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

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General: D_2O, DMSO-d_6, and $CDCl_3$ were purchased from Cambridge Isotope Laboratory Inc; tetra p-sulfonatophenyl porphyrin from Tokyo Chemical Industry (TCI); $(Rh(CO)_2Cl)_2$ from Strem Chemicals Inc; and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. ^1H NMR spectra were recorded on a Bruker AVII$^+$-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 $Na_3[(TSPP)Rh^{III}(D_2O)_2]$ (1): Synthesis and the equilibrium distribution of $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$, $[(TSPP)Rh^{III}(D_2O)(OD)]^{-4}$, and $[(TSPP)Rh^{III}(OD)_2]^{-5}$ were reported in the previously published papers. ^1H NMR (D_2O, 400 MHz) δ(ppm): 9.15 (s, 8H, pyrrole), 8.44 (d, 8H, o-phenyl, $J_{^1H-^1H}$=8Hz), 8.25 (d, 8H, m-phenyl, $J_{^1H-^1H}$=8Hz).

Typical procedure for preparation of (TSPP)Rh-$CH_2CH(OD)R$ in water: Alkenes (0.01mmol) and **1** (1.1mg, 0.001mmol) were dissolved in 0.4 mL borate buffer D_2O solution (pH = 9.0) in vacuum adapted NMR tubes at room temperature, respectively. The progress of the reaction was monitored by ^1H NMR spectroscopy.

Typical procedure for β-hydrogen elimination of (TSPP)Rh-$CH_2CH(OD)R$ in water: The (TSPP)Rh-$CH_2CH(OD)R$ complexes were prepared according to the procedure given above, which exclusively converted $(TSPP)Rh^{III}$ into (TSPP)Rh-$CH_2CH(OD)R$. The excess of alkenes and solvent D_2O were pumped out. Fresh D_2O was added into the NMR tube and subjected to three freeze-pump-thaw cycles. The initial ^1H NMR was recorded to show the formation of Rh-$CH_2CH(OD)R$ and a clean range from 0 to 4 ppm. The sample

(TSPP)Rh-$CH_2CH(OD)R$ 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 ^1H NMR spectroscopy. When the reactions reached completion where all (TSPP)Rh-$CH_2CH(OD)R$ complexes were converted to ketones and (TSPP)Rh^I which shows a characteristic ^1H NMR singlet peak at 8.31 ppm, the product ketones were extracted by $CDCl_3$. Both ^1H NMR and GC-MS confirmed the product ketones. A parallel samples of (TSPP)Rh-$CH_2CH(OH)R$ dissolved in H_2O was also heated under the same reaction condition, and extracted by $CDCl_3$.

Kinetic simulations for reaction of (TSPP)Rh^{III} with pentene:

$[(TSPP)Rh^{III}(D_2O)_2]^{-3}(\mathbf{1}) \rightleftharpoons$

$[(TSPP)Rh^{III}(D_2O)(OD)]^{-4}\ (\mathbf{2}) + D^+ \quad K_1$ (1)

$[(TSPP)Rh^{III}(D_2O)(OD)]^{-4} \rightleftharpoons$

$[(TSPP)Rh^{III}(OD)_2]^{-5}\ (\mathbf{3}) + D^+ \quad K_2$ (2)

$[(TSPP)Rh\text{-}OD(D_2O)]^{-4} + CH_2{=}CHR \rightleftharpoons$

$[(TSPP)Rh\text{-}CH_2CH(OD)R(D_2O)]^{-4}(\mathbf{4})\ K_3$ (3)

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

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

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

$[\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] + [\mathbf{4}]=c_{(Rh^T)}$

$c_0 = [CH_2{=}CHR]$

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

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

$$\begin{aligned}\frac{d[\mathbf{4}]}{dt} &= k_3[\mathbf{2}]c_0 - k_{-3}[\mathbf{4}] \\ &= \beta - \alpha[\mathbf{4}]\end{aligned}$$

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

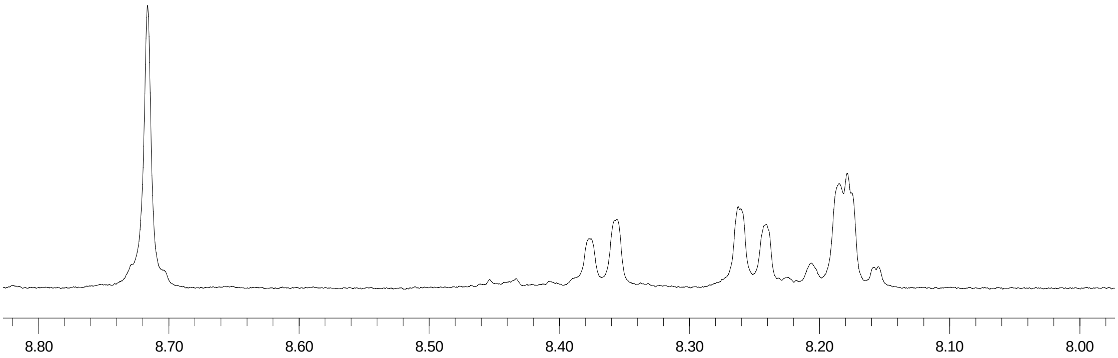
so $[\mathbf{4}]_t = \dfrac{\beta}{\alpha}(1 - e^{-\alpha t})$

= (8.5±0.1)×10^{-7}, =(5.5±0.1)×10^{-4} are obtained from simulation, and k_3=(2.3±0.1)×10^{-1} $Lmol^{-1}s^{-1}$, k_{-3}=(10.0±1.0)×10^{-5} s^{-1}, and K_3 = (2.3±0.1)×10^3 are derived when $c_{(Rh^T)} = 1.9\times10^{-3}$

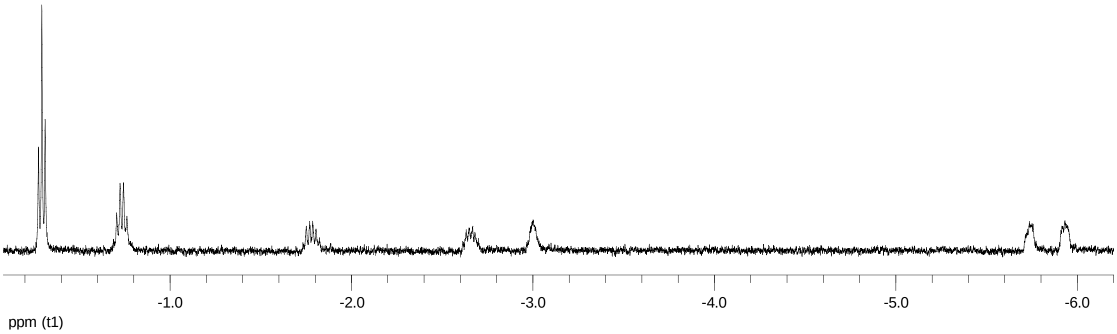
M and $c_0 = [CH_2{=}CHCH_2CH_2CH_3] = 2.1\times10^{-3}$ M are used.

