hammett correlation plot for the **1**-catalyzed ethylbenzene oxidation.

benzene by **2** in 1,2-dichloroethane [containing 2% pyrazole (Hpz)] at 313 K (Fig. 3). Under pseudo-first-order conditions, that is, [alkane] ≫ [Ru], an experimental rate law: rate = k_{obs} [Ru] (where k_{obs} = pseudo-first-order rate constant) was established. The second-order rate constant was evaluated to be $(7.7 \pm 0.4) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. For the stoichiometric oxidation of ethylbenzene-d_5, the second-order rate constant was determined to be $(0.87 \pm 0.1) \times 10^{-4}$ dm^3 mol^{-1} s^{-1} at 313 K, which then translates to a primary kinetic isotope effect (k_H/k_D) = 8.9. This KIE for the stoichiometric reaction is comparable to the related value (k_H/k_D = 11) for the catalytic reaction.

Analogous to the catalytic reactions, both electron-donating and -withdrawing substituents promote the stoichiometric ethylbenzene oxidation. Linear correlation with σ_p^+ and $\sigma_{JJ}^{\bullet}$ for the second-order rate constants ($\log k_{rel}$) has been established: $\log k_{rel} = +0.56\sigma_{JJ}^{\bullet} - 0.36\sigma_p^+$; the reaction constants ($\rho_{JJ}^{\bullet}$ and ρ_p^+) are comparable to those ($\rho_{JJ}^{\bullet} = 0.78$; $\rho_p^+ = -0.71$) for the catalytic reaction. These findings suggest that the transition states of the catalytic and stoichiometric ethylbenzene oxidations are similar, presumably proceeding via a hydrogen atom abstraction mechanism.

The nature of the active species for the **1**-catalyzed alkane oxidation was further scrutinized using *cis*-decalin as a mechanistic probe. When *cis*-decalin was treated with **1** (1 mol %) and Cl_2pyNO in dry benzene, *cis*-9-decalol was formed exclusively in >98% yield without any *trans*-alcohol being detected. Herein, we found that dioxoruthenium(VI) complex **2** did not effectively oxidize *cis*-decalin under similar conditions. Yet by using [Ru^{VI}(TMP-β-Br_8)O_2] [H_2TMP-β-Br_8 = *meso*-tetrakis-(2,4,6-trimethylphenyl)-β-octabromoporphyrin] as an oxidant, the *cis*-decalin oxidation proceeded non-stereoselectively and both *cis*- and *trans*-9-decalol were obtained in a ratio of 80:20. The disparate results for the catalytic and stoichiometric decalin oxidations raises doubts about the involvement of dioxoruthenium(VI) complexes for the **1**-catalyzed asymmetric hydroxylation.

Moreover, we employed cumene as another probe substrate to evaluate the mechanism of the catalytic and the stoichiometric reactions. Under the **1**-catalyzed conditions [cumene (0.5 mmol), Cl_2pyNO (0.55 mmol) and **1** (0.5 μmol)], cumyl alcohol was formed in 80% yield along with a small amount of acetophenone (9%). However, under the stoichiometric conditions, we found that the reaction of cumene with **2** gave cumyl alcohol and acetophenone in 20% and 40% yield, respectively. Taken together the results of *cis*-decalin and cumene oxidations, the observed stereoretention and high

