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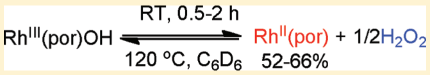
Reduction of Rhodium(III) Porphyrin Hydroxide to Rhodium(II) Porphyrin

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

Supporting Information

ABSTRACT: Highly reactive rhodium(III) porphyrin hydroxides were formed from the ligand substitution of rhodium porphyrin halides in benzene and were rapidly reduced to rhodium(II) porphyrins and hydrogen peroxide. Thus hydroxide acted as the reducing agent. Oxidative addition of rhodium(II) porphyrin with hydrogen peroxide proceeded rapidly at room temperature to give back rhodium(III) porphyrin hydroxides. Rhodium(II) porphyrins and H_2O_2 therefore were thermally reversible with rhodium porphyrin hydroxides.

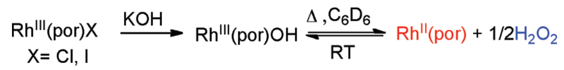


The chemistry of late transition metal hydroxides has generated much interest because of the mismatch of hard ligand and soft metal.[1] Late transition metal hydroxides have rich chemistry.[1c,2−4] Bergman and co-workers have reported that iridium(III) hydroxide complexes exhibit high chemical reactivity in metathesis reaction with alcohol[2] and insertion of alkenes.[2] Furthermore, Periana and Goldberg found the carbon−hydrogen bond activation of benzene by iridium(III) hydroxide and rhodium(I) hydroxide complexes, respectively.[3,4] Recently, Milstein et al. published that a dihydroxo ruthenium(II) pincer complex, generated from the reaction with water, liberated O_2 upon irradiation and is a promising catalyst for water splitting.[5]

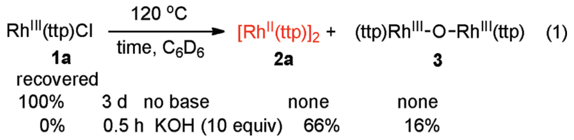
Late transition metal hydroxides with supporting porphyrin (por) ligands are less reported and bear unique chemistry. Wayland and co-workers discovered that the hydrophilic $[Rh^{III}(tspp)OH(H_2O)]^{4-}$ (tspp = tetrasulfonatophenylporphyrinato dianion) can be generated from the reaction between $[Rh^{II}(tspp)(H_2O)]_2^{8-}$ and H_2O.[6] These hydrophilic metalloporphyrin hydroxides also show high chemical reactivity in olefin insertion.[7] Recently, Wayland et al. have estimated the bond dissociation bond energy of a Rh(por)−OMe bond, which turns out to be fairly low (~46 kcal/mol at 298 K).[8] This weak Rh−OMe bond provides a thermodynamic basis to understand and predict the high reactivity of this and related species.

Our previous work on the base-promoted carbon−hydrogen bond activation[9] and carbon−carbon bond activation[10] by rhodium(III) porphyrin halides has prompted us to synthesize rhodium(III) porphyrin hydroxides from the reaction of rhodium(III) porphyrin halides with hydroxide by ligand substitution in order to examine its intrinsic and bond activation chemistry. We now report the synthesis of Rh^{III}(por)OH and the reduction to Rh^{II}(por) as a dimer or monomer depending on the sterics of porphyrin and H_2O_2 as well as the converse formal oxidative addition of rhodium(II) porphyrin with H_2O_2 (Scheme 1).

Scheme 1



Rh^{III}(ttp)Cl **1a** (ttp = tetratolylporphyrinato dianion) was thermally stable in benzene-d_6 at 120 °C for 3 d, but reacted smoothly in the presence of KOH (10 equiv) in benzene-d_6 at 120 °C in 0.5 h to give $[Rh^{II}(ttp)]_2$ **2a** in 66% yield (eq 1).[12] KOH has promoted the reduction of **1a** to **2a**. In addition, 16% yield of the μ-oxo dimer, (ttp)Rh^{III}-O-Rh^{III}(ttp) **3**, which likely forms from the competitive self-condensation of Rh^{III}(ttp)OH **4**, was also obtained (eq 1).[13] We thus proposed that the ligand substitution of Rh^{III}(ttp)Cl with hydroxide ion occurs to yield the highly reactive Rh^{III}(ttp)OH intermediate (Scheme 1).[13,14] As no phenol and biphenyl were detected in the reaction mixture by GC-MS analysis, benzene is not the reducing agent in the conversion of Rh^{III}(ttp)OH to $[Rh^{II}(ttp)]_2$. We suggest that hydroxide ion is the reducing agent. Hydroxide ion can donate one electron to the Rh^{III} center to yield Rh^{II} and itself is oxidized to a hydroxyl radical.[14] This type of reduction has been reported in the first-row transition metal porphyrin hydroxides of manganese, iron, and cobalt.[14]



