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Dual Role of Pyridine *N*-Oxides in Ruthenium Porphyrin-Catalyzed Asymmetric Epoxidation of Olefins

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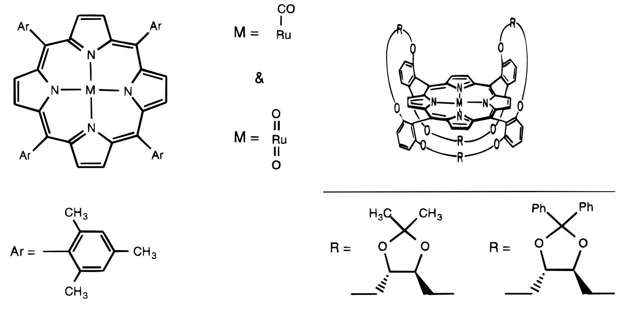
The most important intermediates in the ruthenium porphyrin-catalyzed epoxidation of olefins by pyridine *N*-oxides are shown to be *N*-oxide-coordinated $Ru^{IV}{=}O$ complexes. With a chiral ruthenium porphyrin catalyst, the enantioselective epoxidation of terminal aromatic olefins proceeds with up to 80% ee.

Introduction

Ruthenium porphyrins were recently shown by Hirobe and co-workers to be highly efficient catalysts for the epoxidation of olefins by aromatic *N*-oxides,[1,2] and in the presence of mineral acids even for the oxygenation of unactivated alkanes.[3] Mechanistic investigations revealed that in both processes the main intermediates during catalysis are not the well-known *trans*-dioxoruthenium(VI) porphyrins,[4] which do not react with alkanes and whose reactivity toward alkenes is limited. The most recent evidence is in favor of monooxoruthenium porphyrin intermediates, ruthenium(V) in the reactions with alkanes and either ruthenium(IV) or ruthenium(VI) in the epoxidation of alkenes,[5,6] albeit the possible involvement of nonoxometal species in the epoxidation process has not been ruled out.[5,7] In both processes, the occupant of the coordination site trans to the Ru═O moiety could not be identified yet, but has been proposed to be either halide, perchlorate, solvent, or *N*-oxide.[5−7] The last proposal is most intriguing, since *N*-oxide coordination has recently been found to be crucial in the somewhat related catalytic asymmetric epoxidation of olefins by chiral manganese salen complexes.[8] The ruthenium porphyrin system is, however, much more complicated because the *N*-oxide serves both as oxidant and as potential ligand.

Scheme 1. Structures of Ruthenium Catalysts



(TMP)Ru(CO) & (TMP)Ru(O)$_2$

1-Ru(CO) & **1**-Ru(O)$_2$ **2**-Ru(CO) & **2**-Ru(O)$_2$

Our initial results from the first asymmetric version of the Hirobe system—much higher ees with 2,6-dichloropyridine-*N*-oxide than with iodosylbenzene in the chiral ruthenium porphyrin [**1**-Ru(CO) in Scheme 1]-catalyzed epoxidation of olefins—suggest that this chiral probe could serve as an excellent mechanistic tool.[9] Accordingly, we have now performed four sets of experiments directed toward the elucidation of the structure, reactivity, and selectivity of the active oxidant: (*a*) spectroscopic examination of the stoichiometric reaction of isolated (TMP)Ru(O)$_2$ with 2,3-dimethyl-2-butene; (*b*) determination of the relative reactivities of ring-substituted styrenes with iodosylbenzene and 2,6-dichloropyridine-*N*-oxide, both with (TMP)Ru(O)$_2$ as catalyst; (*c*) **2**-Ru(O)$_2$-catalyzed epoxidation of styrene by different pyridine-*N*-oxides;[10] (*d*) (TMP)-Ru(O)$_2$-catalyzed epoxidation of styrene by enantiopure pyridine-*N*-oxides [the X-ray crystal structure of **4**-(−) is shown in Scheme 2 to demonstrate its chiral domain]. The results show that both the reactivity and the enantioselectivity of the processes in which the olefins react with *trans*-dioxoruthenium(VI) porphyrins [(TMP)Ru(O)$_2$, **1**-Ru(O)$_2$, **2**-Ru(O)$_2$] are too low to account for the results under catalytic conditions, and that pyridine-*N*-oxide-coordinated oxoruthenium(IV) porphyrins are the most potent and the most selective intermediates.

