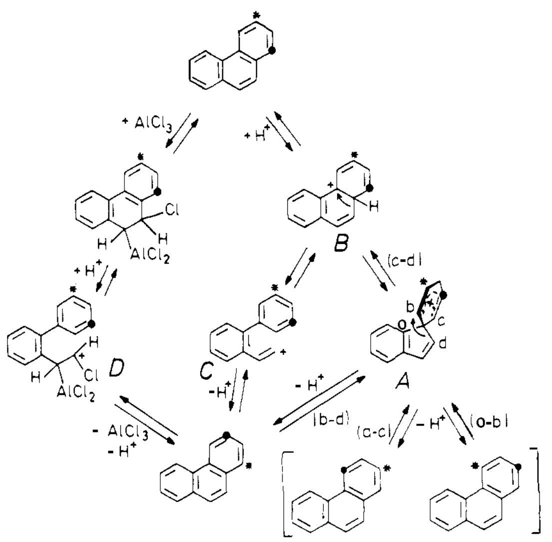
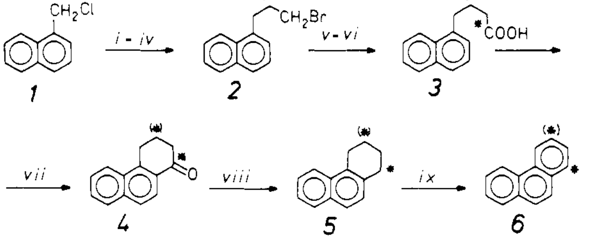
Scheme I[a]



[a] Possible reaction mechanisms: In the mechanism involving intermediate A, letters a–d denote carbon atoms which become bonded as indicated on the arrows. The two bracketed products do not appear in the automerization of [1-$^{13}$C]phenanthrene.

of the $^{13}$C label in other positions of the ring containing the label, explaining the minor amount of C-4 transfer from C-3.

The syntheses of [1-$^{13}$C]- and [3-$^{13}$C]phenanthrene were based on 1-(chloromethyl)naphthalene (**1**), using nine synthetical steps. Synthons having one carbon ($^{13}$CO$_2$) and two carbons (malonate) were attached to 1-(chloromethyl)naphthalene in an order depending on the desired position of the label. The labeling started by carbonation with $^{13}$CO$_2$ (generated from Ba$^{13}$CO$_2$ of 55–80% content) of the corresponding Grignard derivative **1** or **2**. The ultimate precursor of the appropriately labeled phenanthrene was 4-(1-naphthyl)butanoic acid (**3**). Cyclization in the presence of polyphosphoric acid (PPA) yielded 1,2,3,4-tetrahydrophenanthren-1-one (**4**). Clemmensen reduction of **4**, followed by dehydrogenation of the 1,2,3,4-tetrahydrophenanthrene (**5**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), afforded the labeled phenanthrene (**6**).



(i) NaCH(CO$_2$Et)$_2$, (ii) H$_2$O/H$^+$, (iii) LiAlH$_4$/THF, (iv) PBr$_3$, (v) Mg, (vi) $^{13}$CO$_2$/H$^+$, (vii) PPA, (viii) Zn(Hg)/HCl, (ix) DDQ.

For **3** (1-$^{13}$C), read the (i)–(vi) sequence, while for **3** (3-$^{13}$C), the order is (v), (vi), (iii), (iv), (i), (vii)–(ix).

In conclusion, we presented evidence for the first example of catalyzed automerization of a condensed polycyclic benzenoid hydrocarbon which takes place under normal chemical conditions. We are engaged in a thorough study of the catalytic phenanthrene automerization and in reinvestigating the same reaction of [1-$^{13}$C]naphthalene.

**Acknowledgment.** We thank Professors R. M. Roberts (University of Texas at Austin), C. Roussel (University of Marseille, France), and I. Pogany (Polytechnic, Bucharest, Roumania) for fruitful discussions, material, and technical assistance and A. Petride for preparative GLC purifications.

