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Reactivity and Equilibrium Thermodynamic Studies of Rhodium Tetrakis(3,5-disulfonatomesityl)porphyrin Species with H_2, CO, and Olefins in Water

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Aqueous (D_2O) solutions of tetrakis(3,5-disulfonatomesityl)porphyrin rhodium(III) aquo/hydroxo complexes ($[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ (**1**), $[(TMPS)Rh^{III}(OD)(D_2O)]^{-8}$ (**2**), and $[(TMPS)Rh^{III}(OD)_2]^{-9}$ (**3**)) react with hydrogen (D_2) to form an equilibrium distribution with a rhodium hydride ($[(TMPS)Rh–D(D_2O)]^{-8}$ (**4**)) and a rhodium(I) complex ($[(TMPS)Rh^{I}(D_2O)]^{-9}$ (**5**)). Equilibrium constants (298 K) are measured that define the distribution for all five of these (TMPS)Rh species in this system as a function of the dihydrogen (D_2) and hydrogen ion (D^+) concentrations. The hydride complex $[(TMPS)Rh–D(D_2O)]^{-8}$ is a weak acid in D_2O ($K_a(298\ K) = 4.3 \times 10^{-8}$). Steric demands of the TMPS porphyrin ligand prohibit formation of a Rh(II)–Rh(II)-bonded complex, related rhodium(I)–rhodium(III) adducts, and intermolecular association of alkyl complexes which are prominent features of the rhodium tetra(*p*-sulfonatophenyl)porphyrin ((TSPP)Rh) system. The rhodium(II) complex ($[(TMPS)Rh^{II}(D_2O)]^{-8}$) reacts with water to form hydride and hydroxide complexes and is not observed in D_2O. The (TMPS)Rh–OD and (TMPS)Rh–D bond dissociation free energies (BDFE) are virtually equal and have a value of approximately 60 kcal mol^{-1}. Reactions of $[(TMPS)Rh–D(D_2O)]^{-8}$ in water with CO and olefins produce rhodium formyl and alkyl complexes which have equilibrium thermodynamic values comparable to the values for the corresponding substrate reactions of $[(TSPP)Rh–D(D_2O)]^{-4}$.

Introduction

Organometallic transformations in water[1−10] and catalytic processes in aqueous media[11−14] are major contemporary areas of transition metal catalysis research. Our immediate primary objectives in this area are to evaluate the reactivity patterns of metalloporphyrins in water and to identify the dominant energy terms that differentiate substrate reaction behavior in organic and aqueous media.[7−10] Prior papers in this series have described reactions of tetra(*p*-sulfonatophenyl)porphyrin rhodium ((TSPP)Rh) complexes in water with H_2/D_2, D_2O, CO, aldehydes, and olefins that form hydride, hydroxide, formyl, α- and β-hydroxyalkyl, and alkyl complexes.[7−10] Equilibrium thermodynamic studies for this wide range of (TSPP)Rh substrate reactions in water provide one of the most comprehensive sets of thermodynamic measurements for organometallic reactions.[8−10] The (TSPP)-rhodium(II) complex ($[(TSPP)Rh^{II}(D_2O)]^{-4}$) in water forms