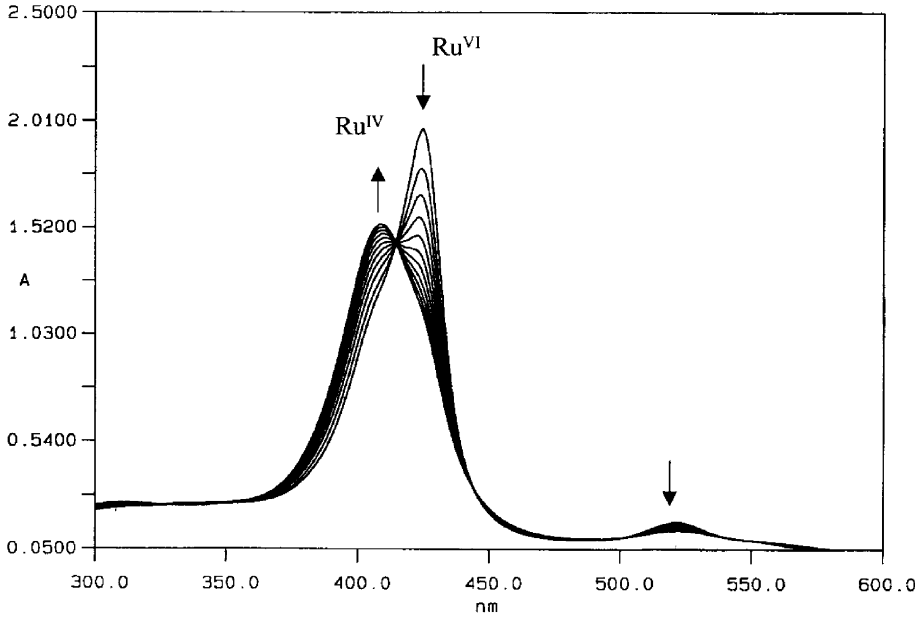


Figure 3. UV–vis spectral trace for the stoichiometric ethylbenzene oxidation by [Ru^{VI}(D_4-Por*)O_2] (**2**) in 1,2-dichloroethane (with 2% pyrazole) at 313 K.

Table 2. Competitive cycloalkane oxidations using the '$Ru^{IV}(D_4\text{-Por}^*)Cl_2] + Cl_2pyNO$' system

Entry	Alkanes	% Conversion	Products (% yield)[a]	Relative reactivity[b]
1	Cyclohexane + cyclohexane-d_{12}	60	Cyclohexanol (35%) Cyclohexanone (60%)	1
		1.4	Cyclohexanol-d_{12} (35%) Cyclohexanone-d_{10} (60%)	0.24 ($k_H/k_D = 4.2$)
2	Cyclooctane + cyclohexane	14.2	Cyclooctanol (53%) Cyclooctanone (38%)	1
		2.4	Cyclohexanol (30%) Cyclohexanone (62%)	0.17
3	Cyclooctane + *cis*-decalin	11.8	Cyclooctanol (50%) Cyclooctanone (35%)	1
		13.0	*cis*-9-Decalol (92%)	8.7
4	Cyclooctane + adamantane	8.2	Cyclooctanol (54%) Cyclooctanone (32%)	1
		36.8	Adamantanol (92%)	24.1

Reaction conditions: To a 1:1 mixture of cycloalkanes (1 mmol) and Ru catalyst (1 μmol) was added Cl_2pyNO (1.1 mmol) under argon, and the mixture was stirred at room temperature for 36 h. Aliquots were taken and analyzed by GC–MS for product identification and quantitation.
[a] % Yield were based on the amount of alkane consumed.
[b] Calculated from alkane conversion; statistical factor corrected.

alcohol-to-ketone ratio for the catalytic reaction implies a more efficient radical recombination step subsequent to the hydrogen atom abstraction step.[14]

The participation of free radical intermediates for the **1**-catalyzed alkane oxidation has also been evaluated using cyclohexane as substrate. However, **3** was chosen to be the catalyst because of its higher activity than **1** for the cyclohexene oxidation. As shown in Table 2, cyclohexane was oxidized to a mixture of cyclohexanol (35%) and cyclohexanone (60%; entry 1), and a primary kinetic isotope effect (KIE) of 4.2 was registered based on a competitive experiment (entry 1). Apparently, the reaction involves the formation of the cyclohexyl radical, since trace (ca. 1%) cyclohexyl chloride was detected when the oxidation was carried out in the presence of CCl_4. Furthermore, the reaction rate was largely reduced by the addition of a free-radical scavenger (hydroquinone).