Results and Discussion

Relative Reactivities of Potential Intermediates. The first step in the current investigations was the ^1H NMR examination of the reactivities of the intermediates potentially formed during catalysis. The reaction was initiated by adding an about

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(1) Higuchi, T.; Ohtake, H.; Hirobe, M. *Tetrahedron Lett.* **1989**, *30*, 6545.

(2) (a) Aromatic *N*-oxides transfer their oxygen atom only to ruthenium porphyrins,[1,3,5] whereas manganese porphyrins catalyze the opposite reaction, that is, oxidation of pyridine to its oxide: Thellend, A.; Battioni, P.; Sanderson, W.; Mansuy, D. *Synthesis* **1997**, 1387. (b) For the limited utilization of aliphatic *N*-oxides in combination with first-row metalloporphyrins, see: Bruice, T. C.; Dicken, C. M.; Balasubramanian, P. N.; Woon, T. C.; Lu, F.-L. *J. Am. Chem. Soc.* **1987**, *109*, 3436 and references therein.

(3) Ohtake, H.; Higuchi, T.; Hirobe, M. *J. Am. Chem. Soc.* **1992**, *114*, 10660.

(4) Groves, J. T.; Quinn R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. Groves, J. T.; Ahn, K.-H.; Quinn R. *J. Am. Chem. Soc.* **1988**, *110*, 4217.

(5) Ohtake, H.; Higuchi, T.; Hirobe, M. *Tetrahedron Lett.* **1992**, *33*, 2521; *Heterocycles* **1995**, *40*, 867.

(6) Groves, J. T.; Bonchio, M.; Carofiglio, T.; Shalyaev, K. *J. Am. Chem. Soc.* **1996**, *118*, 8961.

(7) Higuchi, T.; Hirobe, M. *J. Mol. Catal. A: Chemical* **1996**, *113*, 403.

(8) Finney, N. S.; Posipisil, P. J.; Chang, S.; Palucki, M.; Konsler, R. G.; Hanse, K. B.; Jacobsen, E. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1720.

(9) Gross, Z.; Ini, S.; Kapon, M.; Cohen S. *Tetrahedron Lett.* **1996**, *37*, 7325.

(10) The ruthenium complex of porphyrin **2** was chosen because we have recently shown that the enantioselectivity obtained with the iron(III) complex of **2** was significantly larger than with that of **1**; see: Gross, Z.; Ini, S. *J. Org. Chem.* **1997**, *62*, 5514.

