

## Reactivity and kinetic-mechanistic studies of regioselective reactions of rhodium porphyrins with unactivated olefins in water that form $\beta$ -hydroxyalkyl complexes and conversion to ketones and epoxides

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**General:** D<sub>2</sub>O, DMSO-*d*<sub>6</sub>, and CDCl<sub>3</sub> were purchased from Cambridge Isotope Laboratory Inc; tetra p-sulfonatophenyl porphyrin from Tokyo Chemical Industry (TCI); (Rh(CO)<sub>2</sub>Cl)<sub>2</sub> from Strem Chemicals Inc; and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. <sup>1</sup>H NMR spectra were recorded on a Bruker AVII<sup>+</sup>-400 spectrometer at ambient temperature and the chemical shifts were referenced to 3-trimethylsilyl-1 propanesulfonic acid sodium salt. GC-MS results were obtained by the Agilent 7890A/5975C GC/MSD system equipped with the DB-17MS(30m, 0.25mm, 0.25um) column.

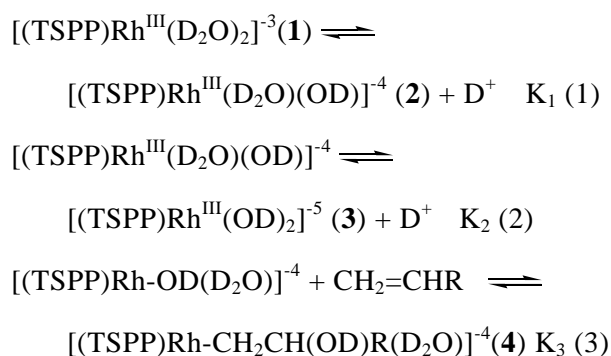
**Preparation of Na<sub>3</sub>[(TSPP)Rh<sup>III</sup>(D<sub>2</sub>O)<sub>2</sub>] (1):** Synthesis and the equilibrium distribution of [(TSPP)Rh<sup>III</sup>(D<sub>2</sub>O)<sub>2</sub>]<sup>-3</sup>, [(TSPP)Rh<sup>III</sup>(D<sub>2</sub>O)(OD)]<sup>-4</sup>, and [(TSPP)Rh<sup>III</sup>(OD)<sub>2</sub>]<sup>-5</sup> were reported in the previously published papers. <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz)  $\delta$ (ppm): 9.15 (s, 8H, pyrrole), 8.44 (d, 8H, o-phenyl, J<sub>1H-1H</sub>=8Hz), 8.25 (d, 8H, m-phenyl, J<sub>1H-1H</sub>=8Hz).

**Typical procedure for preparation of (TSPP)Rh-CH<sub>2</sub>CH(OD)R in water:** Alkenes (0.01mmol) and **1** (1.1mg, 0.001mmol) were dissolved in 0.4 mL borate buffer D<sub>2</sub>O solution (pH = 9.0) in vacuum adapted NMR tubes at room temperature, respectively. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy.

**Typical procedure for  $\beta$ -hydrogen elimination of (TSPP)Rh-CH<sub>2</sub>CH(OD)R in water:** The (TSPP)Rh-CH<sub>2</sub>CH(OD)R complexes were prepared according to the procedure given above, which exclusively converted (TSPP)Rh<sup>III</sup> into (TSPP)Rh-CH<sub>2</sub>CH(OD)R. The excess of alkenes and solvent D<sub>2</sub>O were pumped out. Fresh D<sub>2</sub>O was added into the NMR tube and subjected to three freeze-pump-thaw cycles. The initial <sup>1</sup>H NMR was recorded to show the formation of Rh-CH<sub>2</sub>CH(OD)R and a clean range from 0 to 4 ppm. The sample

(TSPP)Rh-CH<sub>2</sub>CH(OD)R was heated in a water bath at 60°C (or 80°C) for a period of hours, and the progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. When the reactions reached completion where all (TSPP)Rh-CH<sub>2</sub>CH(OD)R complexes were converted to ketones and (TSPP)Rh<sup>I</sup> which shows a characteristic <sup>1</sup>H NMR singlet peak at 8.31 ppm, the product ketones were extracted by CDCl<sub>3</sub>. Both <sup>1</sup>H NMR and GC-MS confirmed the product ketones. A parallel samples of (TSPP)Rh-CH<sub>2</sub>CH(OH)R dissolved in H<sub>2</sub>O was also heated under the same reaction condition, and extracted by CDCl<sub>3</sub>.