^{1}H NMR data of β-hydroxy alkyl rhodium porphyrin complexes formed from reaction 3:

(a) **(TSPP)Rh-$CH_2CH(OD)(CH_2)_2CH_3$** (400 MHz, D_2O) δ(ppm): 8.71 (8H, pyrrole), 8.40-8.12 (16H, phenyl), -5.93 (m, $1H_A$), -5.74 (m, $1H_B$), -3.00 (m, 1H), -2.64 (m, $1H_A$), -1.78 (m, $1H_B$), -0.73 (m, 2H), -0.29 (t, 3H).

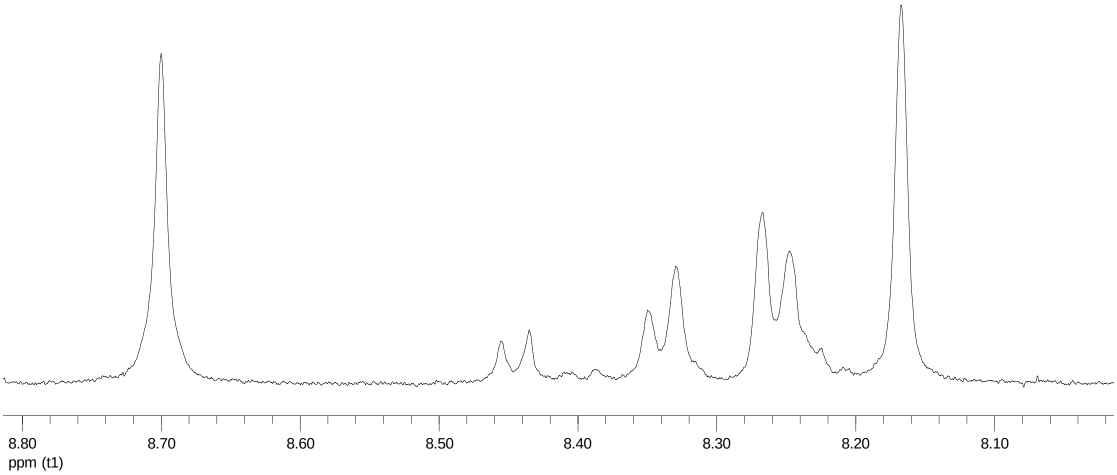


^{1}H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)(CH_2)_2CH_3$ in D_2O

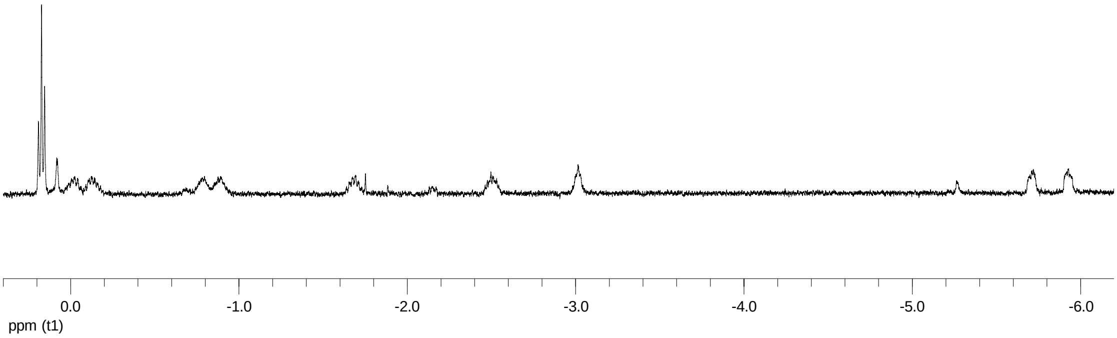


^{1}H NMR spectra of -$CH_2CH(OD)(CH_2)_2CH_3$ in (TSPP)Rh-$CH_2CH(OD)(CH_2)_2CH_3$ in D_2O

(b) **(TSPP)Rh-$CH_2CH(OD)(CH_2)_3CH_3$** (400 MHz, D_2O) δ(ppm): 8.70 (8H, pyrrole), 8.38-8.12 (16H, phenyl), -5.93 (m, $1H_A$), -5.71 (m, $1H_B$), -3.02 (m, 1H), -2.50 (m, $1H_A$), -1.69 (m, $1H_B$), -0.89 (m, $1H_A$), -0.79 (m, $1H_B$), -0.13 (m, $1H_A$), -0.02 (m, $1H_B$), 0.17 (t, 3H).

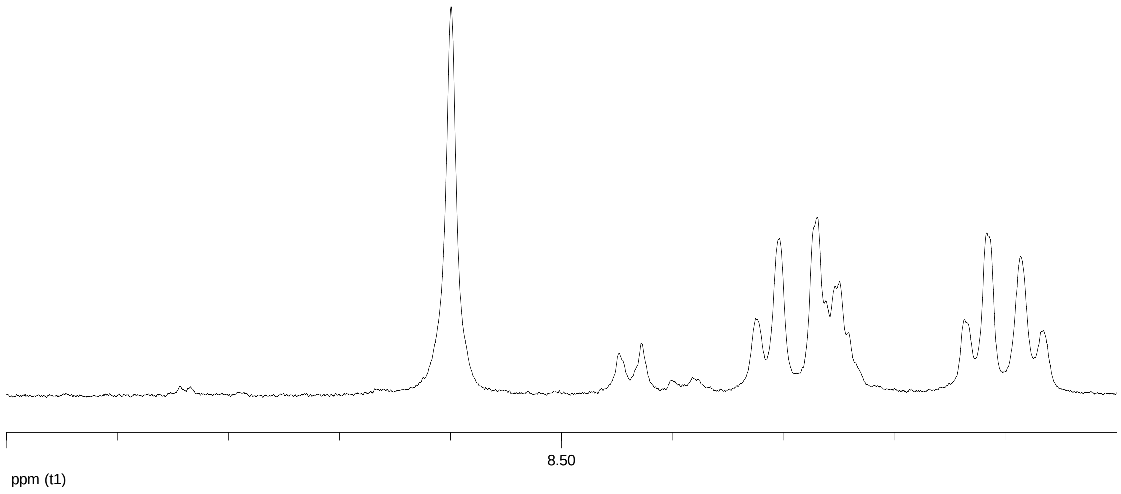


^1H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)(CH_2)_3CH_3$ in D_2O

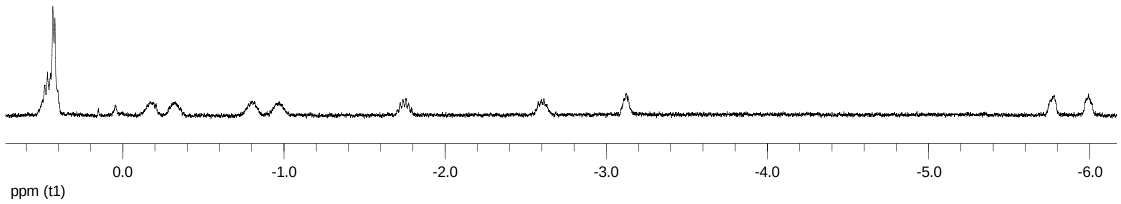


^1H NMR spectra of -$CH_2CH(OD)(CH_2)_3CH_3$ in (TSPP)Rh-$CH_2CH(OD)(CH_2)_3CH_3$ in D_2O

(c) **(TSPP)Rh-$CH_2CH(OD)(CH_2)_4CH_3$** (400 MHz, D_2O) δ(ppm): 8.60 (8H, pyrrole), 8.32-8.07 (16H, phenyl), -5.99 (m, 1H_A), -5.77 (m, 1H_B), -3.12 (m, 1H), -2.60 (m, 1H_A), -1.75 (m, 1H_B), -0.97 (m, 1H_A), -0.80 (m, 1H_B), -0.32 (m, 1H_A), -0.18 (m, 1H_B), 0.43 (m, 2H), 0.47 (t, 3H).

