Supporting Information for

Reduction of Rhodium(III) Porphyrin Hydroxide to Rhodium(II) Porphyrin

Kwong Shing Choi, Tsz Ho Lai, Siu Yin Lee, and Kin Shing Chan*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong,
People’s Republic of China

E-mail: ksc@cuhk.edu.hk

Contents
1. Optimization of Base-Promoted Reduction of Rh\textsuperscript{III}(ttp)Cl
2. Reaction between [Rh\textsuperscript{II}(ttp)]\textsubscript{2} and H\textsubscript{2}O\textsubscript{2(aq)}
3. Reduction of Rh(ttp)I by KOH with PPh\textsubscript{3} as H\textsubscript{2}O\textsubscript{2} trap
4. Experimental Section
5. \textsuperscript{1}H NMR spectra and high-resolution mass spectra
6. Reference
1. Optimization of Base-Promoted Reduction of Rh$^{III}$(ttp)Cl

Table S1. Optimization of Base-Promoted Reduction of Rh$^{III}$(ttp)Cl 1a

<table>
<thead>
<tr>
<th>entry</th>
<th>base (10 equiv)</th>
<th>time</th>
<th>yield of 2a /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>3 d</td>
<td>none*</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$O$^b$</td>
<td>3 d</td>
<td>none*</td>
</tr>
<tr>
<td>3</td>
<td>K$_2$CO$_3$</td>
<td>6.5 h</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>KOH</td>
<td>0.5 h</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>NaOH</td>
<td>0.5 h</td>
<td>68</td>
</tr>
</tbody>
</table>

* Rh(ttp)Cl recovered quantitatively. $^b$ 100 equiv.

Rh$^{III}$(ttp)Cl was found to be stable in benzene-$d_6$ at 120 °C for 3 d with and without H$_2$O (100 equiv) (Table S1, entries 1 and 2, eq S1). Upon the addition of K$_2$CO$_3$ (10 equiv) to Rh$^{III}$(ttp)Cl in benzene-$d_6$ at 120 °C in 6.5 h, [Rh$^{II}$(ttp)]$_2$ 2a was formed in 68% yield (Table S1, entry 3). The reaction time was decreased to 0.5 h when KOH (10 equiv) was used and 2a was formed in 66% yield (Table S1, entry 4). Besides, 1a reacted with NaOH (10 equiv) at 120 °C in 0.5 h to give 2a in a similar yield of 68% (Table S1, entry 5).
2. Reactions between [Rh\textsuperscript{II}(ttp)]\textsubscript{2} 2a and H\textsubscript{2}O\textsubscript{2(aq)}

A. Reaction between [Rh\textsuperscript{II}(ttp)]\textsubscript{2} 2a and excess H\textsubscript{2}O\textsubscript{2(aq)} (10 equiv)

[Rh\textsuperscript{II}(ttp)]\textsubscript{2} 2a reacted with excess H\textsubscript{2}O\textsubscript{2(aq)} (10 equiv) in benzene-\textit{d}_6 at r.t. in 5 minutes to give unidentified decomposition products which likely formed from porphyrin ring oxidation (eq S2, Figure S1).

\[
\begin{align*}
[\text{Rh}^{\text{II}}(\text{ttp})]_2 + \text{H}_2\text{O}_2 & \xrightarrow{\text{5 min, r.t}} \text{decomposed} \\
2\text{a} & \text{ (10 equiv)} & \text{benzene-\textit{d}_6}
\end{align*}
\]

(B) \( t = 5 \text{ min} \)

Unidentified products (H\textsubscript{2}O\textsubscript{2 caused the decomposition of [Rh\textsuperscript{II}(ttp)]\textsubscript{2})

(A) \( t = 0 \text{ h} \)

\begin{align*}
2\text{a}_{\text{Ph}} & \quad 2\text{a}_{\text{pyr}} & \quad 2\text{a}_{\text{Ph}}
\end{align*}