**Registry No.** **1**, 86-52-2; **2**, 27650-86-8; [$\beta$-$^{11}$C]-**2**, 118018-25-0; [1-$^{13}$C]-**3**, 66229-92-3; [3-$^{13}$C]-**3**, 118018-26-1; [1-$^{13}$C]-**4**, 69062-73-3; [3-$^{13}$C]-**4**, 118018-27-2; [1-$^{13}$C]-**5**, 118018-28-3; [3-$^{13}$C]-**5**, 118018-29-4; [1-$^{13}$C]-**6**, 118018-30-7; [3-$^{13}$C]-**6**, 118018-31-8; AlCl$_3$, 7446-70-0; NaCH(CO$_2$Et)$_2$, 996-82-7; NaAlCl$_4$, 7784-16-9; barium [$^{13}$C]carbonate, 51956-33-3; [4-$^{13}$C]phenanthrene, 118018-32-9.

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(7) Wynberg, H.; Wolf, A. P. *J. Am. Chem. Soc.* **1963**, *85*, 3308.

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# The Resonance Raman Spectrum of a Ferrylporphyrin Cation Radical and Its Photodegradation in the Presence of Methanol

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The intense interest in ferryl porphyrin $\pi$-cations continues in view of their proposed intermediacy in a number of important heme enzyme-mediated oxidative processes.[1] Characterization of model compounds by resonance Raman (RR) spectroscopy assumes importance inasmuch as the technique offers promise for detection and structural characterization of the key intermediates in the enzyme systems.[2] We therefore wish to report results of our efforts to obtain the RR spectrum of the most thoroughly studied example of such models; namely, ferryltetramesitylporphine $\pi$-cation radical, (OFe)TMP$^{\bullet+}$. In addition, we show that the previously reported RR spectrum of this species,[3] which is in conflict with our own results, actually corresponds to that of a photoproduct.

Solutions of (OFe)TMP$^{\bullet+}$ were prepared at low temperatures (−78 °C) in purified CH$_2$Cl$_2$ with *m*-chloroperoxybenzoic acid (mCPBA) and yielded a visible spectrum which was identical with that reported.[4] The RR spectrum of this solution exhibited a well-defined band at 802 cm$^{-1}$ which shifted to 767 cm$^{-1}$ when $^{18}$O-labeled (mCPBA)[5] was employed (Figure 1, A and C). In order to demonstrate that the 802-cm$^{-1}$ feature does not correspond to the acylperoxo-coordinated precursor [TMPFe$^{3+}$(mCPBA$^-$)], a sample was prepared with isotopically scrambled oxidant.[6] As seen in Figure 1B, only the 802- and 767-cm$^{-1}$ features are observed. If the spectra corresponded to such a precursor, trace B is expected to exhibit three bands at 802, 767, and ~784 cm$^{-1}$, the last being that associated with the $^{16}$O-$^{18}$O-Fe and $^{18}$O-$^{16}$O-Fe linkages. Thus, the unique 802-cm$^{-1}$ feature is most reasonably assigned to $\nu$(Fe–O) of the ferryl fragment of (OFe)TMP$^{\bullet+}$.

It is important to note that the higher frequency RR spectrum observed for this species (Figure 2A) is also consistent with the $\pi$-cation radical formulation. Specifically, there is a dramatic decrease in the intensity of all macrocycle modes, $\nu_4$ downshifts

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(1) (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032–1033. (b) Schappacher, M.; Weiss, R.; Montiel-Montoya, R.; Trautwein, A.; Tabard, A. *J. Am. Chem. Soc.* **1985**, *107*, 3736–3738. (c) Chin, D.; Balch, A. L.; LaMar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446–1448. (d) Shin, K.; Goff, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 3140–3142.

(2) (a) Ogura, T.; Kitagawa, T. *J. Am. Chem. Soc.* **1987**, *109*, 2177–2179. (b) Oertling, W. A.; Babcock, G. T. *J. Am. Chem. Soc.* **1985**, *107*, 6406–6407. (c) Oertling, W. A.; Babcock, T. T. *Biochemistry* **1988**, *27*, 3331–3338. (d) Paeng, K.-J.; Kincaid, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 7913–7915.

(3) Hashimoto, S.; Tatsuno, Y.; Kitagawa, T. *J. Am. Chem. Soc.* **1987**, *109*, 8096–8097.

(4) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evance, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884–2886.

(5) (a) This shift is in good agreement with that expected based on the harmonic oscillator model. (b) $^{18}$O-mCPBA and the scrambled oxygen analogue were prepared as described in ref 5c,d. (c) Johnson, R. A. *Tetrahedron Lett.* **1976**, *5*, 331–332. (d) Braun, G. In *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, Wiley: New York, p 431.