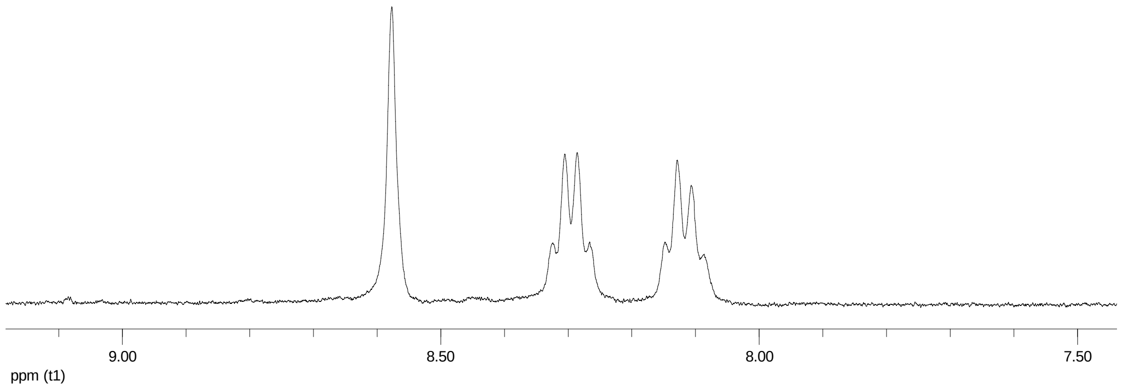


^{1}H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)(CH_2)_4CH_3$ in D_2O



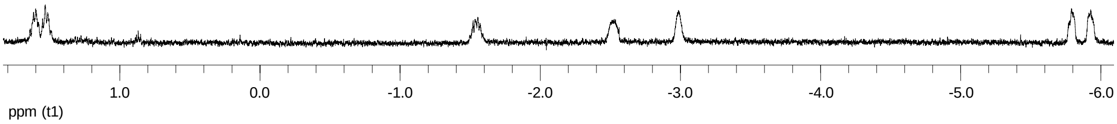
^{1}H NMR spectra of -$CH_2CH(OD)(CH_2)_4CH_3$ in (TSPP)Rh-$CH_2CH(OD)(CH_2)_4CH_3$ in D_2O.

(d) **(TSPP)Rh-$CH_2CH(OD)CH_2CH_2OD$** (400 MHz, D_2O) δ(ppm): 8.58 (8H, pyrrole), 8.40-8.00 (16H, phenyl), -5.93 (m, 1H_A), -5.78 (m, 1H_B), -2.98 (m, 1H), -2.51 (m, 1H_A), -1.55 (m, 1H_B), 1.53 (m, 1H_A), 1.60 (m, 1H_B).



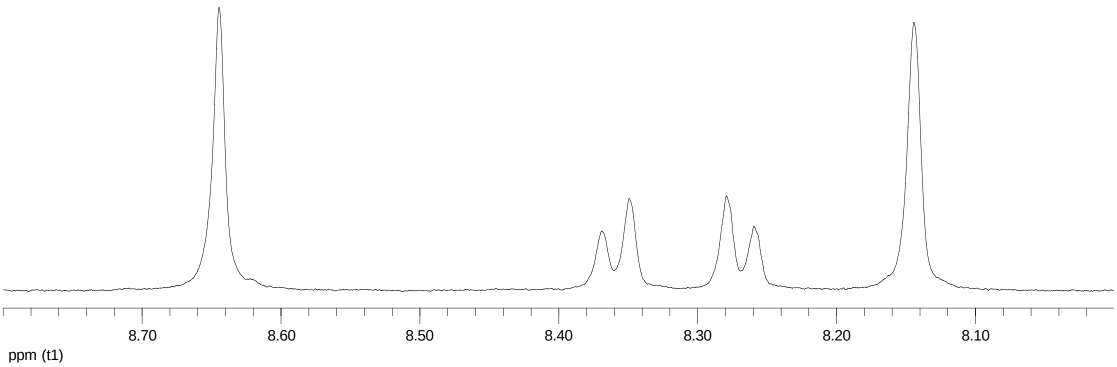
^{1}H NMR spectra of pyrrole and phenyl hydrogens of

(TSPP)Rh-$CH_2CH(OD)CH_2CH_2OD$ in D_2O

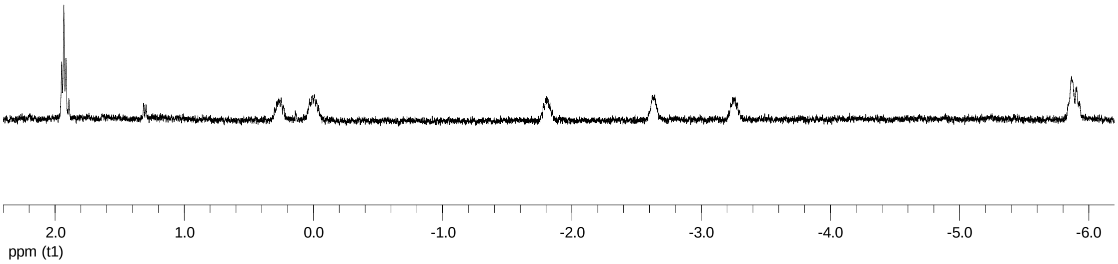


^1H NMR spectra of -$CH_2CH(OD)CH_2CH_2OD$ in (TSPP)Rh-$CH_2CH(OD)CH_2CH_2OD$ in D_2O

(e) **(TSPP)Rh-$CH_2CH(OD)(CH_2)_2CH_2OD$** (400 MHz, D_2O) δ(ppm): 8.65 (8H, pyrrole), 8.40-8.10 (16H, phenyl), -5.80~-5.95 (m, 2H), -3.25 (m, 1H), -2.63 (m, $1H_A$), -1.80 (m, $1H_B$), 0.00 (m, $1H_A$), 0.27 (m, $1H_B$), 1.93 (t, 2H).