\( \text{ppm (T)} \)

\( 9.50 - 9.00 \quad 8.50 - 8.00 \quad 7.50 \)

\textbf{Figure S1.} \textsuperscript{1}H NMR (400 MHz) spectra in benzene-\textit{d}_6. (A) [Rh\textsuperscript{II}(ttp)]\textsubscript{2} 2a; (B) Unidentified products from the reaction mixture at r.t. for 5 min, where pyr and Ph designated the pyrrole and phenyl hydrogens, respectively, in species 2a.
B. Reaction between [Rh$^{II}$](ttp)$_2$ 2a and H$_2$O$_2$(aq) (1 equiv)

\[
[Rh^{II}(ttp)]_2 + H_2O_2(aq) \xrightarrow{1 \text{ h}, \text{ r.t.}} [Rh^{II}(ttp)]_2 + H_2O \quad (S3)
\]

Unidentified products (H$_2$O$_2$ caused the decomposition of [Rh$^{II}$(ttp)$_2$]$_2$

\[
(C) \ t = 1 \text{ h (at } 120^\circ \text{C}) \quad 2a_{pyr} \quad 2a_{Ph}
\]

\[
(B) \ t = 1 \text{ h (at r.t.)} \quad 4_{pyr} \quad 4_{Ph} \quad 4_{Ph}
\]

\[
(A) \ t = 0 \text{ h} \quad 2a_{pyr} \quad 2a_{Ph}
\]

Figure S2. $^1$H NMR (400 MHz) spectra in benzene-$d_6$. (A) [Rh$^{II}$(ttp)$_2$] 2a; (B) Rh$^{III}$(ttp)OH 4 from reaction mixture at r.t for 1 h; (C) [Rh$^{II}$(ttp)$_2$] 2a from reaction mixture at 120 °C for 1 h, where pyr and Ph designated the pyrrole and phenyl hydrogens, respectively, in species 2a and 4.

For the reaction between [Rh$^{II}$(ttp)$_2$] 2a and H$_2$O$_2$ (1 equiv) (eq S3), no (ttp)Rh$^{III}$-O-Rh$^{III}$(ttp) 3 was obtained. Since the reaction contained plenty of water (commercial available H$_2$O$_2$ is 35% aqueous solution, which was used in this experiment), (ttp)Rh$^{III}$-O-Rh$^{III}$(ttp) 3 was likely hydrolyzed to regenerate Rh$^{III}$(ttp)OH (eq S4).

\[
(ttp)Rh^{III}$-O-Rh$^{III}$(ttp) + H$_2$O \xrightarrow{} 2Rh^{III}$(ttp)OH \quad (S4)
3a. Reduction of Rh(ttp)I by KOH with PPh3 as H₂O₂ trap

\[
\text{Rh(ttp)I} + \text{KOH (10 equiv)} \xrightarrow{\text{PPh₃ (1 equiv)}} \text{O=PPPh₃} \quad \text{(S6)}
\]

\[\text{O=PPPh₃ generated from the reaction of PPh₃ with H₂O₂}\]

\[\text{(B) } t = 4 \text{ d (at 60} ^\circ \text{C)}\]

\[\text{(A) } t = 0 \text{ h}\]

\[\text{ppm (δ)}\]

**Figure S3.** ¹H NMR (400 MHz) spectra in benzene-\(d_₆\). (A) Rh(ttp)I 1c; (B) O=PPPh₃ from reaction mixture at 60 °C for 4 d, where pyr and Ph designated the pyrrole and phenyl hydrogens, respectively, in species 1c.
4. Experimental Section

Unless otherwise noted, all reagents were purchased from commercial suppliers and directly used without further purification. $^1$H NMR was recorded on a Bruker AV-400 at 400MHz. Chemical shifts were referenced with the residual solvent protons in C$_6$D$_6$ ($\delta = 7.15$ ppm), and CD$_3$OD (3.31 ppm) as the internal standard. Chemical shifts ($\delta$) were reported as part per million (ppm) in ($\delta$) scale downfield from TMS.

