

## Co-ordination of Styrene Oxide to a Sterically Hindered Ruthenium(II) Porphyrin

John T. Groves,\* Yuanzhang Han, and Donna Van Engen

Department of Chemistry, Princeton University, Princeton, New Jersey 08544, U.S.A.

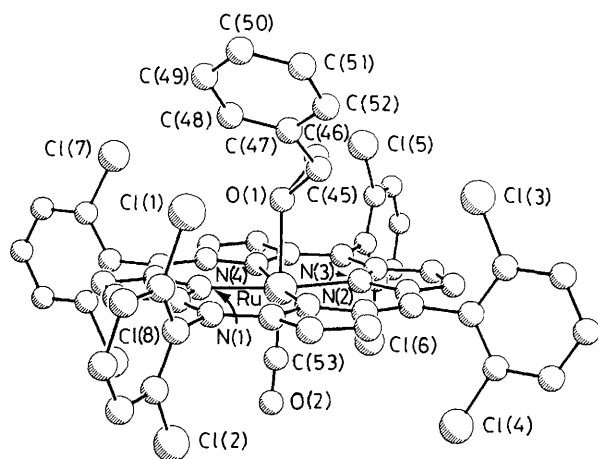
The crystal and molecular structure of an adduct of styrene oxide and tetra-(2,6-dichlorophenyl)porphyrinato-carbonylruthenium(II) reveals co-ordination of the epoxide ring at 49° with respect to the mean porphyrin plane such that there are close non-bonded interactions between the oxirane protons and a porphyrin pyrrole ring and between the styrene oxide phenyl carbons and one chlorine.

Ruthenium porphyrins have been shown to be competent catalysts for epoxidation of alkenes<sup>1</sup> under aerobic conditions and the *cis-trans* isomerization of epoxides under anaerobic conditions.<sup>2</sup> Both processes have exhibited a marked stereoselectivity. In the former case, *cis*-alkenes are signifi-

cantly more reactive toward epoxidation than *trans*-alkenes while in the latter, *cis*-epoxides co-ordinate more readily to ruthenium(II) porphyrins than do the corresponding *trans*-isomers. Here we describe the characterization and *X*-ray crystal structure of an adduct of styrene oxide and tetra-(2,6-dichlorophenyl)porphyrinato-carbonylruthenium(II), [Ru<sup>II</sup>TDCPP(CO)(styrene oxide)], the first metallo-epoxide structure which affords insight regarding the nature of these stereoselectivities.

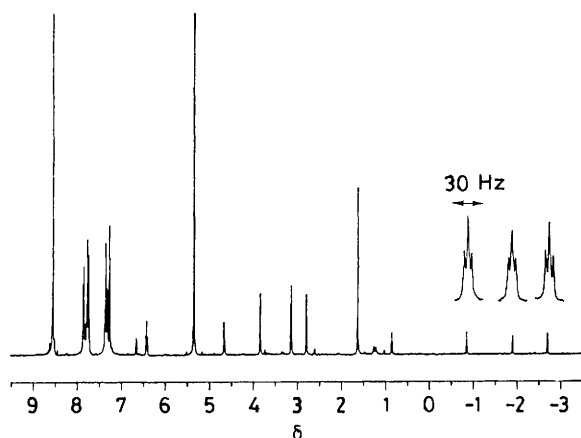
Ru<sup>II</sup>TDCPP(CO)(MeOH) (1) was prepared following literature procedures.<sup>3-5</sup> The styrene oxide adduct Ru<sup>II</sup>TDCPP(CO)(styrene oxide) (2) was isolated by diffusion of pentane into a solution of (1) in dichloromethane-styrene oxide (20:1). Single crystals of (2) suitable for *X*-ray crystallographic analysis were obtained upon evaporation of a dichloromethane-benzene-styrene oxide (10:10:1) solution of (2) over 48 h.