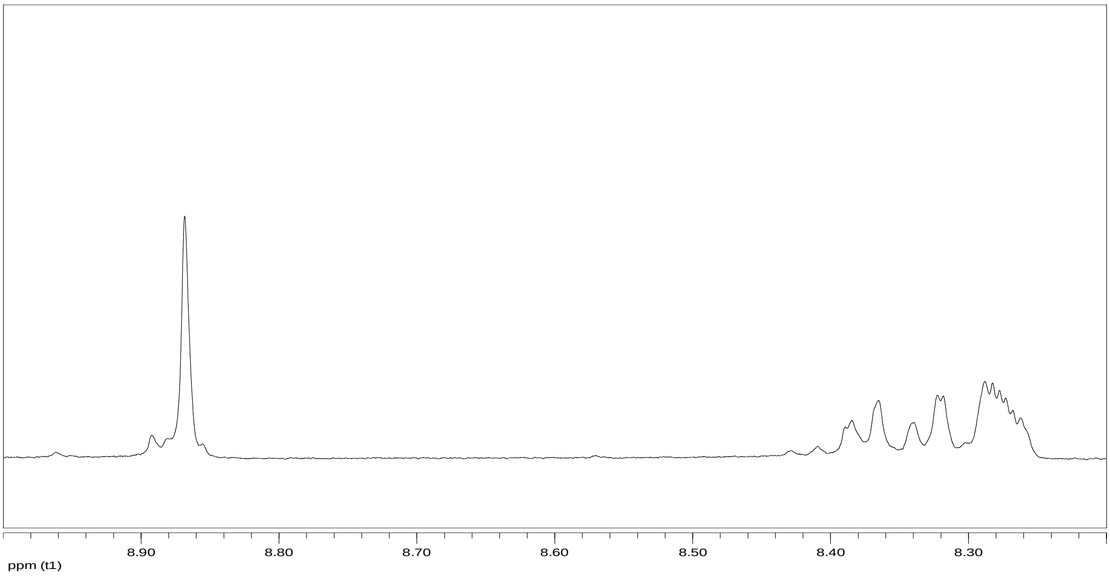


^1H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)(CH_2)_2CH_2OD$ in D_2O

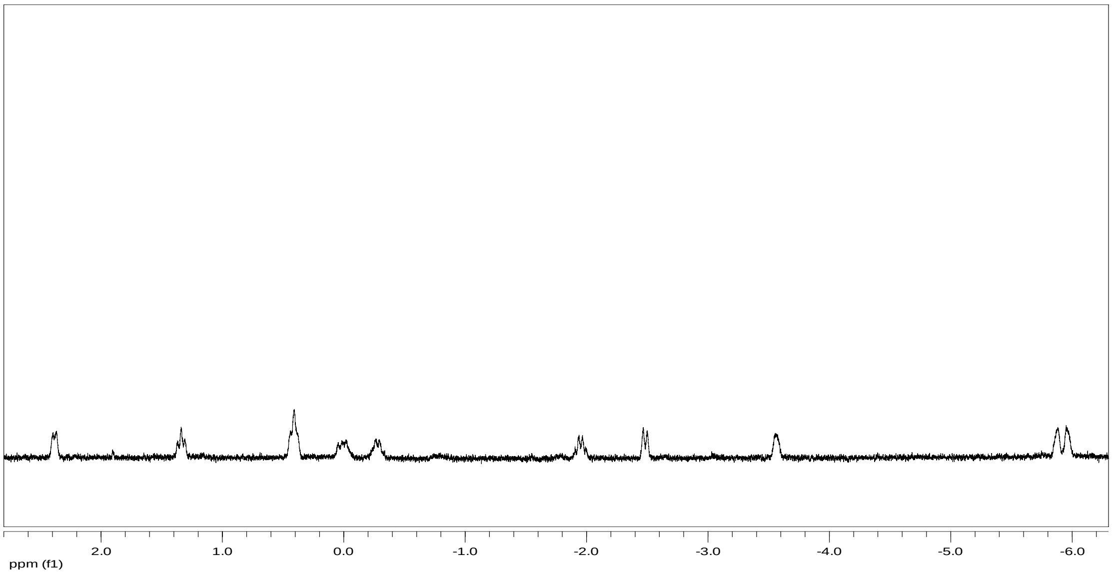


^1H NMR spectra of -$CH_2CH(OD)(CH_2)_2CH_2OD$ in (TSPP)Rh-$CH_2CH(OD)(CH_2)_2CH_2OD$ in D_2O

(f) **(TSPP)Rh-$CH_2CH(OD)(CH_2)_3CH_2OD$** (400 MHz, D_2O) δ(ppm): 8.87 (8H, pyrrole), 8.41-8.25 (16H, phenyl), -5.96 (m, $1H_A$), -5.88 (m, $1H_B$), -3.56 (m, 1H), -2.48 (m, $1H_A$), -1.95 (m, $1H_B$), -0.28 (m, $1H_A$), 0.01 (m, $1H_B$), 0.41 (m, 2H), 1.34 (m, $1H_A$), 2.38 (m, $1H_B$).

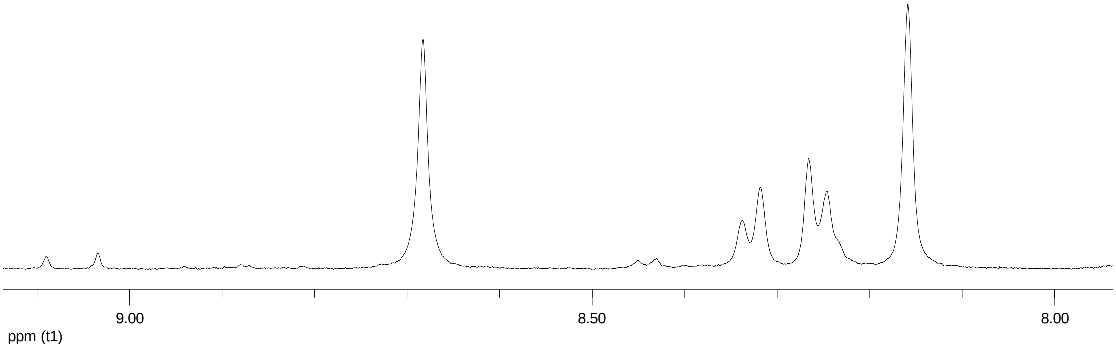


^1H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)(CH_2)_3CH_2OD$ in D_2O

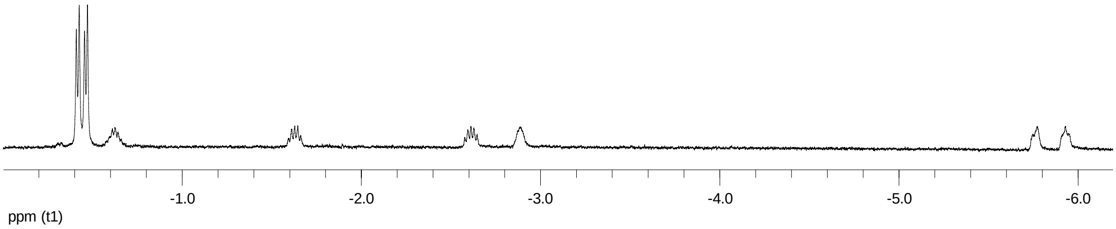


^1H NMR spectra of -$CH_2CH(OD)(CH_2)_3CH_2OD$ in (TSPP)Rh-$CH_2CH(OD)(CH_2)_3CH_2OD$ in D_2O

(g) **(TSPP)Rh-$CH_2CH(OD)CH_2CH(CH_3)_2$** (400 MHz, D_2O) δ(ppm): 8.68 (8H, pyrrole), 8.40-8.15 (16H, phenyl), -5.93 (m, $1H_A$), -5.77 (m, $1H_B$), -2.89 (m, 1H), -2.61 (m, $1H_A$), -1.63 (m, $1H_B$), -0.62 (m, 1H), -0.46 (d, 3H), -0.41 (d, 3H).