(6) The term "scrambled oxidant" is used to indicate that the oxidant consists of a mixture of isotopes having $-^{16}$O$-^{16}$O–C–, –O$^{16}-^{18}$O–C–, –O$^{18}$O–$^{16}$O–C–, and $-^{18}$O$-^{18}$O–C– linkages.

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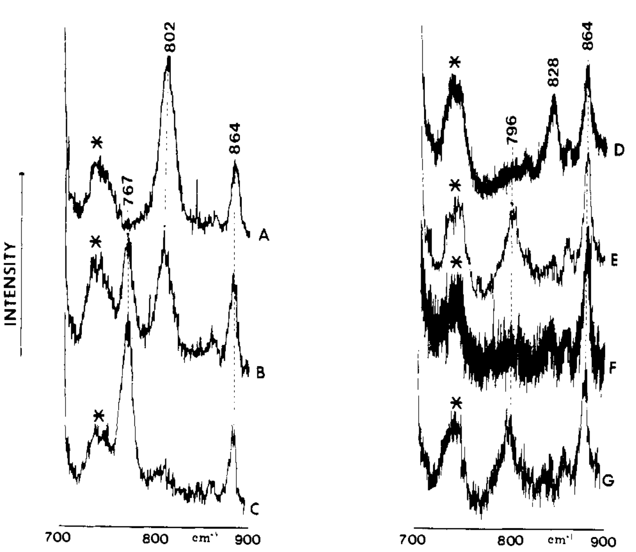

**Figure 1.** Low-frequency resonance Raman spectra of the green complex observed at −80 °C: (A) the $^{16}$O derivative without methanol; (B) the $^{16}$O–$^{18}$O derivative without methanol; (C) the $^{18}$O derivative without methanol; (D) the $^{16}$O derivative with methanol; (E) the $^{18}$O derivative with methanol; (F) the $^{18}$O derivative with methanol at 1/2 mW laser power, with line focussing (G) the $^{18}$O derivative with methanol at 18 mW laser power, with line focussing; (same sample as in trace F). The spectra were obtained with 406.7-nm excitation wavelength (20 mW laser power, except traces F and G). Asterisks indicate $CH_2Cl_2$ solvent bands.

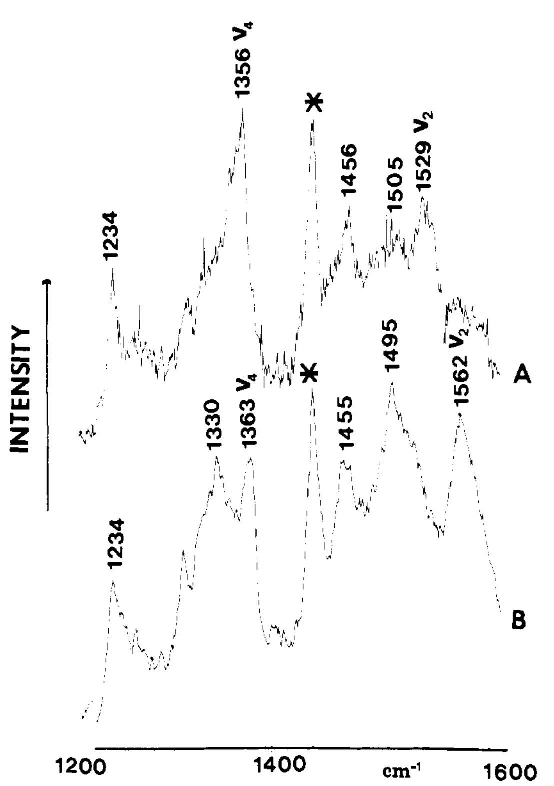

**Figure 2.** High-frequency resonance Raman spectra of the green complex observed at −80 °C: (A) without methanol; (B) with methanol; spectra were obtained with 406.7-nm excitation wavelength, 20 mW laser power.

by ~10 cm$^{-1}$ to 1356 cm$^{-1}$ and $\nu_2$ downshifts by ~30 cm$^{-1}$ to 1529 cm$^{-1}$.[7,8]

Recently, Hashimoto and Kitagawa[3] reported the results of similar studies but with (5/1) $CH_2Cl_2/CH_3OH$ solutions. They observed a weak feature at 828 cm$^{-1}$ which was ascribed to $\nu$(Fe–O) of (OFe)TMP$^{•+}$. The spectra we obtain upon duplicating these experiments are shown in Figure 1 (D and E) and Figure 2B. The low-frequency spectra (Figure 1, D and E) are essentially identical with those previously reported.[3] While the high-frequency region was not reported by the previous workers, that shown in Figure 2B corresponds to the low-frequency spectra shown in Figure 1 (i.e., they were obtained at the same time).