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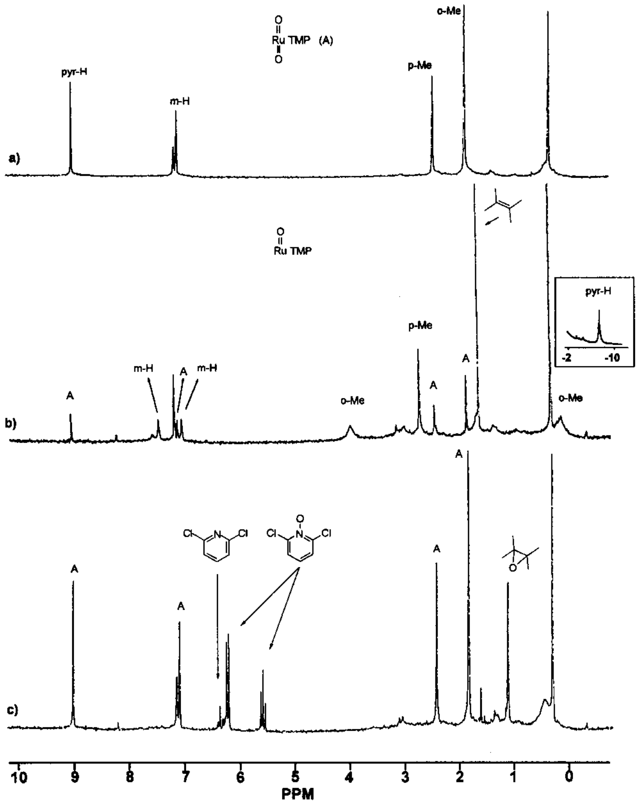
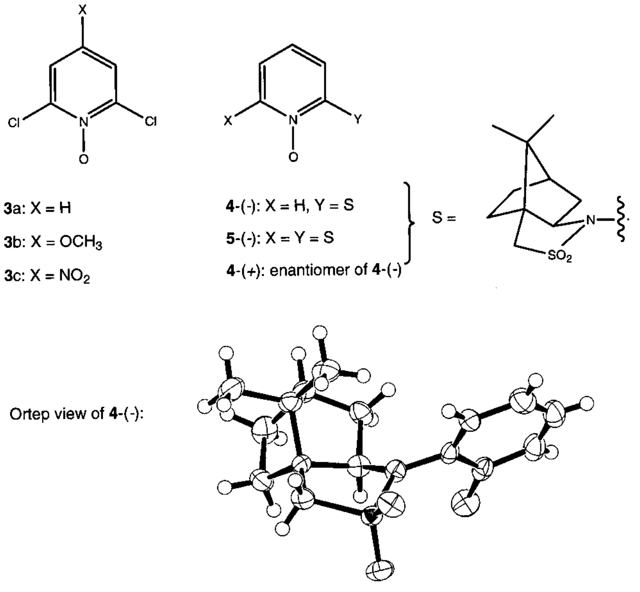


Figure 1. (a) A 9-mM solution of (TMP)Ru(O)$_2$ in benzene-d_6. (b) The same solution, 85 min after addition of ∼1 equiv of 2,3-dimethyl-2-butene. (c) The same solution as in b, 5 min after the addition of 5 equiv of 2,6-dichloropyridine-*N*-oxide (**3a**).

Scheme 2. Structures of Oxidants



equimolar amount of 2,3-dimethyl-2-butene to a benzene-d_6 solution of isolated (TMP)Ru(O)$_2$ (Figure 1a). This resulted in a very slow conversion to (TMP)Ru(O),[11] as demonstrated by the spectrum shown in Figure 1b, which presents about 80% conversion after 85 min. Next, the addition of 5 equiv of 2,6-dichloropyridine-*N*-oxide (**3a**) resulted in the very fast conversion (complete in <5 min) of all the remaining olefin to its epoxide and the quantitative regeneration of (TMP)Ru(O)$_2$

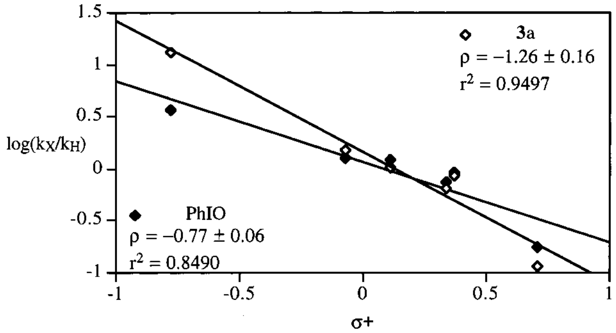
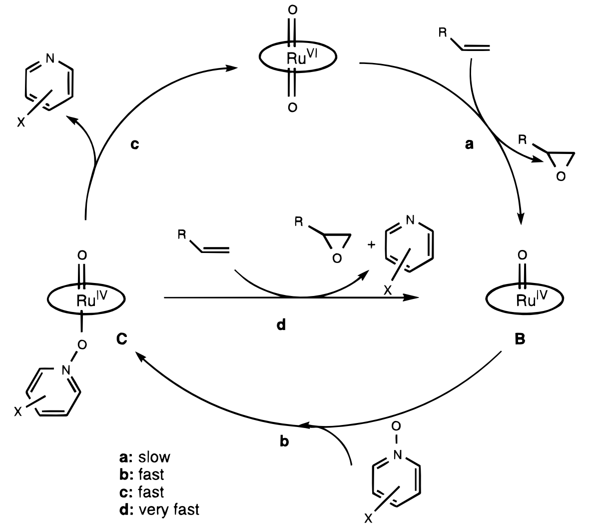


Figure 2. Hammett plots for the (TMP)Ru(O)$_2$-catalyzed reactions of ring-substituted styrenes with **3a** (empty symbols) and iodosylbenzene (filled symbols), respectively.