We also investigated the competitive oxidation of cyclooctene/cycloalkanes in CH_2Cl_2 at 298 K using the '**3** + Cl_2pyNO' protocol. The relative reactivities per H atom (normalized) follow the order: adamantane (24.1) > *cis*-decalin (8.7) > cyclooctane (1) > cyclohexane (0.2). This reactivity pattern is parallel with the C–H bond strength that a 2° C–H bond is stronger than a 3° C–H bond. The employment of such competitive experiments to distinguish between radical and Gif chemistry has been proposed.[15] It is apparent that the 'Ru-porphyrin/Cl_2pyNO' system in this work behaves differently from the Gif system towards alkane oxidation. The substantial increase in the reactivity from cyclohexane to adamantane is consistent with the stability of the alkyl radicals generated through H-atom abstraction, that is, 3° C–H bonds are weaker than the 2° C–H bonds.

With regard to the nature of the active species for the **1**-catalyzed ethylbenzene oxidation, Groves et al. proposed some highly reactive oxoruthenium(V) porphyrin intermediates that were responsible for catalytic alkane oxidation by aromatic *N*-oxides.[10] It is not unreasonable to assume that an oxoruthenium(V) species would behave differently from *trans*-dioxoruthenium(VI) complexes.[11a,13] Indeed, our earlier work on asymmetric alkene epoxidation also revealed similar disparities in stereoretention for *cis*-alkene oxidation under the catalytic and stoichiometric conditions.[8]

3. Conclusion

A catalytic protocol based on a homochiral D_4-symmetric ruthenium porphyrin catalyst and Cl_2pyNO as terminal oxidant has been developed for enantioselective hydroxylation of aromatic hydrocarbons. Results from the mechanistic study and product analysis are consistent with a mechanism involving hydrogen atom abstraction. The **1**-catalyzed alkane oxidations exhibit moderate-to-good enantioselectivity and high stereoretention of the alcohol products.

4. Experimental

4.1. General experimental

The alkanes employed herein were obtained commercially and purified either by distillation or crystallization, and their purities verified by GLC prior to use. Solvents were of analytical grade and purified by distillation over CaH_2 or sodium/benzophenone. 2,6-Dichloropyridine *N*-oxide was prepared by the literature method.[16] The synthesis and characterization of $[Ru^{II}(D_4\text{-Por}^*)(CO)(MeOH)]$ **1**[8b] and $[Ru^{VI}(D_4\text{-Por}^*)O_2]$ **2**[8b] were reported elsewhere.

4.2. Preparation of dichlororuthenium(IV) porphyrin $[Ru^{IV}(D_4\text{-Por}^*)Cl_2]$ 3

A solution of $[Ru^{II}(D_4\text{-Por}^*)(CO)(MeOH)]$ (10 mg, 8 μmol) in CCl_4 (20 mL) was refluxed overnight, fol-

lowed by evaporation of the solvent and subsequent washing with MeOH. The transformation of [Ru^{II}-(D_4-Por*)(CO)(MeOH)] to [Ru^{IV}(D_4-Por*)Cl_2] resulted in a color change from orange to dark red-brown, accompanied by a shift of the Soret band (λ_{max} from 414 to 411 nm in CH_2Cl_2). Its ^1H NMR spectrum shows broad signals and the occurrence of one paramagnetically shifted pyrrole proton signal at −52.3 ppm (in $CDCl_3$, 500 MHz), which are characteristic of dihalogeno ruthenium(IV) porphyrins. Magnetic susceptibility measurements for **3** by Evans Method gave μ_{eff} of 3.1 μ_B at 298 K, consistent with two unpaired electrons in the ground state. Yield >95%. ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 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). ESI-MS *m/z*: 1314 (M^+), 1280 (M^+−Cl). UV–vis (CH_2Cl_2) λ_{max}/nm (log ε): 411 (5.12), 517 (4.03). μ_{eff} (Evan's method) = 3.14 μ_B (solid, room temperature).