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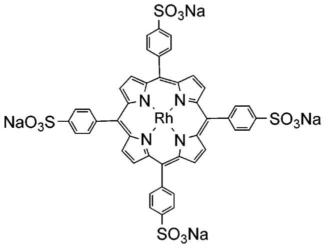
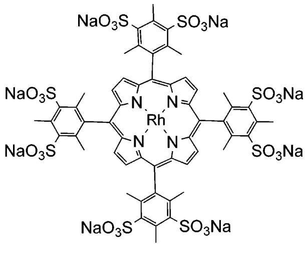
a $Rh^{II}-Rh^{II}$-bonded dimer $[(TSPP)Rh(D_2O)]_2^{-8}$; $[(TSPP)Rh^{I}(D_2O)]^{-5}$ forms metal−metal-bonded $Rh^{I}{:}Rh^{III}-X$ adducts with $(TSPP)Rh^{III}$ species, and the alkyl complexes ((TSPP)-Rh−R) have a marked tendency to form oligomers in solution. One of the objectives of this study is to evaluate whether the use of the larger steric demand tetrakis(3,5-disulfonatomesityl)porphyrin (TMPS) ligand will block oligomer formation and prohibit formation of $Rh^{II}-Rh^{II}$. This article reports on the aqueous solution reactivity patterns for the (TMPS)Rh system and thermodynamics for substrate reactions for comparison with results from the lower steric demand (TSPP)Rh system.[7−10]



(TSPP)Rh



(TMPS)Rh

Experimental Section

General Procedures. All manipulations were performed on a high-vacuum line equipped with a Welch Duo-Seal vacuum pump or in an inert atmosphere box unless otherwise noted. Substrates were degassed by freeze−pump−thaw cycles immediately before use. Reagent grade hydrogen and carbon monoxide were purchased from Matheson Gas Products and used without further purification.

^1H NMR spectra were obtained on a Bruker AC-360 spectrometer interfaced to an Aspect 300 computer at ambient temperature. Chemical shifts were referenced to 3-trimethylsilyl-1-propanesulfonic acid sodium salt. The pD measurements were performed with an Orion 9802 electrode connected to an Orion 410 pH meter. The pD values were derived by adding 0.451 to the meter readings. ($pD = pH_{reading} + 0.451$, (25 °C)).[15]

Syntheses of $(TMPS)Rh^{III}_{aq}$ ($[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ (1), $[(TMPS)Rh^{III}(OD)(D_2O)]^{-8}$ (2), $[(TMPS)Rh^{III}(OD)_2]^{-9}$ (3)), $[(TMPS)Rh-D(D_2O)]^{-8}$ (4), and $[(TMPS)Rh^{I}(D_2O)]^{-9}$ (5)). Tetramesitylporphyrin (TMP)[16] and its sulfonated derivative $Na_8(TMPS)H_2$[17] were synthesized by literature methods.

$(TMPS)Rh^{III}_{aq}$. A 15 mL methanol solution of $Na_8(TMPS)H_2$ (100 mg, 0.06 mmol) and $[RhCl(CO)_2]_2$ (14 mg, 0.04 mmol) was refluxed overnight. After the reaction was cooled to room temperature, two drops of 3% aqueous H_2O_2 solution was added to the reaction which oxidizes rhodium(I) to rhodium(III). After the reaction solution was stirred at room temperature for 10 min, the solvent was removed, and the product was purified on a silica gel column with methanol as the eluent. A greater than 90% isolated yield of $[Na_7(TMPS)Rh^{III}(L)_2]$ complex (L = coordinated methanol) was obtained. Dissolution in D_2O results in an equilibrium distribution of the bisaquo complex $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ (**1**), monohydroxo complex $[(TMPS)Rh^{III}(OD)(D_2O)]^{-8}$ (**2**), and bishydroxo complex $[(TMPS)Rh^{III}(OD)_2]^{-9}$ (**3**). ^1H NMR of $(TMPS)Rh^{III}_{aq}$ (360 MHz, neutral D_2O): δ 8.87 (s, 8 H, pyrrole), 3.19 (s, 12 H, *p*-methyl), 2.12 (s, 24 H, *m*-methyl).