It is obvious that distinctly different RR spectra are obtained in the presence of methanol. In this case, the RR spectrum is much less "radical-like", exhibiting $\nu_2$ (1562 cm$^{-1}$) and $\nu_4$ (1363 cm$^{-1}$) frequencies which are insignificantly different from their values (1565 and ~1369 cm$^{-1}$) for (the nonradical) (OFe)TMP.[7c,d] Furthermore, the weak (oxygen) isotope-sensitive 828-cm$^{-1}$ feature occurs at a frequency which is suspiciously close to the $\nu$(Fe–O) of the six-coordinate DMF adduct of a (nonradical) ferrylporphyrin, previously reported at 829 cm$^{-1}$.[9] Thus, the RR spectrum obtained in the presence of methanol is somewhat similar to those of ferrylporphyrins. However, it is important to emphasize that the presence of methanol does not preclude the formation nor dramatically decrease the stability of the ferrylporphyrin $\pi$-cation[1] (i.e., the solutions prepared in the presence of methanol do contain the target compound).

These facts, along with our experimental results, led us to suspect that the spectra obtained in the presence of methanol may be associated with a photoproduct. In order to investigate this possibility, we have obtained spectra at very low photon fluxes by employing the line-focussing technique using a cylindrical lens.[10] In Figure 1F is shown the spectrum of the $^{18}$O analogue of (OFe)TMP$^{•+}$ in (5/1) $CH_2Cl_2/CH_3OH$ using very low laser power (~1/2 mW, line focussed). The intensity of the 796-cm$^{-1}$ feature, previously assigned to $\nu$(Fe–$^{18}$O) of (OFe)TMP$^{•+}$, is much weaker than the nearby solvent band (labeled by an asterisk). Upon increasing the power to 18 mW (line focussed), the 796-cm$^{-1}$ feature increases in intensity relative to the solvent band. Such behavior is obviously consistent with our contention that the 828-cm$^{-1}$ feature (796 cm$^{-1}$ for the $^{18}$O analogue) is associated with a photoproduct. In contrast, the intensity of the 802-cm$^{-1}$ feature (Figure 1A) *decreases* upon increasing the laser power, indicating that the species associated with this feature is not a photoproduct. While studies are underway to investigate the details of this photochemical process in the presence of methanol,[15] we note that the (six-coordinate, ferryl porphyrin $\pi$-cation radical) active site of horseradish peroxidase compound I (HRP-I) is known to be subject to efficient photodegradation.[2,11]

In conclusion, we assign the relatively strong 802-cm$^{-1}$ feature to $\nu$(Fe–O) of the target compound and point out that the corresponding macrocycle modes ($\nu_4$ and $\nu_2$) are consistent with RR spectral data for known metalloporphyrin $\pi$-cations.[8b,c] This assignment indicates that upon radical cation formation the $\nu$(Fe–O) of the ferryl fragment shifts down by ~40 cm$^{-1}$ (the $\nu$(Fe–O) of the corresponding (OFe)TMP occurs at 843 cm$^{-1}$). It is important to note that the magnitude and direction of this shift lends strong support to our recent RR study of HRP-I.[2d] There we assigned a 737-cm$^{-1}$ feature to $\nu$(Fe–O), a frequency which is 39 cm$^{-1}$ lower than $\nu$(Fe–O) of (the nonradical) HRP-compound II.[12] Apparently, other factors being held constant, formation of the ferryl porphyrin $\pi$-cation leads to a ~40-cm$^{-1}$

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(7) (a) The downshifts are referred to the corresponding values of $\nu_2$ and $\nu_4$ observed for (the nonradical) (OFe)TMP spectra in ref 7b,c. (b) Hasimoto, S.; Tatsuno, Y.; Kitagawa, T. *Proceedings of the Tenth International Conference on Raman Spectroscopy*; Peticolas, W. L., Hudson, B., Eds.; University of Oregon: Eugene, OR, 1986; pp 1–28. (c) Paeng, I. R.; Shiwaku, H.; Nakamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 1995–1996. (d) Paeng, I. R.; Nakamoto, K., unpublished results.