Scheme 3. Proposed Primary Steps During Catalysis



(Figure 1c). Addition of more olefin at this stage resulted in its fast transformation to epoxide, without any observable ruthenium porphyrin intermediates. Our conclusions from this set of experiments are depicted in Scheme 3. The reaction sequence starts in **a**, the slow epoxidation of the olefin by (TMP)Ru(O)$_2$ to form (TMP)Ru(O) (**B** in the Scheme 3). (TMP)Ru(O) does not react further with the olefin, that is, it is the least reactive intermediate in the system. However, the reaction of (TMP)-Ru(O) with the *N*-oxide is very fast (**b**). The observation that the reaction of the olefin with the combination of (TMP)Ru(O) and *N*-oxide is much faster than its reaction with (TMP)Ru-(O)$_2$ clearly proves that the latter complex is irrelevant to the major catalytic cycle. In other words, the catalytic reaction does not proceed through pathway **c**, but via pathway **d**. Because olefins are inert toward only (TMP)Ru(O) or the *N*-oxide, the best candidate for the most reactive intermediate is the *trans*-*N*-oxide-coordinated (TMP)Ru(O) (**C** in Scheme 3).

Different Selectivities of Potential Intermediates. Additional information was obtained by comparing the relative reactivities of ring-substituted styrenes in their (TMP)Ru(O)$_2$-catalyzed reactions with iodosylbenzene and **3a**, respectively. The Hammett plots (Figure 2) demonstrate that the amount of charge transfer from catalyst to olefin in the transition state is significantly smaller with iodosylbenzene [$\rho^+ = -0.77$, (TMP)-Ru(O)$_2$ is the active intermediate] than in the reactions with **3a** [$\rho^+ = -1.26$, (TMP)(pyr-N−O)Ru(O) is the proposed active intermediate]. This leads to the anticipation of superior enantioselectivities in the chiral ruthenium porphyrin-catalyzed reaction with **3a**, because a relatively late transition state

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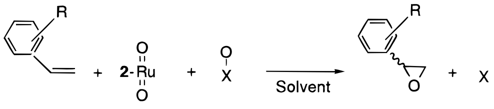
[11] For the NMR of [(TMP)Ru(O)], see: Groves, J. T.; Ahn, K.-H. *Inorg. Chem.* **1987**, *26*, 2831.

Scheme 4. Oxidant and Solvent Effects in **2**-Ru(O)$_2$-Catalyzed Epoxidation of Olefins



solvent, *T*	benzene,[a] 27 °C					CH$_2$Cl$_2$,[b] 18 °C				toluene,[c] −10 °C				
X−O	none	PhIO	**3a**	**3b**[f]	**3c**	none	**3a**	**4**-(+)	**4**-(−)	**3a**				
R	H					H				H	3-Cl	4-Br	4-F	4-Cl
reaction time (h)	13	1	3	2	17	15	3	15	15	24	24	24	24	24
TON[d]	1[e]	2[f]	17	142[g]	10	1[e]	143	35	23	11	135	19	86	149
% ee	45	47	68[h]	68[h]	28	51	58	64	59	**75**	**74**	**75**	**75**	**80**

[a] 0.165 M styrene, styrene/oxidant/catalyst = 620:620:1. [b] 0.13 M styrene, styrene/oxidant/catalyst = 1100:1100:1. [c] 24 h, 0.165 M olefin, olefin/oxidant/catalyst = 1855:1855:1. [d] Turnover number, (mol product)/(mol catalyst). [e] 0.15 mg (0.08 mmol) **2**-Ru(O)$_2$, styrene/catalyst = 390:1. [f] 0.5 M styrene, styrene/oxidant/catalyst = 1880:188:1. [g] 0.165 M styrene, styrene/oxidant/catalyst = 1600:1600:1. [h] At 20 °C. With **3a**, the ee at 27 °C is 65%.

suggests a strong interaction of the incoming olefin with the chiral cavity around the metal.