$[(TMPS)Rh-D(D_2O)]^{-8}$ (4) and $[(TMPS)Rh^{I}(D_2O)]^{-9}$ (5). A 0.3 mL acidic D_2O solution of $(TMPS)Rh^{III}_{aq}$ (3×10^{-3} M, $[D^+] > 10^{-5}$ M) was put into a NMR tube with vacuum adaptor and treated with three freeze−pump−thaw cycles to remove the dissolved air. H_2/D_2 gas (300−500 Torr) was introduced into the NMR tube, and the tube was then flame-sealed. The reaction achieves equilibrium distributions of $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$, H_2/D_2, and $[(TMPS)Rh-D(D_2O)]^{-8}$ species within 2 months at 298 K. The equilibrium constant was evaluated from the intensity integrations of ^1H NMR signals for each species in combination with D^+ concentration measurement and the solubility data of H_2/D_2 in water.[18] A 0.3 mL basic D_2O solution of $(TMPS)Rh^{III}_{aq}$ (3×10^{-3} M, $[D^+] < 10^{-10}$ M) was pressurized with H_2/D_2 (300−500 Torr) using the same procedure. Complete conversion to $[(TMPS)Rh^{I}(D_2O)]^{-9}$ was achieved in 7 days at 298 K. ^1H NMR of $[(TMPS)Rh-D(D_2O)]^{-8}$ (**4**) (D_2O, 360 MHz): δ 8.57 (s, 8H, pyrrole), 3.16 (s, 12H, *p*-methyl), 2.13 (s, 24 H, *m*-methyl). ^1H NMR of $[(TMPS)Rh^{I}(D_2O)]^{-9}$ (**5**): δ 8.03 (s, 8H, pyrrole), 3.01 (s,12 H, *p*-methyl), 2.28 (s, 24 H, *m*-methyl).

Acid Dissociation Constant Measurements for $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ and $[(TMPS)Rh-D(D_2O)]^{-8}$ in Water. The method developed for determining the acid dissociation constants of $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$ and $[(TSPP)Rh-D(D_2O)]^{-4}$ complexes[8] was used to measure the acid dissociation constants of $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ and $[(TMPS)Rh-D(D_2O)]^{-8}$ in D_2O. The mole fraction averaged pyrrole proton resonance for the equilibrium distributions of **1**, **2**, and **3** as a function of the concentration of D^+ ($\delta_{1,2,3(obs)}(pyr) = (K_1K_2\delta_3(pyr) + K_1[D^+]\delta_2(pyr) + [D^+]^2\delta_1(pyr))/(K_1K_2 + K_1[D^+] + [D^+]^2)$) was used in the determination of the acid dissociation constants (298 K) for $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$. Similarly, the mole fraction averaged pyrrole proton resonance for equilibrium distributions of **4** and **5** as a function of the concentration of D^+ ($\delta_{4,5(obs)}(pyr) = (K_5\delta_5(pyr) + [D^+]\delta_4(pyr))/(K_5 + [D^+])$) was used to determine the acid dissociation constant (298 K) for $[(TMPS)Rh-D(D_2O)]^{-8}$. The first and second acid dissociation constants for $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ are $K_1 = 1.0(0.2) \times 10^{-9}$ and $K_2 = 9.7(0.3) \times 10^{-13}$, respectively. The acid dissociation constant for $[(TMPS)Rh\text{-}D(D_2O)]^{-8}$ is $K_5 = 4.3(0.5) \times 10^{-8}$.

Reaction of $[(TMPS)Rh\text{-}D(D_2O)]^{-8}$ with CO. A 0.3 mL D_2O solution of $(TMPS)Rh^{III}_{aq}$ (3×10^{-3} M, $[D^+] > 10^{-5}$ M) was pressurized with 0.8 atm of a mixture of H_2 and CO gases ($H_2/CO = 3:7$). The rhodium formyl complex $[(TMPS)Rh-CDO(D_2O)]^{-8}$ (**6**) was produced and equilibrated with the hydride complex $[(TMPS)Rh-D(D_2O)]^{-8}$. The equilibrium constant was evaluated from intensity integrations of the porphyrin pyrrole hydrogen ^1H NMR signals for rhodium hydride and rhodium formyl complexes, which are at 8.58 and 8.64 ppm, respectively. ^1H NMR (360 MHz, D_2O) for $[(TMPS)Rh-CDO(D_2O)]^{-8}$: δ 8.64 (s, 8H, pyrrole), 3.14 (s, 12H, *p*-methyl), 2.26 (s, 12H, *m*-methyl), 1.95 (s, 12H, *m′*-methyl).