***Kinetic simulations for reaction of (TSPP)Rh<sup>III</sup> with pentene:***



$$\frac{d[\mathbf{4}]}{dt} = k_3[\mathbf{2}]c_0 - k_{-3}[\mathbf{4}]$$

$$[\mathbf{1}] = [\mathbf{2}][\text{D}^+]/K_1,$$

$$[\mathbf{3}] = [\mathbf{2}]K_2/[\text{D}^+],$$

$$[\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] + [\mathbf{4}] = c_{(\text{RhT})}$$

$$c_0 = [\text{CH}_2=\text{CHR}]$$

The concentration of **2** related with **4**,

$$[\mathbf{2}] = \frac{c_{(\text{RhT})} - [\mathbf{4}]}{\frac{[\text{D}^+]}{K_1} + 1 + \frac{K_2}{[\text{D}^+]}}$$

$$\frac{d[\mathbf{4}]}{dt} = k_3[\mathbf{2}]c_0 - k_{-3}[\mathbf{4}]$$

$$= \beta - \alpha[\mathbf{4}]$$

where  $\beta = \frac{k_3 c_{(\text{RhT})} c_0}{\frac{[\text{D}^+]}{K_1} + 1 + \frac{K_2}{[\text{D}^+]}}$ ,  $\alpha = \frac{\beta}{c_{(\text{RhT})}} + k_{-3}$

$$\text{so } [\mathbf{4}]_t = \frac{\beta}{\alpha}(1 - e^{-\alpha t})$$

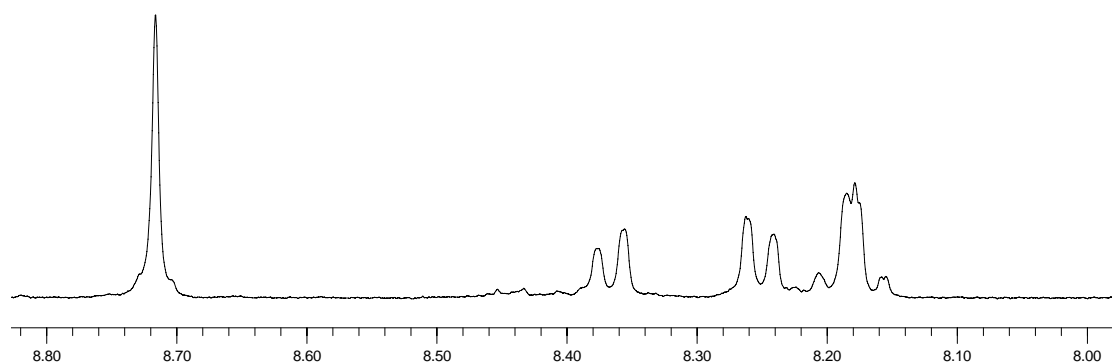
$$= (8.5 \pm 0.1) \times 10^{-7}, \quad = (5.5 \pm 0.1) \times 10^{-4} \text{ are obtained from simulation, and } k_3 = (2.3 \pm 0.1) \times 10^{-1}$$

$$\text{Lmol}^{-1}\text{s}^{-1}, \quad k_{-3} = (10.0 \pm 1.0) \times 10^{-5} \text{ s}^{-1}, \text{ and } K_3 = (2.3 \pm 0.1) \times 10^3 \text{ are derived when } c_{(\text{RhT})} = 1.9 \times 10^{-3}$$