This proposal is supported by a comparison of the *stoichiometric* epoxidation of styrene by **2**-Ru(O)$_2$ (45% ee) with the **2**-Ru(CO)-catalyzed reactions with iodosylbenzene (47%) and various substituted pyridine-*N*-oxides (Scheme 4). The almost identical ees in the first two reactions indicate that **2**-Ru(O)$_2$ is the reactive intermediate with iodosylbenzene. However, the only obvious explanation for both the higher and the lower ees obtained in the reactions of styrene with **3a**−**c** (68% with **3a** and **3b**, and 28% ee with **3c**) is that the substituted pyridine-*N*-oxides are coordinated to the metal in the oxygen atom transfer step to the olefin. A reasonable rationale for the large effect of the *N*-oxides on the enantioselectivity of the process is that they affect the chirotopic environment around the metal center.[12] Supporting evidence for this proposal was obtained by examining the reactions of the two enantiomeric *N*-oxides **4**(−) and **4**(+) (Scheme 4, in CH$_2$Cl$_2$, because of their low solubility in benzene). The different ees—64% with **4**(+) and 59% with **4**(−)—clearly prove that the transition states of the product-forming step with these oxidants are diastereomeric.[13] All these results clearly rule out dioxoruthenium(VI) porphyrin as the common intermediate, indicate that the oxidant is coordinated to oxoruthenium(IV) in the oxygen atom transfer step from catalyst to olefin, and demonstrate the superior enantioselectivity of the *N*-oxide-coordinated intermediates.

Other Potentially Active Intermediates. In the *hydroxylation* process, which differs from the *epoxidation* system in its requirement for either the addition of mineral acids or the one-electron oxidation of the Ru(II) precursor, dihalogeno Ru(IV) and oxoruthenium(V) porphyrins were considered to be the most important intermediates by Hirobe and colleagues[5] and Groves et al.,[6] respectively. The possible involvement of such species in the epoxidation process was investigated by preparing the appropriate complexes of the chiral porphyrins. The dichlororuthenium(IV) porphyrin [**1**-Ru(Cl)$_2$] was obtained from the reaction of **1**-Ru(CO) with CCl$_4$,[14] and the porphyrin-oxidized [**2**-Ru(CO)(ClO4)] complex—the proposed precursor of oxoruthenium(V)—via one-electron oxidation of **2**-Ru(CO) with Fe(ClO$_4$)$_3$.[6] Next, the epoxidaton of styrene by **3a** in the presence of catalytic amounts of the various ruthenium complexes was compared. The ees of the styrene oxide produced in the reactions catalyzed by **1**-Ru(O)$_2$ (48%) vs **1**-Ru(Cl)$_2$ (23%), and by **2**-Ru(CO) (58%) vs [**2**-Ru(CO)(ClO4)] (41% ee),[15] together with the reduced chemical yields obtained with **1**-Ru(Cl)$_2$ and [**2**-Ru(CO)(ClO4)], leads us to conclude that dihalogeno Ru(IV) and Ru(V) species are not important intermediates in the *epoxidation* process.

Which Oxygen is Transferred to the Olefin.? Returning to Scheme 3, it remains uncertain if the olefin approaches the ruthenium complex from the oxometal or the *N*-oxide coordination site (the upper and lower sites, respectively, of intermediate **C**). In an attempt to resolve the last point, the two enantiopure *N*-oxides **4**(−) and **5**(−) shown in Scheme 2 were utilized as the oxygen atom sources. If olefins react with the oxygen atom of the coordinated *N*-oxide, some level of chiral induction might be expected, even with a nonchiral catalyst.[16] However, the styrene oxide obtained from the (TMP)Ru(O)$_2$-catalyzed reaction of styrene with the enantiopure *N*-oxides was found to be racemic. This strongly suggests, although it does not absolutely prove, that olefins approach the intermediate **C** from the oxometal bond. Interestingly, Katsuki and colleagues have most recently demonstrated that in the much more flexible manganese salen complexes, asymmetric induction occurs with the aid of chiral ligands and a nonchiral catalyst.[17]