Coupling constants ($J$) were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a ThermoFinnigan MAT 95 XL mass spectrometer. Fast atom bombardment spectra were performed with 3-nitrobenzyl alcohol (NBA) as the matrix.

Unless otherwise stated, all thermal reactions conducted in sealed NMR tube were protected from light by wrapping with aluminum foil and were heated in a GC instrument. The yields of rhodium porphyrin complexes in all reactions were NMR yields estimated by the integrals of $^1$H NMR spectra with benzene residue as the internal standard. The yields of rhodium porphyrin complexes were calculated based on the number of mole of rhodium porphyrin contained.

The synthesis of Rh$^{III}$[ttp]Cl$_1$, [Rh$^{III}$[ttp]]$_2$, and Rh$^{III}$[tmp]I$^3$ were followed by literature methods.

**General Procedure for Reactions of Rh$^{III}$[ttp]Cl 1a with base in benzene-$d_6$.** A stock solution of Rh$^{III}$[ttp]Cl 1a in benzene-$d_6$ (3 mL, 0.00165 M, 4.95 mmol) was prepared. The solutions were degassed for five freeze-thaw-pump cycles and stored under N$_2$. H$_2$O was degassed for five freeze-thaw-pump cycles and stored under N$_2$. Stock solutions of K$_2$CO$_3$ (1.0 mL, 0.0825 M, 82.5 mmol), KOH (1.0 mL, 0.0825 M, 82.5 mmol), and NaOH (1.0 mL, 0.0825 M, 82.5 mmol) in water were prepared and degassed for five freeze-thaw-pump cycles and stored under N$_2$ respectively.

**A. Reaction of Rh$^{III}$[ttp]Cl 1 in neat benzene-$d_6$.** The Rh$^{III}$[ttp]Cl 1a stock solution (0.5 mL, 0.00165 M, 0.825 mmol) was transferred to a Teflon screw capped NMR tube under N$_2$ and degassed for five freeze-thaw-pump cycles, then flame-sealed under vacuum. The reaction mixture was heated at 120 °C. No reaction occurred after 3 days.
B. Reaction of Rh\textsuperscript{III}(ttp)Cl \textit{1a} with H\textsubscript{2}O (100 equiv). The Rh\textsuperscript{III}(ttp)Cl \textit{1a} stock solution (0.5 mL, 0.00165 M, 0.825 mmol) and degassed H\textsubscript{2}O (1.50 \mu L, 82.5 mmol) were transferred to a Teflon screw capped NMR tube under N\textsubscript{2}. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was heated at 120 °C. No reaction occurred after 3 days.

C. Reaction Rh\textsuperscript{III}(ttp)Cl \textit{1a} with of K\textsubscript{2}CO\textsubscript{3} (10 equiv). The K\textsubscript{2}CO\textsubscript{3} stock solution (0.1 mL, 0.0825 M, 8.25 mmol) was transferred to a Teflon screw capped NMR tube under N\textsubscript{2} and most water was removed by vacuum pump (10\textsuperscript{-3} torr) for 3 h. The Rh\textsuperscript{III}(ttp)Cl \textit{1a} stock solution (0.5 mL, 0.00165 M, 0.825 mmol) was transferred to the NMR tube under N\textsubscript{2}. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was heated at 120 °C for 6.5 h, [Rh\textsuperscript{II}(ttp)]\textsubscript{2} \textit{2a} (68%, NMR yield) was formed. \textsuperscript{6}\textsuperscript{1}\textsuperscript{H} NMR of [Rh\textsuperscript{II}(ttp)]\textsubscript{2} \textit{2a}: (C\textsubscript{6}D\textsubscript{6}, 400 MHz) δ 2.50 (s, 12 H), 7.15 (m-phenyl H are obscured by solvent), 7.75 (d, 4 o-phenyl H, J = 7.2 Hz.), 8.64 (s, 8 H), 9.65 (d, 4 o-phenyl H, J = 7.2 Hz).