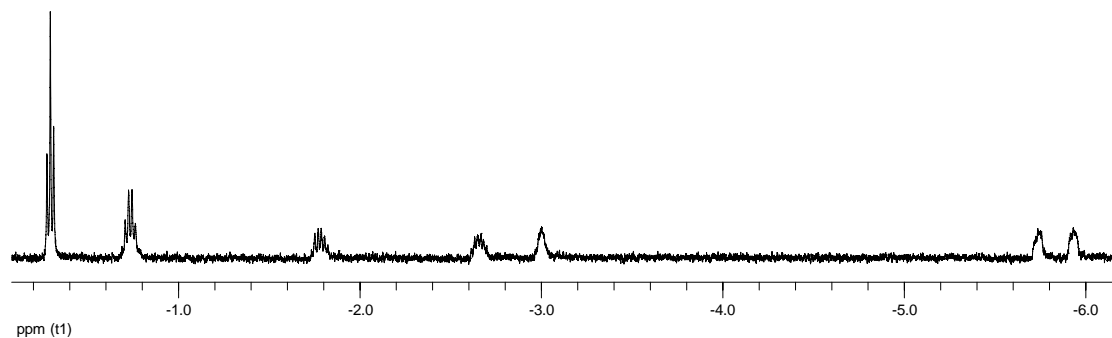
M and  $c_0 = [\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3] = 2.1 \times 10^{-3}$  M are used.

***<sup>1</sup>H NMR data of  $\beta$ -hydroxy alkyl rhodium porphyrin complexes formed from reaction 3:***

(a) **(TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>** (400 MHz, D<sub>2</sub>O)  $\delta$ (ppm): 8.71 (8H, pyrrole), 8.40-8.12 (16H, phenyl), -5.93 (m, 1H<sub>A</sub>), -5.74 (m, 1H<sub>B</sub>), -3.00 (m, 1H), -2.64 (m, 1H<sub>A</sub>), -1.78 (m, 1H<sub>B</sub>), -0.73 (m, 2H), -0.29 (t, 3H).

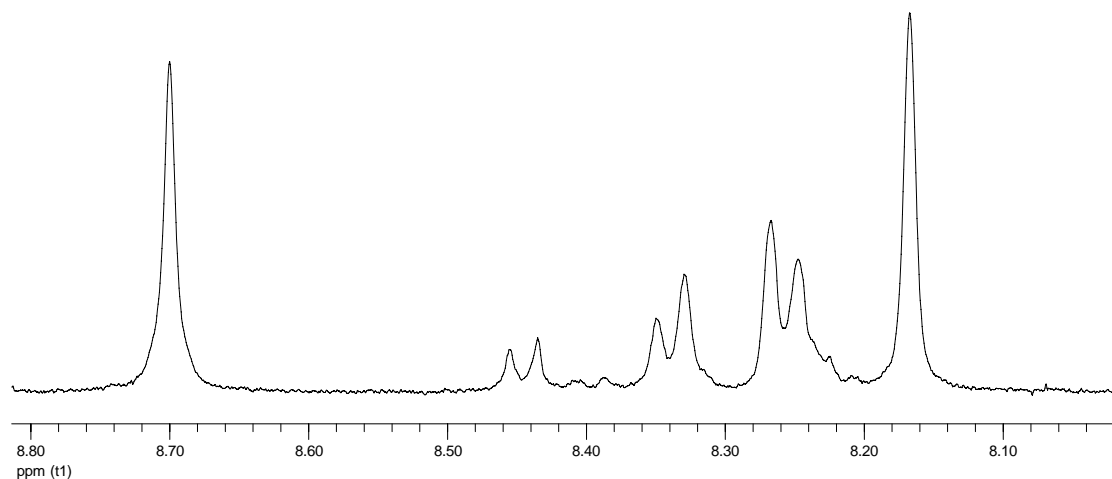


<sup>1</sup>H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> in D<sub>2</sub>O