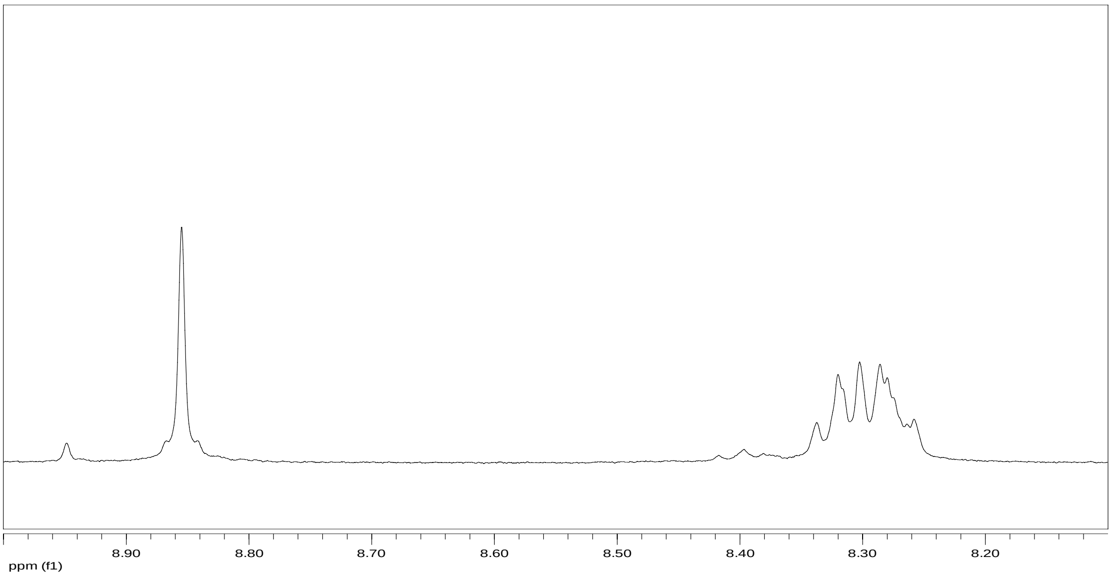


^{1}H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)CH_2CH(CH_3)_2$ in D_2O

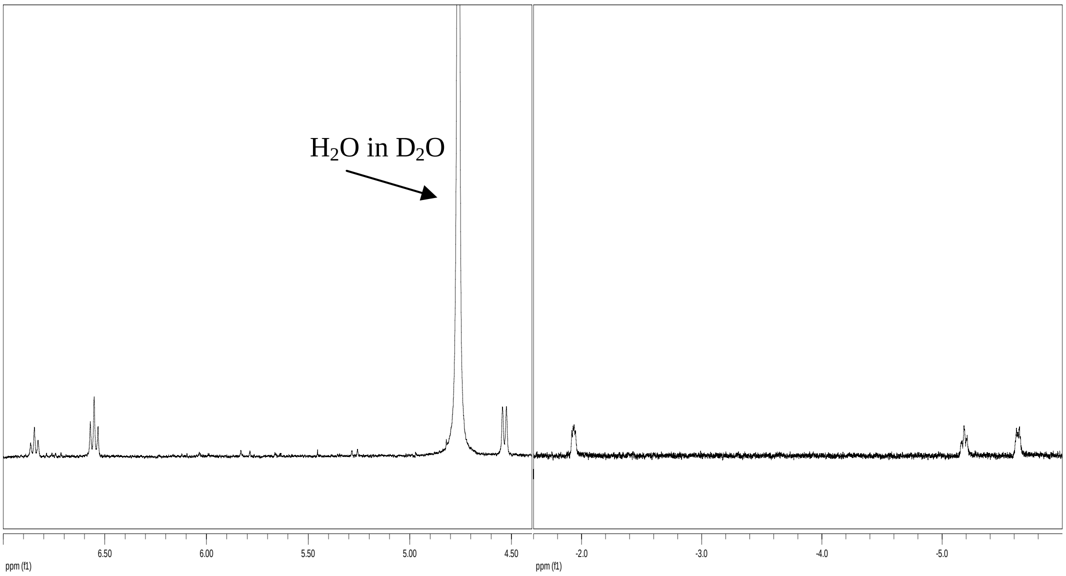


^{1}H NMR spectra of -$CH_2CH(OD)CH_2CH(CH_3)_2$ in (TSPP)Rh-$CH_2CH(OD)CH_2CH(CH_3)_2$ in D_2O

(h) **(TSPP)Rh-$CH_2CH(OD)Ph$** (400 MHz, D_2O) δ(ppm): 8.86 (8H, pyrrole), 8.36-8.22 (16H, phenyl), -5.63 (m, $1H_A$), -5.18 (m, $1H_B$), -1.93 (m, 1H), 4.53 (d, 2H), 6.55 (t, 2H), 6.85 (t, 1H).