Summary and Conclusions

The current investigation provides quite strong evidence that the *N*-oxide-coordinated oxoruthenium(IV) complexes are the most reactive as well as most selective intermediates in the ruthenium porphyrin-catalyzed epoxidation of olefins by aromatic *N*-oxides. As far as enantioselectivity is concerned, the

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(12) Preliminary molecular modeling investigations for the coordination complexes of **3a**−**c** with **2**-Ru(CO) reveal that the geometries of the complexes with **3a** and **3b** as ligands were practically identical, and very different from that with **3c** (no optimized geometry could be obtained for the latter).

(13) It might be argued that the chiral environment produced by nonbonding access of chiral pyridine-*N*-oxides to **2**-Ru(O)$_2$ affects the results. This proposal has been checked by adding (1*S*)-(−)-2,10-camphorsultam, the chiral moiety of **4**(−), to the reactions with **3a**. No effect was found.

(14) For the preparation of a large variety of dihalogenoruthenium(IV) porphyrins and analysis of their ^{1}H NMR spectra, see: Gross, Z.; Barzilay, C. M. *J. Chem. Soc., Chem. Commun.* **1995**, 1287; Gross, Z.; Mahammed, A.; Barzilay, C. M. *J. Chem. Soc., Chem. Commun.* **1998**, 1505.

(15) With the ruthenium complexes of both porphyrin **1** and **2**, indentical ees were obtained with the Ru(CO) and Ru(O)$_2$ complexes, but the chemical yields with the Ru(O)$_2$ complexes were much higher.

(16) For the effectiveness of the same chiral moiety as in **4** and **5** for the asymmetric cyclopropanation of styrene, see: (a) Haddad, N.; Galili, N. *Tetrahedron: Asymmetry* **1997**, *8*, 3367. (b) Gross, Z.; Galili, N.; Simkhovich, L. *Tetrahedron Lett.* **1999**, *40*, 1571.

(17) Hashihayata, T.; Ito, Y.; Katsuki, T. *Tetrahedron* **1997**, *53*, 9541.

major role of the *N*-oxides seems to be their effect on the chiral environment on the opposite coordination site, around the oxoruthenium bond. Finally, the importance of the current system is emphasized by the **2**-Ru(O)$_2$-catalyzed reactions of several ring-substituted styrenes with **3a** (Scheme 4, at −10 °C). The ees of the produced epoxides were 74−80%, significantly larger than those obtained by epoxidation of this type of olefins by any other chiral metal catalyst. Current efforts in our laboratory are devoted to raise the ees to practically useful values, >90% ee, by additional small modifications in the catalyst's superstructure.

Experimental Section

Physical Methods and Standard Materials. The spectroscopic methods and the treatment of standard materials are described in one of our recent publications.[10]

Preparation of Catalysts. Porphyrins **1** and **2** were available from our previous studies, and **2**-Ru(CO) and **2**-Ru(O)$_2$ were prepared in the same way as **1**-Ru(CO) and **1**-Ru(O)$_2$.[9,10]

2-Ru(CO). $R_f = 1.0$ (alumina, $CH_2Cl_2 \cdot EtOAc$ 1:1); UV−Vis (CH_2Cl_2, λ_{max}, nm): 426 (Soret), 552. ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 4.6 Hz, 2H), 8.26 (two unresolved doublets, 4H), 8.17 (d, J = 4.6 Hz, 2H), 7.58 (dt, J^1 = 9.0 Hz, J^2 = 2.0 Hz, 4H), 7.37 (d, J = 11.0 Hz, 4H), 7.14 (m, 20H), 6.98 (d, J = 7.4 Hz, 4H), 6.44 (t, J = 7.4 Hz, 2H), 6.39 (d, J = 7.6 Hz, 4H), 6.20 (t, J = 7.5 Hz, 4H), 6.09 (t, J = 7.4 Hz, 2H), 5.88 (d, J = 7.7 Hz, 4H), 5.77 (t, J = 7.6 Hz, 4H), 4.89 (d, J = 10.2 Hz, 2H), 4.77 (dd, J^1 = 10.7 Hz, J^2 = 2.3 Hz, 2H), 4.23 (m, 10H), 4.07 (dd, J = 9.5, 3.2 Hz, 2H), 3.98 (m, 4H), 3.35 (t, J = 7.4 Hz, 2H), 2.85 (m, 2H).