The reduction is general for various rhodium tetrakis-4-substituted phenyl porphyrin iodides (Table 1, eq 2). Rh(ttp)I **1c** was reduced in a longer time of 1.5 h than Rh(ttp)Cl but gave a higher yield of 72% (Table 1, entry 2). The reduction rate increases with more electron-deficient porphyrins and is in the order H > Me > MeO-substituted porphyrin (Table 1, entries 1−3). The rhodium dimer yields are all high but in the opposite substituent order.

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Table 1. Reduction of Rhodium(III) Porphyrin Iodide

$$\mathrm{Rh^{III}(por)I} \xrightarrow[80\ ^{\circ}\mathrm{C},\ \mathrm{C_6D_6}]{\mathrm{KOH\ (10\ equiv)}} \mathrm{[Rh^{II}(por)]_2} \qquad (2)$$

entry	por	time (h)	yield of $[Rh^{II}(por)]_2$ /%
1	$tp_{OMe}p$ **1b**	7	**2b** 68%
2	ttp **1c**	1.5	**2a** 72%
3	tpp **1d**	0.5	**2c** 82%

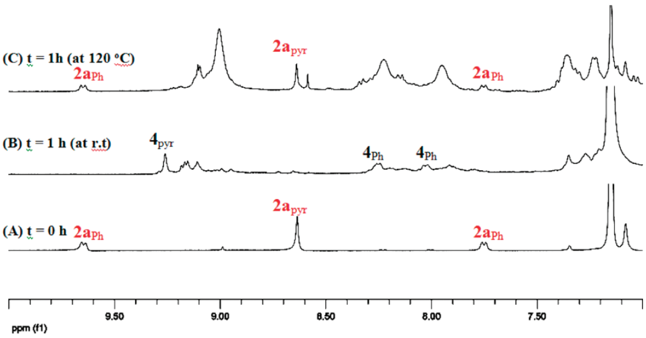

Figure 1. ^1H NMR (400 MHz) spectra in benzene-d_6. (A) $[Rh^{II}(ttp)]_2$ **2a**; (B) $Rh^{III}(ttp)OH$ **4** from reaction mixture at rt for 1 h; (C) $[Rh^{II}(ttp)]_2$ **2a** from reaction mixture at 120 °C for 1 h, where pyr and Ph designate the pyrrole and phenyl hydrogens, respectively, in species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

To gain further understanding of the chemistry of Rh(por)OH, we then attempted to synthesize the highly reactive $Rh^{III}(por)OH$ independently by oxidative addition with H_2O_2, analogous to the reaction of pentacyanocobalt(II) with H_2O_2 to give pentacyanocobalt(III) hydroxide.[15] $[Rh^{II}(ttp)]_2$ was thus treated with a stoichiometric amount of $H_2O_{2(aq)}$[16] in benzene-d_6 at rt in 1 h (eq 3, Figure 1A,B). A new rhodium porphyrin species formed and only exhibits porphyrin resonances without any axial ligand signal in its ^1H NMR spectrum. The high-resolution mass spectrum shows the molecular ion at *m*/*z* 788.1997[17] and is assigned to be $Rh^{III}(ttp)OH$.[13] However, the absence of a $Rh^{III}(ttp)O-H$ ^1H NMR signal is likely due to the rapid exchange with residual water in solvent. To demonstrate that $Rh^{III}(ttp)OH$ is indeed an intermediate for the formation of $[Rh^{II}(ttp)]_2$ via reduction, this reaction mixture was heated at 120 °C. To our delight, $Rh^{III}(ttp)OH$ was reduced to $[Rh^{II}(ttp)]_2$ in 30% yield in 0.5 h (eq 3, Figure 1C), which indirectly supports the formation of H_2O_2 coproduct. Furthermore, eq 3 is reversible, its equilibrium constant is hard to measure due to the rapid base-catalyzed disproportionation of H_2O_2 to O_2 and H_2O.[18]