Reactions of $[(TMPS)Rh^{I}(D_2O)]^{-9}$ and $[(TMPS)Rh\text{-}D(D_2O)]^{-8}$ with Ethene and Propene. A 0.3 mL D_2O solution of freshly prepared $[(TMPS)Rh-D(D_2O)]^{-8}/[(TMPS)Rh^{I}(D_2O)]^{-9}$ (3×10^{-3} M) in a vacuum-adapted NMR tube was degassed followed by vacuum transfer of ethene or propene (300−500 Torr) into the solution, then dihydrogen gas (300−500 Torr) was reintroduced

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Scheme 1. Simultaneous Equilibria that Occur in the (TMPS)Rh(III)/D_2 System in Water

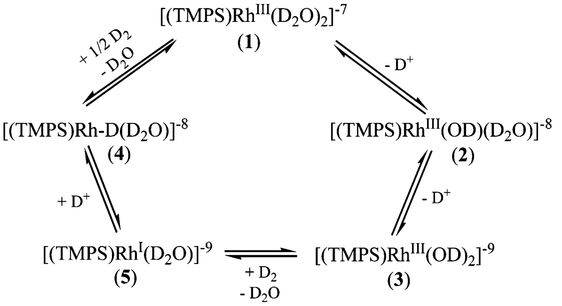

Table 1. Characteristic Pyrrole ^1H NMR (D_2O) Chemical Shifts for (TMPS)Rh Species

(TMPS)Rh species	pyrrole
$[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ (**1**)	8.87
$[(TMPS)Rh^{III}(OD)(D_2O)]^{-8}$ (**2**)	8.75
$[(TMPS)Rh^{III}(OD)_2]^{-9}$ (**3**)	8.63
$[(TMPS)Rh\text{-}D(D_2O)]^{-8}$ (**4**)	8.58
$[(TMPS)Rh^{I}(D_2O)]^{-9}$ (**5**)	8.03
$[(TMPS)Rh-CDO(D_2O)]^{-8}$ (**6**)	8.64

into the sample to suppress the formation of $(TMPS)Rh^{III}{}_{aq}$ species. Rhodium alkyl complexes $[(TMPS)Rh-CH_2CH_2D(D_2O)]^{-8}$ and $[(TMPS)Rh-CH_2CHDCH_3(D_2O)]^{-8}$ were produced, respectively. Reactions of the rhodium hydride with the olefins are completed within the time needed to obtain ^1H NMR spectra. Reactions of $[(TMPS)Rh^{I}(D_2O)]^{-9}$ with the olefins are much slower and take as long as two months to achieve equilibrium. The equilibrium constants were evaluated from integration of the intensities of ^1H NMR signals for rhodium alkyl and rhodium(I) complexes in combination with concentrations of the small organic substrates in water from solubility data[18] and measurement of D^+ concentration which determines the equilibrium distributions of $[(TMSP)Rh-D(D_2O)]^{-8}$ and $[(TMPS)Rh^{I}(D_2O)]^{-9}$. ^1H NMR (360 MHz, D_2O) of $[(TMPS)Rh-CH_2CH_2D(D_2O)]^{-8}$ (**7**): δ 8.52 (s, 8H, pyrrole), 3.16 (s, 12H, *p*-methyl), 2.28 (s, 12H, *m*-methyl), 2.02 (s, 12H, *m′*-methyl), −2.18 (t, 2H, $-CH_2D$, $J_{1H-1H} = 8$ Hz), −5.45 (t of d, 2H, $-CH_2$, $J_{1H-1H} = 8$ Hz, $J_{103Rh-1H} = 3$ Hz). ^1H NMR (360 MHz, D_2O) of $[(TMPS)Rh-CH_2CHDCH_3(D_2O)]^{-8}$ (**8**): δ 8.49 (s, 8H, pyrrole), 3.14 (s, 12H, *p*-methyl), 2.22 (s, 12H, *m*-methyl), 2.02 (s, 12H, *m′*-methyl), −1.72 (d, 3H, $-CH_3$, $J_{1H-1H}= 8$ Hz), −4.31 (m, H, $-CHD$, $J_{1H-1H} = 8$ Hz), −5.38 (d of d, 2H, $-CH_2$, $J_{1H-1H} = 8$ Hz, $J_{103Rh-1H} = 3$ Hz).