2-Ru(O)$_2$. Samples of the *trans*-dioxoruthenium(VI) porphyrin **2**-Ru(O)$_2$ were freshly prepared by *m*-CPBA oxidation of **2**-Ru(CO) in 99% yield by the procedure of Groves et al.[4] The major changes relative to **2**-Ru(CO) are the color change from orange to brown, accompanied by the shift of the main λ_{max} from 426 nm to 446 nm (CH_2Cl_2), and reduction of the ^1H NMR pyrrole signals from four to two [8.50 ppm (d, J = 4.2 Hz, 4H) and 8.41 ppm (d, J = 4.2 Hz, 4H, in $CDCl_3$, 200 MHz)].

1-Ru(Cl)$_2$. The dihalogeno ruthenium(IV) porphyrin **1**-Ru(Cl)$_2$ was obtained by heating a solution of 1 mg (0.72 μmol) of **1**-Ru(CO) in 3 mL of CCl_4 overnight, followed by evaporation of the solvent. The transformation of **1**-Ru(CO) to **1**-Ru(Cl)$_2$ resulted in a color change from orange to brown, accompanied by the shift of the main λ_{max} from 426 nm to 438 nm (CH_2Cl_2), the disappearance of all diamagnetic ^1H NMR resonances, and the appearance of two paramagnetically shifted pyrrole signals at −53 ppm and −55 ppm (in $CDCl_3$, 200 MHz), characteristic of dihalogeno ruthenium(IV) porphyrins.[14]

2-Ru(CO)(ClO$_4$). The porphyrin-oxidized **2**-Ru(CO)(ClO$_4$) complex was prepared in analogy to the procedure of Groves et al.[6] by adding several portions of dry $Fe(ClO_4)_3$ to a solution of 1 mg (0.53 μmol) of **2**-Ru(CO) in benzene, until the color change from orange [(**2**-Ru(CO)] to green (characteristic of porphyrin oxidation) was complete. The λ_{max} values [410 (Soret), 466, and 674 nm, in benzene] in the visible spectrum of the filtered solution were also as expected for a porphyrin-oxidized complex, a blue shifted Soret band and new red bands at long wavelengths.

Preparation of Oxidants. The *N*-oxides **3a** and **3c** were prepared according to literature procedures,[18] whereas **3b** and the chiral derivatives were prepared by the following procedures.

3b. Five milliliters of a sodium methoxide solution (30 mg of Na in 5 mL of methanol) were added to a suspension of 200 mg (0.96 mmol) of 2,6-dichloro-4-nitropyridine-*N*-oxide in 10 mL of methanol under nitrogen, at 0 °C. The solution was mixed for 4 h at room temperature, washed with 4 mL of water, and extracted with dichloromethane. After evaporation of the solvent the product was isolated by flash chromatography on silica with methanol:ethyl acetate (1:9). By recrystallization from ethyl acetate, 75 mg (40%) of 2,6-dichloro-4-methoxypyridine-*N*-oxide was obtained. ^1H NMR (200 MHz, $CDCl_3$): = 7.01 (s, 2H), 3.85 (s, 3H); $R_f = 0.4$ (silica, methanol:ethyl acetate 1:9); HRMS (EI): e/z 192.9679 (100%), calculated for $C_6H_5Cl_2NO_2$: 192.9698.