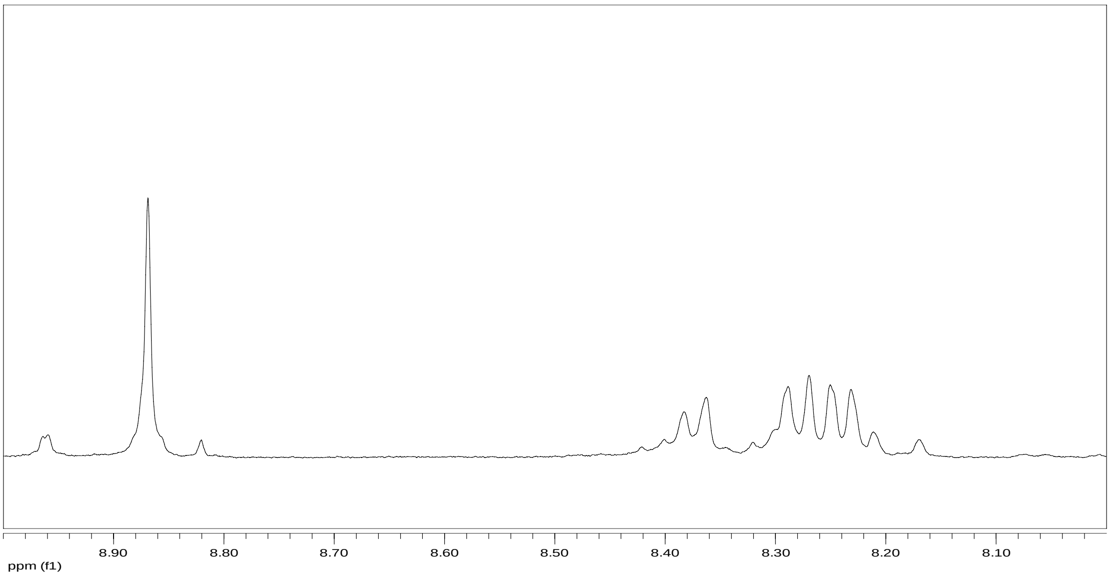


^1H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)Ph$ in D_2O

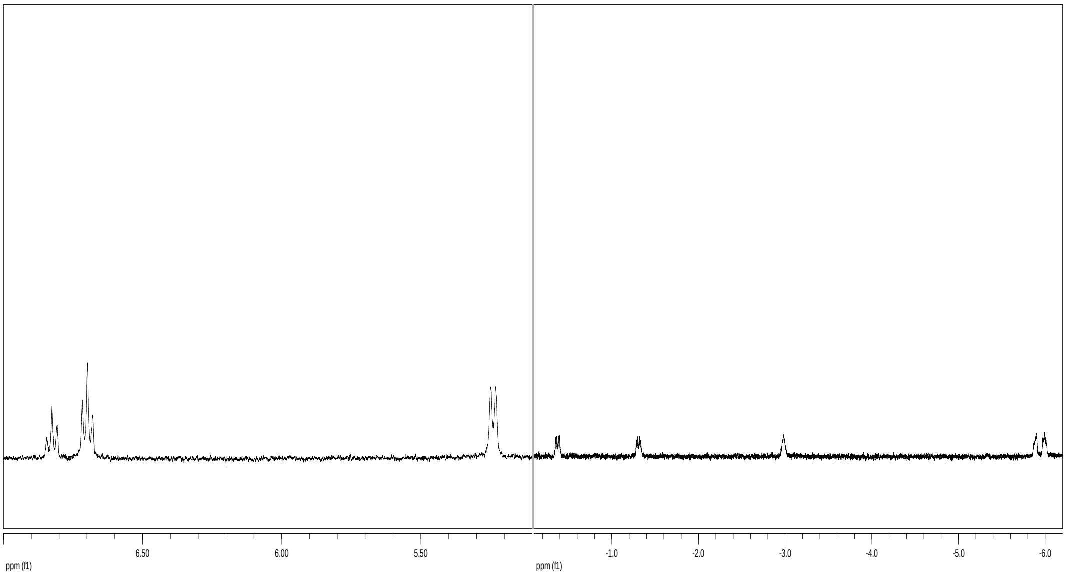


^1H NMR spectra of -$CH_2CH(OD)Ph$ in (TSPP)Rh-$CH_2CH(OD)Ph$ in D_2O

(i) **(TSPP)Rh-$CH_2CH(OD)CH_2Ph$** (400 MHz, D_2O) δ(ppm): 8.87 (8H, pyrrole), 8.44-8.14 (16H, phenyl), -5.99 (m, $1H_A$), -5.89 (m, $1H_B$), -2.98 (m, 1H), -1.31 (m, $1H_A$), -0.37 (m, $1H_B$), 5.24 (d, 2H), 6.70 (t, 2H), 6.83 (t, 1H).

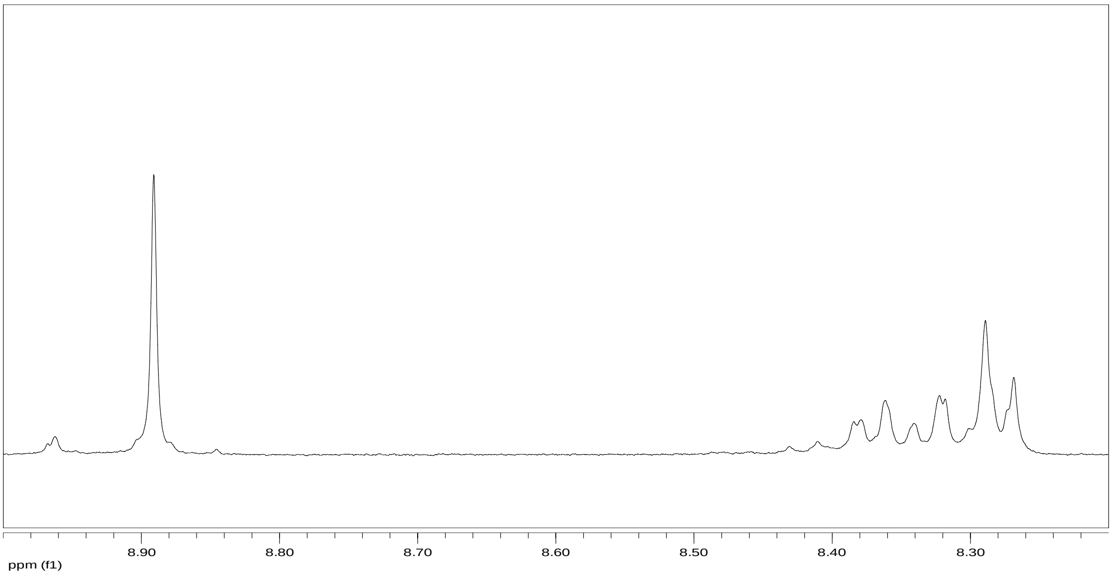


^{1}H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)CH_2Ph$ in D_2O

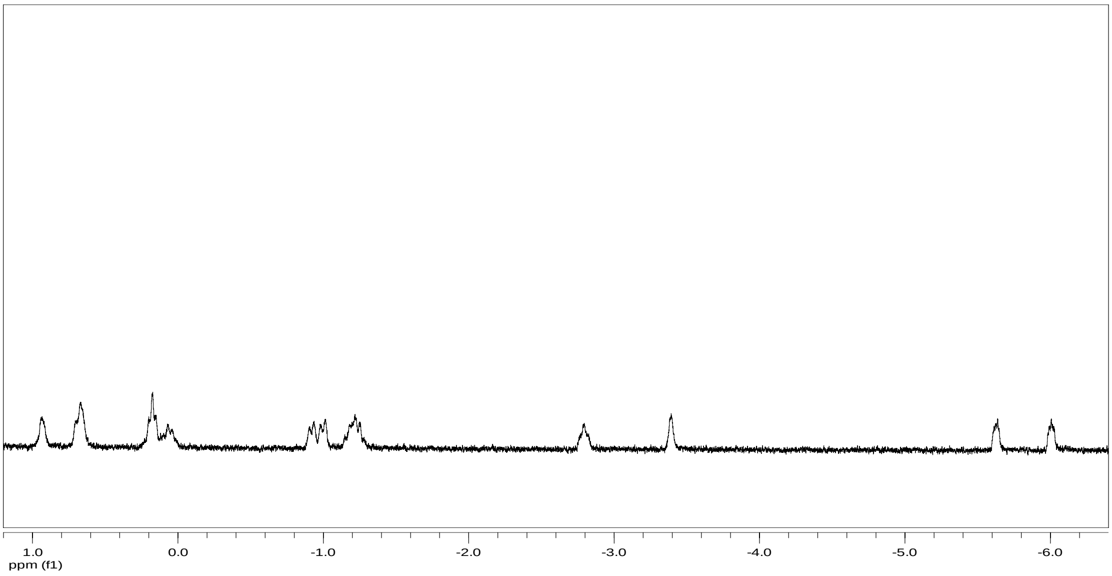


^{1}H NMR spectra of -$CH_2CH(OD)CH_2Ph$ in (TSPP)Rh-$CH_2CH(OD)CH_2Ph$ in D_2O

(j) **(TSPP)Rh-$CH_2CH(OD)$(c-hexyl)** (400 MHz, D_2O) δ(ppm): 8.89 (8H, pyrrole), 8.40-8.25 (16H, phenyl), -6.01 (m, 1H_A), -5.63 (m, 1H_B), -3.39 (m, 1H), -2.79 (m, 1H), -1.13~-1.33 (m, 2H), -0.88~-1.05 (m, 2H), 0.28~-0.01 (m, 3H), 0.77~0.60 (m, 2H), 0.93 (m, 1H).