Reactions of $[(TMPS)Rh^{I}(D_2O)]^{-9}$ with RX (X = I, Br, Cl; R= CH_3, CH_2CH_3, $CH_2CH_2CH_3$) in D_2O. Alkyl halides (1.2 equiv) were introduced by vacuum transfer into a 0.3 mL freshly prepared D_2O solution of $[(TMPS)Rh^{I}(D_2O)]^{-9}$ (3×10^{-3} M, $[D^+] < 10^{-10}$ M) in a NMR tube with vacuum adaptor; rhodium alkyl complexes $[(TMPS)Rh-R(D_2O)]^{-8}$ (R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$) were immediately formed and characterized by ^1H NMR. ^1H NMR (360 MHz, D_2O) of $[(TMPS)Rh-CH_3(D_2O)]^{-8}$ (**9**): δ 8.51 (8H, pyrrole), 3.15 (16H, phenyl), 2.32 (s, 12H, *m*-methyl), 1.95 (s, 12H, *m′*-methyl), −6.2 (br, 3H, $-CH_3$).

Results and Discussion

Aqueous solutions of rhodium(III) tetrakis(3,5-disulfonatomesityl)porphyrin ($(TMPS)Rh^{III}{}_{aq}$) complexes react with dihydrogen to produce equilibrium distributions between five rhodium species including a rhodium hydride, rhodium(I), and three rhodium(III) aquo and hydroxo complexes (Scheme 1). The porphyrin pyrrole ^1H NMR chemical shifts that are used in the identification of the (TMPS)Rh species in D_2O are listed in Table 1. The distribution of these (TMPS)Rh species in D_2O can be readily determined by application of ^1H NMR which provides a means to evaluate equilibrium constants for each reaction.

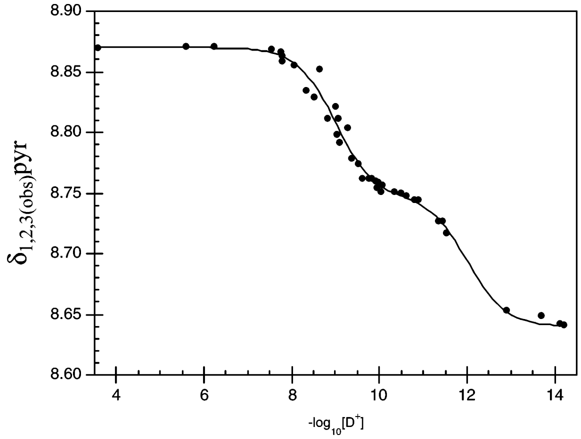

Figure 1. Observed limiting fast-exchange mole fraction-averaged pyrrole ^1H NMR chemical shifts for compounds **1**, **2**, and **3** in D_2O as a function of $-\log [D^+]$. The solid line is the nonlinear least-squares best-fit line giving $K_1(298\ K) = 1.0(0.2) \times 10^{-9}$ and $K_2(298\ K) = 9.7(0.3) \times 10^{-13}$. $\delta_1(pyr) = 8.87$ ppm, $\delta_2(pyr) = 8.75$ ppm, and $\delta_3(pyr) = 8.63$ ppm;.