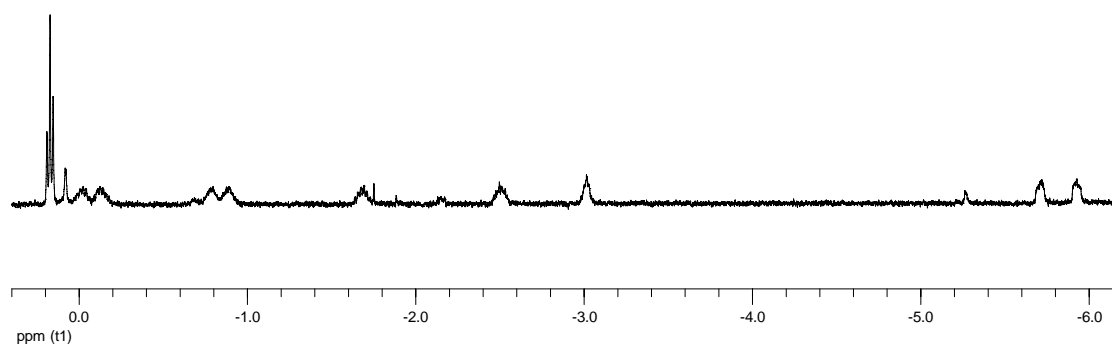


<sup>1</sup>H NMR spectra of -CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> in (TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> in D<sub>2</sub>O

(b) **(TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>** (400 MHz, D<sub>2</sub>O)  $\delta$ (ppm): 8.70 (8H, pyrrole), 8.38-8.12 (16H, phenyl), -5.93 (m, 1H<sub>A</sub>), -5.71 (m, 1H<sub>B</sub>), -3.02 (m, 1H), -2.50 (m, 1H<sub>A</sub>), -1.69 (m, 1H<sub>B</sub>), -0.89 (m, 1H<sub>A</sub>), -0.79 (m, 1H<sub>B</sub>), -0.13 (m, 1H<sub>A</sub>), -0.02 (m, 1H<sub>B</sub>), 0.17 (t, 3H).

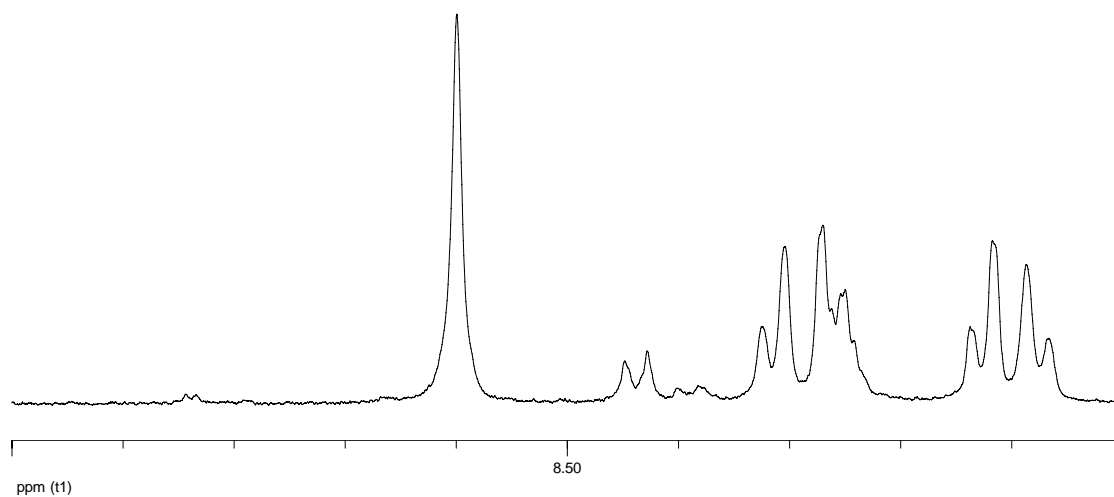


$^1\text{H}$  NMR spectra of pyrrole and phenyl hydrogens of  
(TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> in D<sub>2</sub>O