(8) (a) The downshifts in $\nu_4$ and $\nu_2$ are expected on the basis of extensive studies of the RR spectra of metalloporphyrin $\pi$-cations given in ref 8b,c. (b) Oertling, W. A.; Salehi, A.; Chung, Y. C.; Leroi, G. E.; Chang, C. K.; Babcock, G. T. *J. Phys. Chem.* **1987**, *91*, 5887–5898. (c) Czernuszewicz, R. S.; Macor, K. A.; Li, X. Y.; Kincaid, J. R.; Spiro, T. G., submitted for publication.

(9) Gold, A.; Jayaraj, K.; Doppelt, P.; Weiss, R.; Chottard, G.; Bill, E.; Ding, X.; Trautwein, A. X. *J. Am. Chem. Soc.* **1988**, *110*, 5756–5761.

(10) Shriver, D. F.; Dunn, J. B. R. *Appl. Spectrosc.* **1974**, *28*, 319–323.

(11) Gasyna, Z.; Browett, W. R.; Stillman, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 3633–3640.

(12) (a) Terner, J.; Sitter, A. J.; Reczek, C. M. *Biochem. Biophys. Acta* **1985**, *828*, 73–80. (b) Hashimoto, S.; Tatsuno, Y.; Kitagawa, T. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 2417–2421.

downshift in $\nu$(Fe–O) and implies a substantial weakening of the Fe–O linkage. Finally, it should be pointed out that Spiro and co-workers have shown that conversion of vandyloctaethylporphine to the corresponding radical leads to an *upshift* of $\nu$(V–O) of 13 $cm^{-1}$,[13] We note that this latter complex forms an "$a_{1u}$-like" radical, whereas $(OFe)TMP^{\bullet+}$ and HRP-I are considered to be "$a_{2u}$-like" radicals.[8c,14] While further studies will be needed to investigate this issue in detail, the weakening of Fe–O in "$a_{2u}$-like" and strengthening in "$a_{1u}$-like" systems may prove to hold generally, as was noted in our recent work on HRP-I.[2d]

**Acknowledgment.** We gratefully acknowledge valuable discussions with Dr. K. Macor (University of Notre Dame), Dr. R. Czernuscewicz, and Professor T. Spiro (Princeton University). This work was supported by a grant from the National Institutes of Health (DK-35153). The Raman spectroscopic equipment used in this work was partially funded by the National Science Foundation (CHE-8413956).

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(13) Oliver Su, Y.; Czernuszewicz, R. S.; Miller, L. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 4150–4157.

(14) Browett, W. R.; Gasyna, Z.; Stillman, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 3633–3640.

(15) The extreme photolability of this species in the presence of methanol prevented us from obtaining good quality spectra of the nonphotolyzed material. Further experiments to obtain this spectrum are planned.

# Kinetic Role of the Alkaloid Ligands in Asymmetric Catalytic Dihydroxylation

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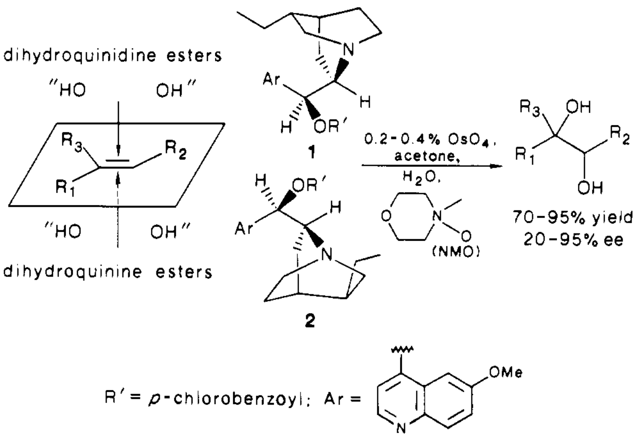
*Received August 25, 1988*

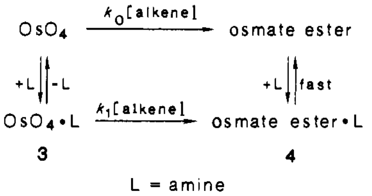
Simple ester derivatives of dihydroquinidine (**1**) and dihydroquinine (**2**) play a complex role as ligands in the osmium-catalyzed dihydroxylation process (Scheme I).[1] In addition to imparting fair to high levels of asymmetry into the diol products, these *cinchona* alkaloid ligands accelerate the rate of addition of olefins to $OsO_4$ by 1–2 orders of magnitude. A major current research goal is to determine the various interactions which occur between the amine ligands and the different osmium species present in the catalytic cycle. Specific aspects which we address in the present study include (a) the number of alkaloid ligands present in the rate-limiting and ee-determining step(s); (b) the role of amines in the reoxidation/hydrolysis steps; and (c) the level of alkaloid required to achieve optimal enantioselectivities. We find that due to the ligand-acceleration phenomenon, ee maximization takes place with extremely low levels of alkaloid, well below the levels required to achieve rate saturation. The kinetic basis for this observation is described.