4(−), 4(+), and 5(−). A 100 mg amount of NaH (4.2 mmol) was placed in a 25-mL flask and washed with hexane. Ten milliliters of dry toluene and 336 mg of (1*S*)-(−)-2,10-camphorsultam (1.56 mmol, Aldrich) were added at room temperature, followed by addition of 200 mg of 2-chloropyridine-*N*-oxide (1.56 mmol, freshly sublimed) after 2 h. The solution was heated at reflux for 12 h, washed with brine, evaporated, and loaded on silica. Unreacted (1*S*)-(−)-2,10-camphorsultam was eluted with CH_2Cl_2, and elution with EtOAc afforded 200 mg of the product, 150 mg (35% yield) after recrystallization from hot MeOH. **4**(−): $[\alpha]_D$ −78° (c = 0.4, $CHCl_3$). Compounds **4**(+) {$[\alpha]_D$ +70° (c = 0.4, $CHCl_3$)} and **5**(−) {$[\alpha]_D$ −128° (c = 0.8, $CHCl_3$)} were prepared by analogous procedures in 26% and 6% yield, respectively. The NMR spectra and HRMS data were fully consistent with the structures shown in Scheme 2. X-ray-quality crystals of **4**(−) were obtained by slow recrystallization from MeOH.

Catalytic Oxidations. (a) With 2-Ru(O)$_2$. The appropriate oxidant (iodosylbenzene or substituted pyridine-*N*-oxide) was added in one portion to a well-stirred N_2-purged benzene solution of accurate amounts of olefin, nitrobenzene (internal standard), and catalyst. Reactions were stopped by freezing the reaction mixture with external liquid N_2. For determination of the chemical yields, aliquots from the reaction mixtures were injected into a nonchiral GC column (HP-5) without any treatment, and the ratio of products compared with the internal standard. The ees were determined by GC, using a Cyclodex-B capillary column, after separation of the reaction products from the catalyst and any unreacted oxidant by bulb-to-bulb vacuum distillation. The reaction times, turnover numbers, and ees for the **2**-Ru(O)$_2$-catalyzed reactions are compiled in Scheme 4, together with all the other variables. The yields relative to the oxidant were 50−100%, and the yields relative to olefin were 1−13%.

(b) With (TMP)Ru(O)$_2$. The reaction conditions for the (TMP)-Ru(O)$_2$-catalyzed competitive epoxidation of ring-substituted styrenes by iodosylbenzene and **3a**, respectively, were as follows: 1 M styrene, 1 M ring-substituted styrene, olefins/oxidant/catalyst = 14 000:345:1, in benzene at 16 °C. After 1 h, the product mixtures were analyzed by GC, and the following product ratio (k_x/k_H = [ring-substituted styrene oxide]/[styrene oxide]) were obtained.

substituent	4-OMe	3-Me	4-Cl	3-F	3-Cl	3-NO$_2$
log(k_x/k_H), with PhIO	0.56	0.10	0.09	−0.12	−0.04	−0.76
log(k_x/k_H), with **3a**	1.11	0.18	0.01	−0.19	−0.07	−0.94

(c) Comparison of 1-Ru(Cl)$_2$ and 1-Ru(O)$_2$. The **1**-Ru(Cl)$_2$-catalyzed epoxidation of styrene by **3a** at an olefin:oxidant:catalyst ratio of 330:330:1, in benzene under argon at room temperature for 1 h, provided styrene oxide with 13.21% yield and 22.7% ee. Under the same reaction conditions, but with **1**-Ru(O)$_2$ as catalyst, 23.20% yield and 48.3% ee were obtained.

(d) Comparison of 2-Ru(CO)(ClO$_4$) and 2-Ru(CO). The **2**-Ru(CO)(ClO$_4$)-catalyzed epoxidation of styrene by **3a** at an olefin:oxidant:catalyst ratio of 664:664:1, in toluene under argon at room temperature for 1.5 h, provided styrene oxide with 0.03% yield and 41% ee. Under the same reaction conditions, but with **2**-Ru(CO) as catalyst, 1.32% yield and 58% ee were obtained.[15]

Acknowledgment. This research was supported by the Israel Science Foundation, under Grant No. 362-95-3. We are also thank Dr. M. Kapon for the X-ray crystal structure determination.

Supporting Information Available: Full X-ray structural data for **4**(−). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Rousseau, R. J.; Robins, R. K. *J. Heterocycl. Chem.* **1965**, *2*, 196.