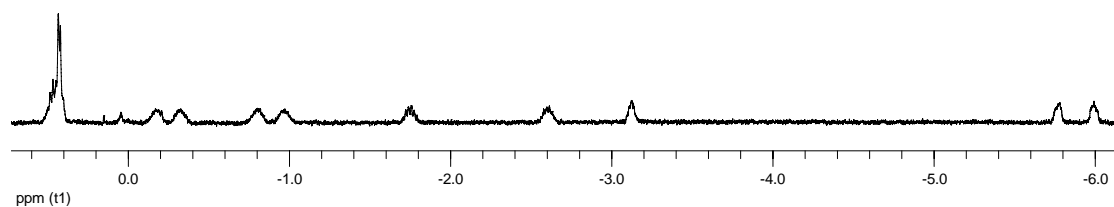


$^1\text{H}$  NMR spectra of -CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> in (TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub> in  
D<sub>2</sub>O

(c) (TSPP)Rh-CH<sub>2</sub>CH(OD)(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub> (400 MHz, D<sub>2</sub>O)  $\delta$ (ppm): 8.60 (8H, pyrrole), 8.32-8.07 (16H, phenyl), -5.99 (m, 1H<sub>A</sub>), -5.77 (m, 1H<sub>B</sub>), -3.12 (m, 1H), -2.60 (m, 1H<sub>A</sub>), -1.75 (m, 1H<sub>B</sub>), -0.97 (m, 1H<sub>A</sub>), -0.80 (m, 1H<sub>B</sub>), -0.32 (m, 1H<sub>A</sub>), -0.18 (m, 1H<sub>B</sub>), 0.43 (m, 2H), 0.47 (t, 3H).

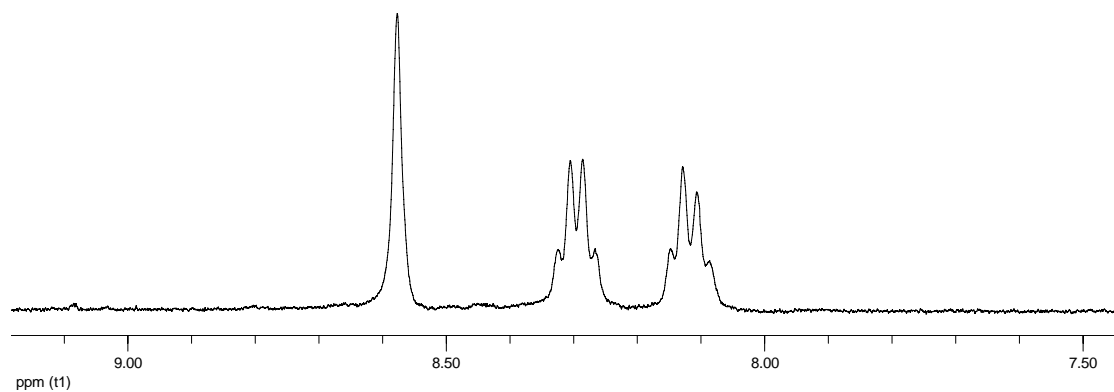


$^1\text{H}$  NMR spectra of pyrrole and phenyl hydrogens of  $(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{OD})(\text{CH}_2)_4\text{CH}_3$  in  $\text{D}_2\text{O}$



$^1\text{H}$  NMR spectra of  $-\text{CH}_2\text{CH}(\text{OD})(\text{CH}_2)_4\text{CH}_3$  in  $(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{OD})(\text{CH}_2)_4\text{CH}_3$  in  $\text{D}_2\text{O}$ .

(d)  $(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{OD})\text{CH}_2\text{CH}_2\text{OD}$  (400 MHz,  $\text{D}_2\text{O}$ )  $\delta(\text{ppm})$ : 8.58 (8H, pyrrole), 8.40-8.00 (16H, phenyl), -5.93 (m,  $1\text{H}_\text{A}$ ), -5.78 (m,  $1\text{H}_\text{B}$ ), -2.98 (m, 1H), -2.51 (m,  $1\text{H}_\text{A}$ ), -1.55 (m,  $1\text{H}_\text{B}$ ), 1.53 (m,  $1\text{H}_\text{A}$ ), 1.60 (m,  $1\text{H}_\text{B}$ ).



$^1\text{H}$  NMR spectra of pyrrole and phenyl hydrogens of



