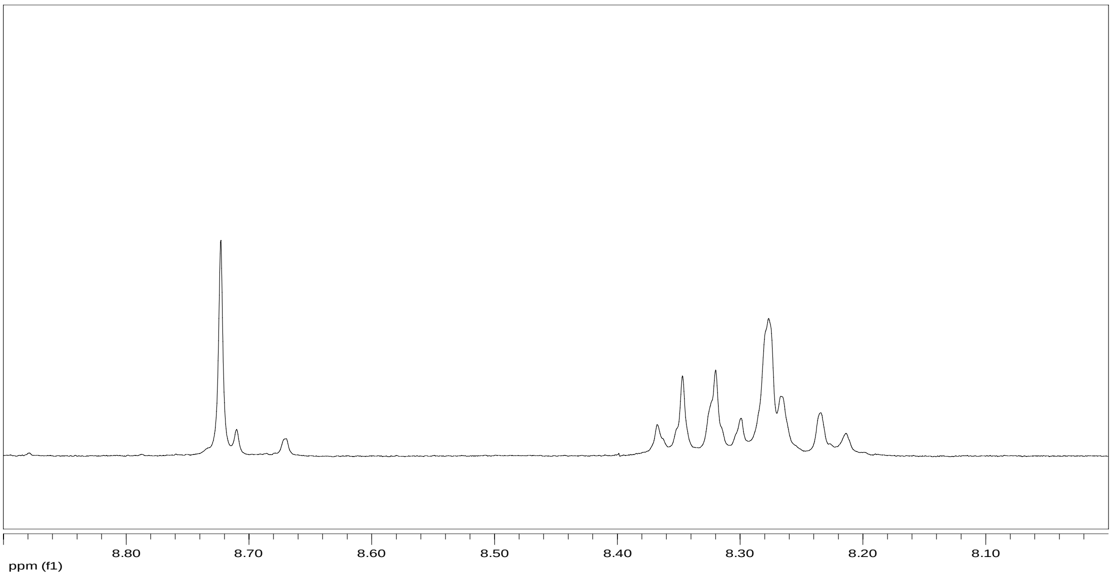


^{1}H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2CH(OD)$(c-hexyl) in D_2O

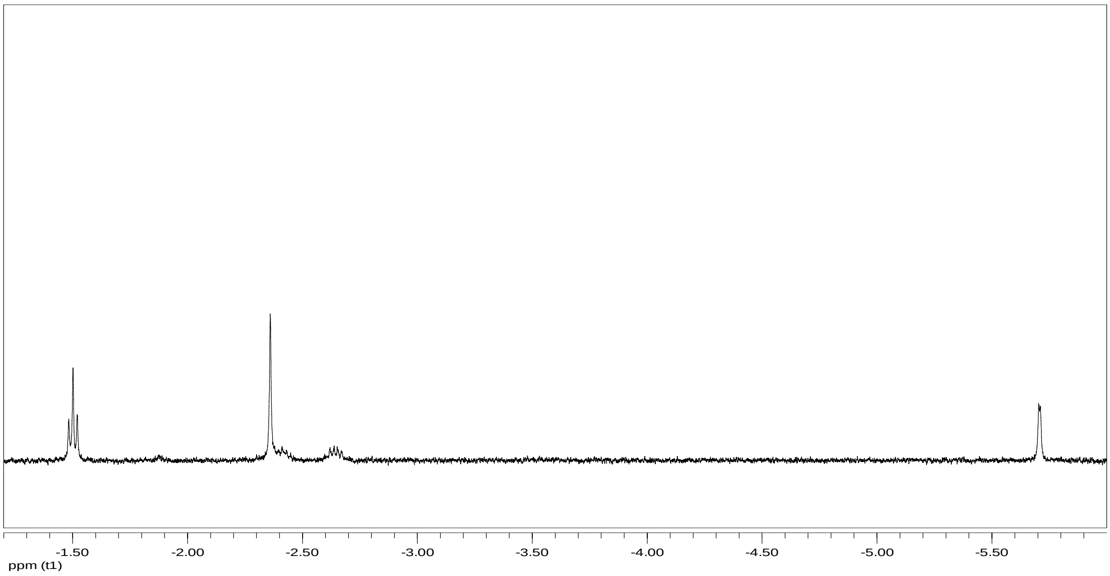


^{1}H NMR spectra of -$CH_2CH(OD)$(c-hexyl) in (TSPP)Rh- $CH_2CH(OD)$(c-hexyl) in D_2O

(k) **(TSPP)Rh-$CH_2C(OD)(Me)(Et)$** (400 MHz, D_2O) δ(ppm): 8.72 (8H, pyrrole), 8.40-8.19 (16H, phenyl), -5.67~-5.74 (m, 2H), -2.64 (m, $1H_A$), -2.41 (m, $1H_B$), -2.36 (s, 3H), -1.50 (t, 3H).



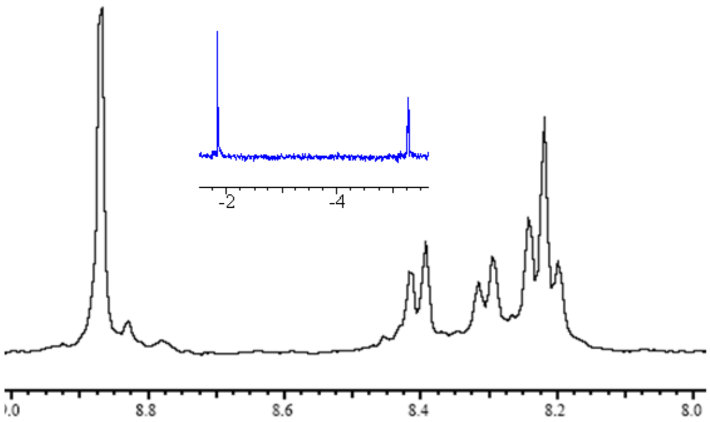
^{1}H NMR spectra of pyrrole and phenyl hydrogens of (TSPP)Rh-$CH_2C(OD)(Me)(Et)$ in D_2O



^{1}H NMR spectra of -$CH_2C(OD)(Me)(Et)$ in (TSPP)Rh-$CH_2C(OD)(Me)(Et)$ in D_2O

^{1}H NMR data of β-carbonyl alkyl rhodium porphyrin complexes:

(a) **(TSPP)Rh-$CH_2C(O)CH_3$**

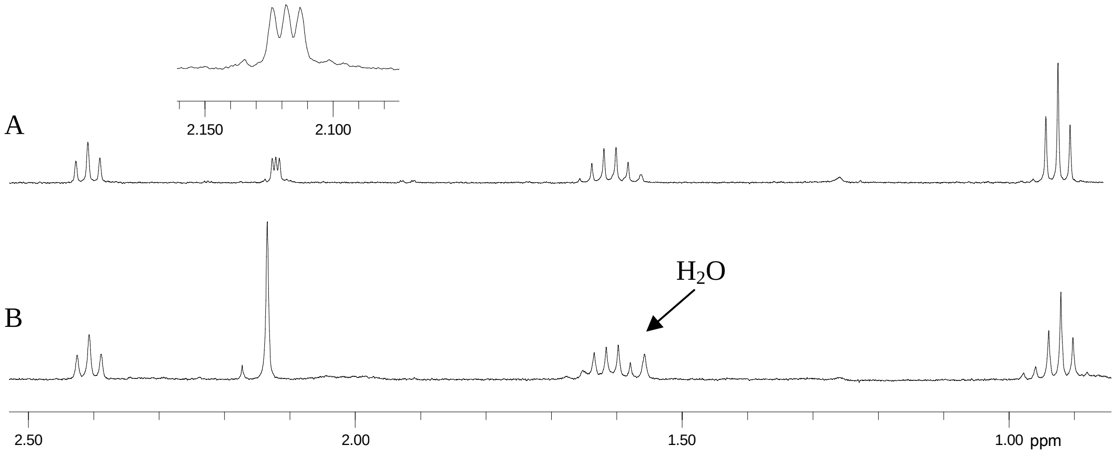


^{1}H NMR of the (TSPP)Rh-$CH_2C(O)CH_3$ from reaction of (TSPP)Rh^I with $ClCH_2C(O)CH_3$ in water, which is identical with compound formed by reaction of (TSPP)Rh^{III} with acetone.

(b) **(TSPP)Rh-$CH_2C(O)(CH_2)_2CH_3$** 8.85 (8H, pyrrole), 8.46-8.18 (16H, phenyl), -5.29 (m, 2H), -2.15 (m, 2H), -0.59 (m, 2H), -0.23 (t, 3H).

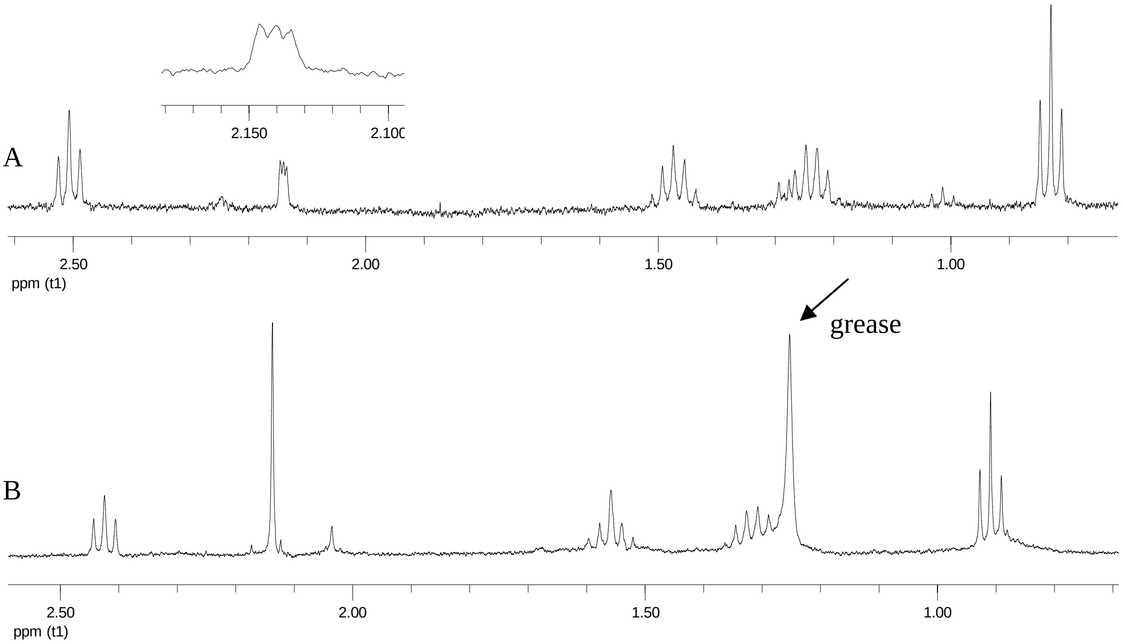
^{1}H NMR data of ketones formed from reaction 5:

(a) ***2-pentanone:***



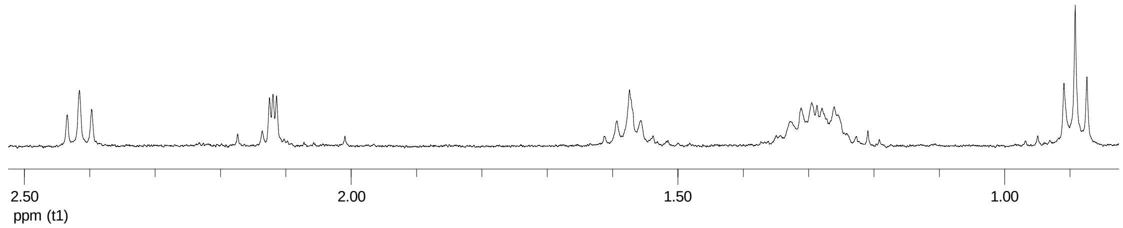
^{1}H NMR (400 MHz; $CDCl_3$) spectrum of 2-pentanone produced from thermal dissociation of (TSPP)Rh-$CH_2CH(OH)CH_2CH_2CH_3$ in D_2O and H_2O. A) $CH_2(D)C(O)CH_2CH_2CH_3$ in D_2O; B) $CH_3C(O)CH_2CH_2CH_3$ (obtained in H_2O).

(b) ***2-hexanone:***



^{1}H NMR (400 MHz) spectrum of 2-hexanone produced from thermal dissociation of (TSPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2CH_3$ in D_2O and H_2O. A) $CH_2(D)C(O)CH_2CH_2CH_2CH_3$ in D_2O; B) $CH_3C(O)CH_2CH_2CH_2CH_3$ (obtained in H_2O) in $CDCl_3$.

(c) ***2-heptanone:***



^{1}H NMR (400 MHz) spectrum of 2-heptanone produced from thermal dissociation of (TSPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2CH_2CH_3$ in D_2O.

(d) 5-hydroxy-2-pentanone (400 MHz; $CDCl_3$) δ(ppm): 3.65 (t, 2H), 2.59 (t, 2H), 2.18 (s, 3H), 1.84 (quintet, 2H).

(e) 6-hydroxy-2-hexanone (400 MHz; $CDCl_3$) δ(ppm): 3.64 (t, 2H), 2.49 (t, 2H), 2.15 (s, 3H), 1.70-1.52 (m, 4H).

(f) acetophenone (400 MHz; $CDCl_3$) δ(ppm): 7.95 (d, 2H), 7.55 (t, 1H), 7.45 (t, 2H), 2.59 (s, 3H).

(g) cyclohexyl methyl ketone (400 MHz; $CDCl_3$) δ(ppm): 2.37-2.28 (m, 1H), 2.13 (s, 3H), 1.91-1.84 (m, 2H), 1.81-1.73 (m, 2H), 1.70-1.63 (m, 1H), 1.39-1.13 (m, 5H).

(h) 2-methyl-benzofuran (400 MHz; $CDCl_3$) δ(ppm): 7.49-7.44 (m, 1H), 7.42-7.37 (m, 1H), 7.20-7.15 (m, 2H), 6.36 (quintet, 1H), 2.45 (d, 3H).