Aquo and Hydroxo $(TMPS)Rh^{III}$ Complexes in Water. Dissolution of $(TMPS)Rh^{III}$ in D_2O results in solutions of the bisaquo complex $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ (**1**) in equilibrium with mono- and bishydroxo complexes ($[(TMPS)Rh^{III}(OD)(D_2O)]^{-8}$ (**2**) and $[(TMPS)Rh^{III}(OD)_2]^{-9}$ (**3**)) (eqs 1 and 2). Rapid interchange of hydrogens from coordinated water and hydroxide with bulk solvent water (T = 275−300 K) results in a single set of mole fraction averaged porphyrin ^1H NMR resonances for the equilibrium distribution of **1**, **2**, and **3** (Table 1). The mole fraction averaged pyrrole proton resonance for equilibrium distributions of **1**, **2**, and **3** as a function of the concentration of D^+ was used in the determination of the acid dissociation constants (298 K) for **1** and **2** by nonlinear least-squares curve fitting to the equation $\delta_{1,2,3(obs)}(pyr) = (K_1K_2\delta_3(pyr) + K_1[D^+]\delta_2(pyr) + [D^+]^2\delta_1(pyr))/(K_1K_2 + K_1[D^+] + [D^+]^2)$[8] (Figure 1)). The acidities for **1** ($K_1 = 1.0(0.2) \times 10^{-9}$) and **2** ($K_2 = 9.7(0.3) \times 10^{-13}$) are somewhat smaller than the values for $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$ and $[(TSPP)Rh^{III}(OD)(D_2O)]^{-4}$ ($K_1 = 1.4(0.2) \times 10^{-8}$ and $K_2 = 2.8(0.3) \times 10^{-12}$)[7,8] and much larger than the acid dissociation constant for pure D_2O (eq 3) ($K_3(298\ K) = 2.44 \times 10^{-17}$).[19]

$$[(TMPS)Rh^{III}(D_2O)_2]^{-7} \rightleftharpoons [(TMPS)Rh^{III}(OD)(D_2O)]^{-8} + D^+ \quad (1)$$

$$[(TMPS)Rh^{III}(OD)(D_2O)]^{-8} \rightleftharpoons [(TMPS)Rh^{III}(OD)_2]^{-9} + D^+ \quad (2)$$

$$D_2O \rightleftharpoons D^+ + OD^- \quad (3)$$

Reactions of H_2/D_2 with Solutions of $(TMPS)Rh^{III}$ in D_2O. The bisaquo complex $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ (**1**) reacts slowly with H_2/D_2 ($P_{H_2} \approx 0.5-0.8$ atm) in acidic D_2O media

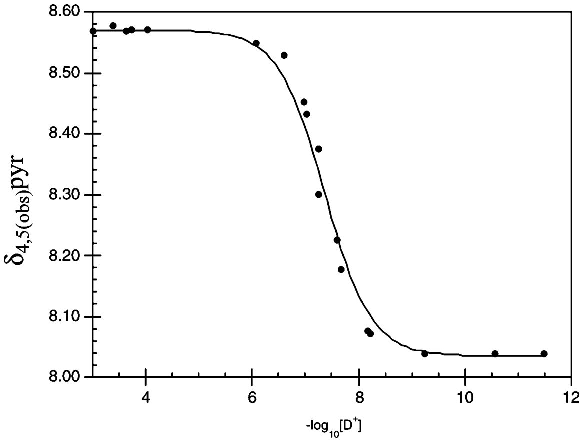

Figure 2. Limiting fast-exchange mole fraction-averaged ^{1}H NMR chemical shifts for $[(TMPS)Rh-D(D_2O)]^{-8}$ (**4**) and $[(TMPS)Rh^I(D_2O)]^{-9}$ (**5**) in D_2O as a function of $-\log [D^+]$. The solid line is the nonlinear least squares best fit line giving $K_5(298\ K) = 4.3(0.5) \times 10^{-8}$: $\delta_4(pyr) = 8.58$ ppm and $\delta_5(pyr) = 8.03$ ppm.