The *X*-ray crystal structure of (2) was solved using standard heavy atom techniques and the SHELXTL package of programs<sup>6</sup> and was refined to a final *R* factor of 0.049.† Three molecules of benzene, two on inversion sites, were located in the difference Fourier map following refinement of the Ru porphyrin with isotropic temperature factors. The ligated



**Figure 1.** A perspective view of the major conformation of Ru<sup>II</sup>TDCPP(CO)(styrene oxide)·2C<sub>6</sub>H<sub>6</sub> (2). Selected bond lengths (Å) and angles (°): Ru-N(1) 2.045(3), Ru-N(2) 2.049(3), Ru-N(3) 2.057(3), Ru-N(4) 2.049(3), Ru-O(1) 2.220(3), Ru-C(53) 1.811(5), O(1)-C(45) 1.414(6), O(1)-C(46) 1.453(9), C(45)-C(46) 1.469(8), C(53)-O(2) 1.149(6); N(1)-Ru-N(2) 89.9(1), N(1)-Ru-N(3) 174.4(1), N(2)-Ru-N(3) 90.1(1), N(1)-Ru-N(4) 90.1(1), N(2)-Ru-N(4) 174.1(1), N(3)-Ru-N(4) 89.3(1), N(1)-Ru-O(1) 85.2(1), N(2)-Ru-O(1) 87.1(1), N(3)-Ru-O(1) 89.2(1), N(4)-Ru-O(1) 87.0(1), O(1)-Ru-C(53) 177.1(2), N(1)-Ru-C(53) 91.9(2), N(2)-Ru-C(53) 92.5(2), N(3)-Ru-C(53) 93.7(2), N(4)-Ru-C(53) 93.4(1), Ru-C(53)-O(2) 177.8(4), Ru-O(1)-C(45) 129.4(3), Ru-O(1)-C(46) 129.4(3), O(1)-C(45)-C(46) 60.5(4), O(1)-C(46)-C(45) 57.9(4), O(1)-C(45)-C(47) 115.7(5), C(45)-O(1)-C(46) 61.6(4); O(1), C(45), C(46)-Ru, N(1-4), C(1-20) 49.

† *Crystal data* for (2): C<sub>53</sub>H<sub>28</sub>Cl<sub>8</sub>N<sub>4</sub>O<sub>2</sub>Ru·2C<sub>6</sub>H<sub>6</sub>, red plates, *M* = 1293.8, triclinic, space group *P* $\bar{1}$ , *a* = 10.747(3), *b* = 12.927(3), *c* = 21.843(5) Å,  $\alpha$  = 95.80(2),  $\beta$  = 95.07(2),  $\gamma$  = 102.81(2)°, *U* = 2924.7(12) Å<sup>3</sup>, *D*<sub>c</sub> = 1.47 g cm<sup>-3</sup>, *F*(000) = 1308,  $\mu$ (Mo-*K* $\alpha$ ) = 6.8 cm<sup>-1</sup>. Crystal dimensions: 0.15 × 0.30 × 0.38 mm<sup>3</sup>. Data collected at 223 K on a Nicolet R3m diffractometer using Mo-*K* $\alpha$  radiation ( $\lambda$  = 0.71069 Å). Using  $\omega$ -2 $\theta$  variable-scan (3.00–29.30° min<sup>-1</sup>) technique, 10284 independent (*R*<sub>int</sub> = 0.013) reflections were collected in the range 3 < 2 $\theta$  < 50° and 8220 reflections with  $|F| \geq 3.0 \sigma(F)$  were used in the refinement. Refinement with 730 parameters converged at *R* = 0.049, *R*<sub>w</sub> = 0.049. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 2.** 500 MHz  $^1\text{H}$  NMR of the mixture of  $\text{Ru}^{\text{II}}\text{TDCPP}(\text{CO})$  (**2**) (5.2 mM) and excess styrene oxide (9.2 mM) in  $\text{CD}_2\text{Cl}_2$  at 233 K. Inset: each trace expanded to 30 Hz width.