D. Reaction Rh\textsuperscript{III}(ttp)Cl \textit{1a} with KOH (10 equiv). The KOH stock solution (0.1 mL, 0.0825 M, 8.25 mmol) was transferred to a Teflon screw capped NMR tube under N\textsubscript{2} and most water was removed by vacuum pump (10\textsuperscript{-3} torr) for 3 h. The Rh\textsuperscript{III}(ttp)Cl \textit{1a} stock solution (0.5 mL, 0.00165 M, 0.825 mmol) was transferred to the NMR tube under N\textsubscript{2}. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was heated at 120 °C for 0.5 h, [Rh\textsuperscript{II}(ttp)]\textsubscript{2} \textit{2a} (66%, NMR yield) was formed. \textsuperscript{3}

The precipitate formed in the reaction D was filtered and it was only sparingly soluble in degassed CD\textsubscript{3}OD. \textsuperscript{1}\textsuperscript{H} NMR of (ttp)\textsuperscript{III}Rh-O-Rh\textsuperscript{III}(ttp) \textit{3}: (CD\textsubscript{3}OD, 400 MHz) δ 2.72 (s, 24 H), 7.61 (d, J = 8.0 Hz, 16 H), 8.12 (d, J = 7.2 Hz, 16 H), 8.90 (s, 16 H). HRMS: Calcd for (C\textsubscript{96}H\textsubscript{72}N\textsubscript{8}Rh\textsubscript{2}O): m/z 1559.3967. Found: m/z 1559.3997. In addition, (ttp)\textsuperscript{III}Rh-O-Rh\textsuperscript{III}(ttp) \textit{3} was air-sensitive and decomposed within 1 h upon exposure to air.

The reaction D was scaled up. Rh\textsuperscript{III}(ttp)Cl \textit{1a} (10 mg, 0.012 mmol) and KOH (7.0 mg, 0.12 mmol)
was added to benzene-$d_6$ (2 mL). The reaction mixture was degassed for five freeze-thaw-pump cycles in a teflon stopper tube and then was heated at 120 °C in an oil bath for 0.5 h. Excess solvent was filtered off, (tp)$_3^{iii}$Rh-O-Rh$_{iii}^{iii}$(ttp) 3 (3 mg, 0.00192 mmol, 16%) was formed.

E. Reaction Rh$_{iii}^{iii}$(ttp)Cl 1a with NaOH (10 equiv). The NaOH stock solution (0.1 mL, 0.0825 M, 8.25 mmol) was transferred to a Telfon screw capped NMR tube under N$_2$ and most water was removed by vacuum pump (10$^{-3}$ torr) for 3 h. The Rh$_{iii}^{iii}$(ttp)Cl 1a stock solution (0.5 mL, 0.00165 M, 0.825 mmol) was transferred to the NMR tube under N$_2$. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was heated at 120 °C for 0.5 h, [Rh$_{ii}^{ii}$(ttp)]$_2$ 2a (68%, NMR yield) was formed.3

General Procedure for Reactions of Rh(tp$_{OMe}$p)I 2b, Rh(ttp)I 2a and Rh(tpp)I 2c with KOH

A stock solution of Rh(tp$_{OMe}$p)I 1b, Rh(ttp)I 1c and Rh(tpp)I 1d in benzene-$d_6$ (2.0 mL, 0.00165 M, 0.0033 mmol) were prepared and degassed for five freeze-thaw-pump cycles and stored under N$_2$, respectively