($[D^+] > 10^{-6}$) to form the hydride complex $[(TMPS)Rh-D(D_2O)]^{-8}$ (**4**) (eq 4). Reaction 4 achieves a conveniently measurable equilibrium distribution of species. The equilibrium constant for reaction 4 ($K_4(298\ K) = 18.2(0.5)$) was evaluated by ^{1}H NMR in combination with D^+ concentration

$$[(TMPS)Rh^{III}(D_2O)_2]^{-7} + D_2 \rightleftharpoons [(TMPS)Rh-D(D_2O)]^{-8} + D^+ + D_2O \quad (4)$$

measurements and the solubility of D_2 in water. The equilibrium constant for the reaction of $(TMSP)Rh^{III}$ with dihydrogen is indistinguishable from the value for the reaction of $(TSPP)Rh^{III}$ with dihydrogen.[8]

Solutions of $(TMPS)Rh^{III}$ in basic media ($[D^+] \approx 10^{-8}$–10^{-11} M), where the $(TMPS)Rh^{III}$ mono- and bishydroxo complexes **2** and **3** predominate, give a much faster reaction with H_2/D_2 than the reactions in acidic media and result in formation of the rhodium(I) complex $[(TMPS)Rh^I(D_2O)]^{-9}$ (**5**).

Acid Dissociation Constant of $[(TMPS)Rh\text{-}D(D_2O)]^{-8}$. Protonation of $[(TMPS)Rh^I(D_2O)]^{-9}$ (**5**) produces the rhodium hydride complex **4** by the reverse of eq 5. Aqueous solutions that contain both **4** and **5** manifest a single mole

$$[(TMPS)Rh-D(D_2O)]^{-8} \rightleftharpoons [(TMPS)Rh^I(D_2O)]^{-9} + D^+ \quad (5)$$

fraction averaged ^{1}H NMR resonance that results from rapid proton interchange between **4** and **5**. A plot of $\delta_{4,5(obs)}$(pyr) for equilibrium distributions of **4** and **5** in D_2O at a series of hydrogen ion (D^+) concentrations is illustrated in Figure 2. The mole fraction-averaged pyrrole proton resonances ($\delta_{4,5(obs)}$(pyr)), as a function of the molar concentration of D^+ was used to determine the acid dissociation constant for the hydride **4** at 298 K ($K_5 = 4.3(0.5) \times 10^{-8}$) by nonlinear least-squares curve fitting to the relationship $\delta_{4,5(obs)}(pyr) = (K_5\delta_5(pyr) + [D^+]\delta_4(pyr))/(K_5 + [D^+])$.

The aqueous acid dissociation constant of $[(TMPS)Rh-D(D_2O)]^{-8}$ ($K_5 = 4.3(0.5) \times 10^{-8}$) is slightly smaller than the value for $[(TSPP)Rh-D(D_2O)]^{-4}$ ($K(298K) = 8.0(0.5) \times 10^{-8}$).[7,8] The electron-releasing property of the mesityl methyl groups and placement of the sulfonate groups in the meta positions can be used to rationalize this observation.

The qualitative relationships between the (TMPS)Rh species (Rh(III), Rh(II), Rh(I), and Rh−D) in D_2O are summarized by the pentagon shown in Scheme 1. Experimentally measured quantitative relationships between the five rhodium porphyrin species **1**−**8** depicted by reactions 1−8 are summarized in Table 2. The most prominent difference between the (TMPS)Rh and (TSPP)Rh systems is that the steric demands of the TMPS ligand preclude formation of a $Rh^{II}-Rh^{II}$-bonded complex. Association of $[(TSPP)Rh\text{-alkyl}(D_2O)]^{-4}$ complexes in water and complex formation of $[(TSPP)Rh^I(D_2O)]^{-5}$ with rhodium(III) species are also blocked for (TMPS)Rh complexes by the large steric demands of the TMPS ligand. The rhodium(II) complex ($(TMPS)Rh^{II}$) is not observed as a monomer in water because of reaction with D_2O that results in disproportionation into $(TMPS)Rh^I$ and $(TMPS)Rh^{III}$ species.