$$\underset{\mathbf{2a}}{\mathrm{[Rh^{II}(ttp)]_2}} + \underset{(1\ \mathrm{equiv})}{\mathrm{H_2O_{2(aq)}}} \xrightarrow[\mathrm{C_6D_6}]{1\ \mathrm{h,\ r.t}} \underset{\mathbf{4}\ (55\%)}{\mathrm{2Rh^{III}(ttp)OH}} \xrightarrow[\mathrm{C_6D_6}]{1\ \mathrm{h,\ 120\ ^{\circ}C}} \underset{\mathbf{2a}\ (30\%)}{\mathrm{[Rh^{II}(ttp)]_2}} + \mathrm{H_2O_2} \qquad (3)$$

The indirect detection of H_2O_2 coproduct was further conducted by carrying out the reduction of Rh(ttp)I with KOH in the presence of Ph_3P (1 equiv) as a H_2O_2 trap. To our delight, Ph_3PO was observed in 43% yield by ^1H NMR spectroscopy. The $[Rh^{II}(ttp)]_2$ yield, however, could not be determined, as it is unstable in the presence of a strong ligand via ligand-induced disproportionation.[19]

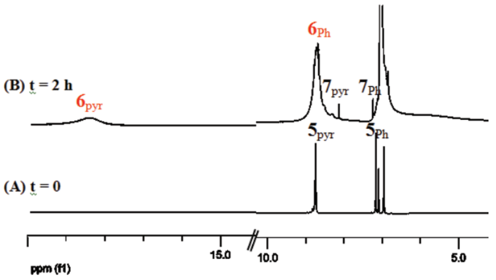

Figure 2. ^1H NMR (400 MHz) spectra in benzene-d_6. (A) $Rh^{III}(tmp)I$ **5**; (B) reaction mixture of $Rh^{II}(tmp)$ **6** and $(tmp)Rh^{III}$-OO-$Rh^{III}(tmp)$ **7**, where pyr and Ph designate the pyrrole and phenyl hydrogens, respectively, in species **5**, **6**, and **7**.

To eliminate the formation of the $Rh^{III}(por)$ μ-oxo complex, reduction of the sterically hindered $Rh^{III}(tmp)I$ (tmp = tetramesitylporphyrinato dianion) was examined.[20] Similarly, $Rh^{III}(tmp)I$ **5** was reduced by KOH (10 equiv) in benzene-d_6 at 120 °C in 2 h to give $Rh^{II}(tmp)$ **6** ($\delta_{pyrrole}$= 18.2 ppm) in 52% yield, and the reported $(tmp)Rh^{III}$-OO-$Rh^{III}(tmp)$ **7** ($\delta_{pyrrole}$= 8.23 ppm) was also observed in 5% yield (eq 4, Figure 2).[20] $(tmp)Rh^{III}$-OO-$Rh^{III}(tmp)$ likely forms from the secondary insertion reaction of **6** with O_2[20] formed by the H_2O_2 disproportionation.[18] Therefore, the formation of $(tmp)Rh^{III}$-OO-$Rh^{III}(tmp)$ supports the generation of H_2O_2, which also undergoes catalyzed disproportionation into O_2 and H_2O.[18]

$$\underset{\mathbf{5}}{\mathrm{Rh^{III}(tmp)I}} \xrightarrow[120\ ^{\circ}\mathrm{C},\ 2\ \mathrm{h},\ \mathrm{C_6D_6}]{\mathrm{KOH\ (10\ equiv)}} \underset{\mathbf{6}\ (52\%)}{\mathrm{Rh^{II}(tmp)}} + \underset{\mathbf{7}\ (5\%)}{\mathrm{(tmp)Rh^{III}\text{-}OO\text{-}Rh^{III}(tmp)}} \qquad (4)$$

In summary, we have reported the reduction of $Rh^{III}(por)$ halides by OH^- to $Rh^{II}(por)$. Further studies are ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental information, compound characterization, and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ksc@cuhk.edu.hk.

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