styrene oxide portion was found to occupy two conformations. A perspective view of the major (72%) conformation of  $\text{Ru}^{\text{II}}\text{TDCPP}(\text{CO})(\text{styrene oxide})\cdot 2\text{C}_6\text{H}_6$  is shown in Figure 1. The minor conformation was similar. The measured Ru–O(1) bond length, 2.220(3) Å, is in accord with the values of 2.21(2) Å for Ru–O(OEt) in  $\text{Ru}^{\text{II}}\text{TTP}(\text{CO})(\text{EtOH})$ <sup>7,8</sup> (TTP = tetraphenylporphyrin) and 2.123(9) Å for Ru–O(thf) (thf = tetrahydrofuran) found in  $\text{Ru}^{\text{II}}\text{TMP}(\text{N}_2)(\text{thf})$ <sup>9</sup> (TMP = tetramesitylporphyrin). The ruthenium atom is displaced from the porphyrin plane toward CO by 0.11 Å. The co-ordinated epoxide ring was found at an angle of 49° with respect to the plane defined by the porphyrin ring. Interestingly, the phenyl group of the co-ordinated epoxide is orientated such that the *para*-carbon is nearly intersected by an extension of the carbon–chlorine(1) bond at a distance of 3.76 Å. The distances from this chlorine to the *ortho*- and *meta*-carbons C(48) and C(49) are 3.53 and 3.48 Å, respectively, and the perpendicular distance from Cl(1) to the phenyl ring is 3.42 Å, very close to the sum of the van der Waals radii for carbon and chlorine. The only other close non-bonded interactions are those of the two oxirane protons which protrude toward the pyrrole ring of the porphyrin. The vertical distances of these protons from the mean plane of the porphyrin are 2.84 and 2.79 Å, also very close to the sum of the nominal radii for these atoms.

It is apparent from the structure that the co-ordinated epoxide in (**2**) is bent, in contrast to the thf ligand in  $\text{Ru}^{\text{II}}\text{TMP}(\text{N}_2)(\text{thf})$  which is nearly perpendicular to the porphyrin plane.<sup>9</sup> The short distance between the oxirane protons and the porphyrin indicate that the most significant steric interaction in this molecule is between the pyrrole ring and the co-ordinated epoxide. A *trans* substituent larger than a hydrogen could not be accommodated by this co-ordination geometry, consistent with the observation that *trans*- $\beta$ -methylstyrene oxide does not co-ordinate as effectively to ruthenium(II) porphyrins<sup>2</sup> under these conditions. It is also interesting that the phenyl substituent of the co-ordinated

epoxide is at a position which minimizes its distance from one of the *ortho*-chloro substituents. We have proposed a transition state for alkene epoxidation by oxometalporphyrins similar to that of the structure of (**2**) to account for the relatively high reactivity of *cis*-(1,2)-disubstituted alkenes toward oxometalporphyrins.<sup>10</sup> Such a side-on approach to the metal-oxo group would allow favourable interactions between the filled  $\pi$ -orbital of the approaching alkene and the metal–oxygen  $\pi$ -antibonding orbitals. While this suggestion has been questioned recently on the basis of molecular graphics imaging and MM2 calculations,<sup>11,12</sup> the structure of (**2**) reported here affords a clear rationale for the experimentally observed stereoselectivities and sensitivity of these preferences to the size of the *ortho* substituent on the phenyl group of the porphyrin.