A. Reaction of Rh(tp$_{OMe}$p)I 1b with KOH. The KOH stock solution (100 µL, 0.0825 M, 0.00825 mmol) was transferred to a Telfon screw capped NMR tube under N$_2$ and most water was removed by vacuum pump (10$^{-3}$ torr) for 3 h. The Rh(tp$_{OMe}$p)I stock solution (500 µL, 0.00165 M, 0.000825 mmol) was transferred to the NMR tube under N$_2$. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was heated at 80 °C for 7 h, [Rh$_{ii}^{ii}$(tp$_{OMe}$p)]$_2$ 2b (68%, NMR yield) was formed.3 $^1$H NMR of [Rh$_{ii}^{ii}$(tp$_{OMe}$p)]$_2$: (C$_6$D$_6$, 400 MHz) δ 3.60 (s, 12 H), 7.15 (m-phenyl H are obscured by solvent), 7.59 (d, 4 H, $J = 7.4$ Hz), 8.69 (s, 8 H), 9.70 (d, 4 H, $J = 7.8$ Hz).

Reaction of Rh(ttp)I 1c with KOH. The KOH stock solution (100 µL, 0.0825 M, 0.00825 mmol) was transferred to a Telfon screw capped NMR tube under N$_2$ and most water was removed by vacuum pump (10$^{-3}$ torr) for 3 h. The Rh(ttp)I stock solution (500 µL, 0.00165 M, 0.000825 mmol) was transferred to the NMR tube under N$_2$. The reaction mixture was degassed for five freeze-thaw-pump
cycles and then flame-sealed under vacuum. The reaction mixture was heated at 80 °C for 1.5 h, 
[Rh^{II}\,(tpp)]_2\,2a \,(72\%, \text{NMR yield}) \text{ was formed.}^4

**C. Reaction of Rh(tpp)I 1c with KOH.** The KOH stock solution (100 \,\mu L, 0.0825 M, 0.00825 mmol) was transferred to a Teflon screw capped NMR tube under N$_2$ and most water was removed by vacuum pump (10$^{-3}$ torr) for 3 h. The Rh(tpp)I stock solution (500 \,\mu L, 0.00165 M, 0.000825 mmol) was transferred to the NMR tube under N$_2$. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was heated at 80 °C for 0.5 h, 
[Rh^{II}\,(tpp)]_2\,2c \,(82\%, \text{NMR yield}) \text{ was formed.}^{21} \text{H NMR of } [\text{Rh}^{III}\,(tpp)]_2\,2c: \,\text{C$_6$D$_6$,} \,400 \text{ MHz} \,\delta \,7.10 \,(d, \,4 \text{ H, } J = 6.6 \text{ Hz}), \,7.23 \,(t, \,4 \text{ H, } J = 6.9 \text{ Hz}), \,7.58 \,(t, \,4 \text{ H, } J = 6.1 \text{ Hz}), \,7.93 \,(t, \,4 \text{ H, } J = 6.7 \text{ Hz}), \,8.49 \,(s, \,8 \text{ H}), \,9.66 \,(d, \,4 \text{ H, } J = 6.5 \text{ Hz}).

**General Procedure for Reactions between [Rh^{III}\,(tpp)]_2\,2a \text{ and } H_2O_{2(aq)}** The stock solution of [Rh^{III}\,(tpp)]_2\,2a \text{ in benzene-$d_6$} \,(2\,mL, \,0.00619 M, \,0.0124 mmol) and two stock solutions of different concentration of H$_2$O$_2$ in D$_2$O (1mL, 3.10 M, 3.10 mol and 1 mL, 0.310 M, 0.310 mol) were prepared. Those solutions were degassed for five freeze-thaw-pump cycles and stored under N$_2$.