The number of alkaloid ligands present in the olefin addition step is a crucial mechanistic question, for this is the step in which both the asymmetric induction and the rate acceleration arise. Osmium tetroxide forms coordinatively saturated 18-electron 1:1 complexes with a variety of 3° amines ($K_{eq}$ = 10–50 $M^{-1}$ at 25 °C in toluene or acetone/water (10:1) for the derivatives of **1** and **2** we have examined),[2] and no evidence has ever been obtained by us or by others[3] for a bis-amine adduct (formally a 20-electron complex). On the other hand, stoichiometric olefin oxidations by $OsO_4$ in the presence of pyridine or ammonia, the only kinetically well-characterized amine-promoted osmylation systems described in the literature, have been shown to obey rate laws with a second-order amine component.[3a,b] In addition, Tomioka and Koga recently proposed a stereochemical model for their stoichiometric asymmetric osmylations in which the rate-limiting and asymmetry-inducing step involves attack, intramolecularly by virtue of chelation, of a second amine.[4] Therefore the question of whether one or two molecules of the alkaloid ligand are involved in these systems was examined.

Scheme I



Scheme II



The rate expression predicted for the pathway outlined in Scheme II involving a single amine ligand is

$$\Delta k = k_2 - k_0 = \frac{(k_1 - k_0)K_{eq}[\text{amine}]}{K_{eq}[\text{amine}] + 1} \qquad (1)$$

where $K_{eq}$ is the binding constant between amine and $OsO_4$, and $k_2$ is the measured second-order rate constant.[5] Kinetic measurements of both the stoichiometric reaction and the catalytic reaction were performed for nine different olefins with varying concentrations of **1** or **2**.[6] Quinuclidine was also examined as a model ligand. In all cases, the relationship in eq 1 was obeyed, as plots of $1/\Delta k$ vs $1/[\text{alkaloid}]$ were strictly linear, rigorously establishing the involvement of only a single amine ligand in the rate/turnover limiting step. Enantiomeric excesses obtained in the catalytic reaction also approached a maximum value with increasing amine concentration, obeying the equation

$$\text{ee} = \frac{(k_f - k_s)K_{eq}[\text{amine}]}{k_1 K_{eq}[\text{amine}] + k_0} \qquad (2)$$

where $k_f$ and $k_s$ are the rate constants for the major and minor enantiomeric pathways, respectively.[5] This behavior, too, is

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(1) Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968.

(2) Binding constants were determined from Scatchard plots or from Benesi–Hildebrand plots of UV–vis data. While derivatives of **1** and **2** each contain two different amine moieties, solution and solid-state studies of $OsO_4$·alkaloid complexes show that binding occurs exclusively through the quinuclidine N and that chelation by coordination of the quinoline N is geometrically impossible. Details of our structural studies will be reported separately: Jacobsen, E. N.; Lippard, S. J.; Markó, I.; Pulla Rao, Ch.; Sharpless, K. B.; Svendsen, J. S., Manuscript in preparation.

(3) (a) Clark, R. L.; Behrman, E. J. *Inorg. Chem.* **1975**, *14*, 1425. (b) Burton, K. *Biochem. J.* **1967**, *104*, 686. (c) Griffith, W. P.; Rossetti, R. *J. Chem. Soc., Dalton Trans.* **1972**.

(4) Tomioka, K.; Nakajima, M.; Iitaka, Y.; Koga, K. *Tetrahedron Lett.* **1988**, *29*, 573.

(5) Derivation of eq 1 and 2 is provided as Supplementary Material.

(6) Kinetics of the stoichiometric reaction were measured by UV–vis spectroscopy under pseudo-first-order conditions with limiting $OsO_4$. In the catalytic reaction, rates were determined by monitoring changes in starting olefin concentration by GC.

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