4.3. General procedure for hydroxylation of alkanes by [Ru^{VI}(D_4-Por*)O_2]

To a degassed CH_2Cl_2 solution (2 mL) containing alkane (1 mmol) and pyrazole (0.3 mmol) was added [Ru^{VI}(D_4-Por*)O_2] (15–30 μmol) under an argon atmosphere. The reaction mixture was stirred at room temperature overnight. The completion of the reaction was indicated by the disappearance of the Soret band of the starting dioxoruthenium(VI) complex. The ruthenium-containing product was removed by filtration over an alumina column using dichloromethane as the eluant, and the filtrate was analyzed by gas chromatography equipped with a chiral capillary column (J&W Scientific Cyclodex-B or B-PM). Internal standard method was employed to quantify the products. The product yields were based on the amount of the oxidant used. Absolute configurations were determined by comparing retention times with the chiral authentic samples.

4.4. General procedure for catalytic asymmetric hydroxylation by Cl_2pyNO

To a mixture of alkane (0.5 mmol) and Cl_2pyNO (0.55 mmol) in dry, degassed benzene (5 mL) was added the catalyst (0.5 μmol), and the solution stirred under an argon atmosphere at room temperature unless otherwise noted. The aliquot was analyzed by GLC for product identification and quantification by the internal standard method. The product yields were based on the amount of alkanes consumed.

4.5. Determination of the relative reactivities (k_{rel}) for catalytic hydroxylation of *para*-substituted ethylbenzenes

A CH_2Cl_2 solution containing ethylbenzene (0.5 mmol), substituted ethylbenzene (0.5 mmol) and Cl_2pyNO (0.55 mmol) was prepared. Catalyst (0.5 μmol) was added and the solution stirred for 12 h. The amount of arylalkanes 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 ethylbenzene; H_f and H_i are the final and initial quantities of ethylbenzene.

4.6. Determination of primary kinetic isotope effect (k_H/k_D) for catalytic oxidation of ethylbenzene and ethylbenzene-d_5

A solution containing ethylbenzene (0.5 mmol), 4-chloroethylbenzene (0.5 mmol), 2,6-dichlorobenzene (0.1 mmol, as the internal standard), and Cl_2pyNO (0.55 mmol) was prepared. Another solution, using ethylbenzene-d_5 instead of ethylbenzene, was also added. Catalyst **1a** (0.5 μmol) was added to both solutions, and the mixtures stirred for 12 h at 298 K. The amounts of ethylbenzene before and after the reactions were determined by GLC analysis. The k_H/k_D value was determined by using the following equations:

$$k_H/k_{Cl} = \log(H_f/H_i)/\log(Cl_f/Cl_i) \quad \text{(i)}$$

$$k_D/k_{Cl} = \log(D_f/D_i)/\log(Cl_f/Cl_i) \quad \text{(ii)}$$

then, k_H/k_D = [Eqs. (i)/(ii)]

Cl_f and Cl_i are the final and initial quantities of the 4-chloroethylbenzene; D_f and D_i are the final and initial quantities of ethylbenzene-d_5. H_f and H_i are the final and initial quantities of ethylbenzene.

4.7. Kinetics measurements

Kinetic measurements were performed on a Hewlett-Packard 8453A Diode Array Spectrophotometer interfaced with an IBM-compatible PC and equipped with a Lauda RM6 circulating water bath by using standard 1.0-cm quartz cuvettes. The temperature of solutions during kinetic experiments was maintained to be within ±0.2 °C.

The rate constants of alkane oxidation by [Ru^{VI}-(Por*)O_2] were measured by monitoring the decrease of the Soret absorption band under the condition that the/alkane concentrations were at least 100-fold in excess of [Ru^{VI}(Por*)O_2]. The pseudo-first-order rate constants (k_{obs}) were obtained by non-linear least-squares fits of ($A_f - A_t$) to time (t) according to the following equation:

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

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

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