The solution  $^1\text{H}$  NMR spectrum of a mixture of  $\text{Ru}^{\text{II}}\text{TDCPP}(\text{CO})$  (5.2 mM) and styrene oxide (14.4 mM, 2.7 equiv.) in  $\text{CD}_2\text{Cl}_2$  shows broad peaks for styrene oxide at 300 K. At 233 K this sample exhibited a sharp spectrum (Figure 2) with resonances indicative of a 2:1 mixture of (**2**) and  $\text{Ru}^{\text{II}}\text{TDCPP}(\text{CO})$ . That the pyrrole protons assigned to (**2**) appear as a sharp singlet suggests that the ligated epoxide rotates freely about the Ru–O(1) axis whereas exchange with the free epoxide is slow at that temperature. The apparent equilibrium constant for styrene oxide co-ordination to  $\text{Ru}^{\text{II}}\text{TDCPP}(\text{CO})$  was determined to be  $2 \times 10^2 \text{ mol}^{-1} \text{ dm}^3$  by integration of these proton resonances. Smaller binding constants of epoxides to cadmium porphyrins have been detected spectrophotometrically<sup>13</sup> and the co-ordination of thiirane to a ( $\text{C}_5\text{H}_4$ )ruthenium(II) complex has been recently reported.<sup>14</sup> A detailed examination of the co-ordination of epoxides as well as thiiranes and aziridines with  $\text{Ru}^{\text{II}}(\text{CO})$  porphyrins will be reported elsewhere.

Support of this research by the National Science Foundation (CHE-8706310) is gratefully acknowledged. The N.S.F. and the N.I.H. provided funds for the purchase of a GC-mass spectrometer with a FAB source.

Received, 12th September 1989; Com. 9/03882E

## References

† Selected spectroscopic data:  $^1\text{H}$  NMR of (**2**) ( $\delta$  in  $\text{CD}_2\text{Cl}_2$  at 233 K): porphyrin, 8.53 (s, pyrrole); 7.84–7.70 (m, *m*, *p*-H); co-ordinated styrene oxide, 6.63 (*p*-H, t,  $J$  7.34 Hz); 6.40 (*m*-H, t,  $J$  7.34 Hz); 4.64 (*o*-H, d,  $J$  7.34 Hz); –0.87 (t, H-*cis* to phenyl); –1.92 (t,  $\text{H}_\alpha$ ); –2.72 (t, H-*trans* to phenyl),  $^2J_{\text{gem}}$  4.4  $^3J_{\text{trans}}$  3.67,  $^3J_{\text{cis}}$  4.40 Hz; for free styrene oxide,  $\delta$  7.35–7.23 (m, phenyl-H); 3.82 (dd,  $\text{H}_\alpha$ ); 3.12 (dd, H-*trans* to phenyl); 2.77 (dd, H-*cis* to phenyl);  $^2J_{\text{gem}}$  5.50,  $^3J_{\text{trans}}$  2.57,  $^3J_{\text{cis}}$  4.04 Hz.

- J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790.
- J. T. Groves, K.-H. Ahn, and R. Quinn, *J. Am. Chem. Soc.*, 1988, **110**, 4217.
- P. S. Traylor, D. Dolphin, and T. G. Traylor, *J. Chem. Soc., Chem. Commun.*, 1984, 279.
- C. L. Hill and M. M. Williamson, *J. Chem. Soc., Chem. Commun.*, 1985, 1228.
- J. T. Groves and R. Quinn, *Inorg. Chem.*, 1984, **23**, 3844.
- G. M. Sheldrick, SHELXTL 1980. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data. University of Göttingen, Federal Republic of Germany.
- J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 2141.
- J. P. Collman, J. I. Brauman, J. P. Fitzgerald, P. D. Hampton, Y. Naruta, J. W. Sparapanny, and J. A. Ibers, *J. Am. Chem. Soc.*, 1988, **110**, 3477.
- M. J. Camenzind, B. R. James, D. Dolphin, J. W. Sparapanny, and J. A. Ibers, *Inorg. Chem.*, 1988, **27**, 3054.
- J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 5786.
- D. Ostovic and T. C. Bruice, *J. Am. Chem. Soc.*, 1988, **110**, 6906.
- D. Ostovic and T. C. Bruice, *J. Am. Chem. Soc.*, 1989, **111**, 6511.
- P. Dumas and P. Guerin, *Can. J. Chem.*, 1978, **56**, 925.
- J. Amarasekera, T. B. Rauchfuss, and S. R. Wilson, *J. Am. Chem. Soc.*, 1988, **110**, 2332.