**A. Reaction between [Rh(tpp)]_2\,2a \text{ and } H_2O_{2(aq)} \,(10 \text{ equiv).}** The [Rh^{III}\,(tpp)]_2\,2a \text{ stock solution (0.5 mL, 0.00619 M, 3.10 mmol) and the } H_2O_2 \text{ stock solution (10 } \mu L, \,3.10 \text{ M, 31.0 mmol) were transferred to a Teflon screw capped NMR tube under N$_2$. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was left at r.t. for 0.5 min, 
[Rh^{III}\,(tpp)]_2\,2a \text{ was completely decomposed.}

**B. Reaction between [Rh^{III}\,(tpp)]_2\,2a \text{ and } H_2O_{2(aq)} \,(1 \text{ equiv).}** The [Rh^{III}\,(tpp)]_2\,2a \text{ stock solution (0.5 mL, 0.00619 M, 3.10 mmol) and the } H_2O_2 \text{ stock solution (10 } \mu L, \,0.310 \text{ M, 0.310 mmol) were transferred to a Teflon screw capped NMR tube under N$_2$. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was left at r.t. After 1 h, Rh^{III}\,(tpp)OH \,4 \,(55\%, \text{NMR yield}) \text{ was formed. HRMS: Calcd for (C}_{48}H_{37}O_{12}N_{4}Rh)^+: m/z
1H NMR of Rh^{III}(ttp)OH 4: (C_{6}D_{6}, 400 MHz) δ 2.40 (s, 12 H), 8.02 (d, \( J = 7.4 \) Hz, 8 H), 8.24 (d, \( J = 7.2 \) Hz, 8 H), 9.25 (s, 8 H). The Rh^{III}(ttp)O-H signal is not observed in 1H NMR spectrum, likely due to the rapid exchange with residual water in solvent. The same reaction mixture was then heated at 120 °C for 0.5 h, [Rh^{II}(ttp)] 2a (30%, NMR yield) was formed.

**Reaction Rh^{III}(ttp)I with KOH in the presence of 1 equiv of PPh₃.** The KOH stock solution (100 µL, 0.334 M, 0.0334 mmol) was transferred to a Teflon screw capped NMR tube under N₂ and most water was removed by vacuum pump (10⁻³ torr) for 3 h. Rh^{III}(ttp)I (3.0 mg, 0.0033 mmol) and PPh₃ (0.9 mg, 0.0034 mmol) were then added. Degassed benzene-d₆ (0.50 mL) were then added under N₂. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum. The reaction mixture was left at 60°C for 4 d, Ph₃PO (43%, NMR yield) was formed.

**Reaction Rh^{III}(tmp)I 5 with KOH (10 equiv) at 120 °C.** A stock solution of Rh^{III}(tmp)I 5 in benzene-d₆ (3.0 mL, 0.00165 M, 4.95 mmol) and KOH (1.0 mL, 0.0825 M, 82.5 mmol) in water were prepared and degassed for five freeze-thaw-pump cycles and stored under N₂ respectively.

A KOH stock solution (0.1 mL, 0.0825 M, 8.25 mmol) were transferred to a Teflon screw capped NMR tube under N₂ and most water was removed by vacuum pump (10⁻³ torr) for 3 h. The Rh^{III}(tmp)I 5 stock solution (0.5 mL, 0.00165 M, 0.825 mmol) was transferred to the NMR tube under N₂. The reaction mixture was degassed for five freeze-thaw-pump cycles and then flame-sealed under vacuum.

The reaction mixture was heated at 120 °C for 2 h, Rh^{II}(tmp) 6 (52%, NMR yield) and (tmp)Rh^{III}-OO-Rh^{III}(tmp) 7 (5%, NMR yield) were formed. 3.5 1H NMR of Rh^{II}(tmp) 6 (C₆D₆, 400 MHz) δ 3.55 (bs, 24 H), 3.50 (s, 12 H), 8.87 (br s, 8 H), 18.2 (br s, 8 H). 1H NMR of (tmp)Rh^{III}-OO-Rh^{III}(tmp) 7 (C₆D₆, 400 MHz) 6.93 (s, 8 H), 7.22 (s, 8 H), 8.23 (s, 16 H), mesityl H are obscured by Rh^{II}(tmp) H (δ 3.60).

**5. 1H NMR spectra and high-resolution mass spectra**

1H NMR (CD₃OD, 400 MHz ) of (ttp)^{III}Rh-O-Rh^{III}(ttp) 3
Reference


S11