Bond Dissociation Free Energy Difference between Rh−OD and Rh−D. The difference in the Rh−OD and Rh−D bond dissociation free energies (BDFE) can be obtained by using reaction 9 in Table 3 ($[(TMPS)Rh^{III}(OD)(D_2O)]^{-8} + D_2 \rightleftharpoons [(TSPP)Rh-D(D_2O)]^{-8} + D_2O$). The difference in the $(Rh-OD)_{aq}$ and $(Rh-D)_{aq}$ bond dissociation free energies (BDFE) is derived by expressing $\Delta G_9°$ in terms of a BDFE for each bond formed or broken in reaction 9 ($\Delta G_9° = -14.0$ kcal mol^{-1} $= (Rh-OD)_{aq} + (D-D)_{aq} - (Rh-D)_{aq} - (D-OD)_{aq}$; $((Rh-OD)_{aq} - (Rh-D)_{aq}) = -14.0 - (D-D)_{aq} + (D-OD)_{aq} = -14.0 - 103.4 + 117.6 = 0.2$ kcal mol^{-1};[19,20,21] $(Rh-OH)_{aq} - (Rh-H)_{aq} \approx 1.2$ kcal mol^{-1}).

The difference of ~0.2 kcalmol^{-1} between the $[(TMPS)Rh-OD]_{aq}$ and $[(TMPS)Rh-D]_{aq}$ BDFE is slightly smaller than the 1.8 kcal mol^{-1} BDFE difference between (TSPP)Rh−OD and (TSPP)Rh−D.[8] A BDFE of 60(2) kcal mol^{-1} has been previously estimated for the (TSPP)Rh−D and the (TMPS)Rh−D BDFE is undoubtedly also close to 60 kcal mol^{-1}.

Reaction of $[(TMPS)Rh^{II}(D_2O)]^{-8}$ with D_2O. The rhodium(II) complex $[(TMPS)Rh^{II}(D_2O)]^{-8}$ is not observed by ^{1}H NMR at the conditions where $[(TSPP)Rh^{II}(D_2O)]^{-4}$ dimerizes by $Rh^{II}-Rh^{II}$ bonding to form $[(TSPP)Rh^{II}(D_2O)]_2^{-8}$. The lack of observation of $[(TMPS)Rh^{II}(D_2O)]^{-8}$ is undoubtedly the result of reaction of the Rh(II) complex with water (eq 17). Using BDFE value of 60 kcal mol^{-1} for the (TMPS)Rh−D and (TMPS)Rh−OD and 117.6 kcal mol^{-1} for the BDFE of D−OD in water[8] gives an estimate of −2.4 kcal mol^{-1} for $\Delta G_{17}°$ (298 K).

$$2\ [(TMPS)Rh^{II}(D_2O)]^{-8} + D-OD \rightleftharpoons [(TMPS)Rh-D(D_2O)]^{-8} + [(TMPS)Rh-OD(D_2O)]^{-8} \quad (17)$$

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(19) Values are obtained from *J. Phys. Chem. Ref. Data*, 1982, *11*, supplement 2. Standard state used is 298.15 K and 0.1 MPa.

Table 2. Measured and Calculated Equilibrium Constants (K_n) and $\Delta G°$(298 K) (kcal mol^{-1}) for (TMPS)Rh Reactions in D_2O[a]

	(TMPS)Rh reactions	K_n (298 K)	$\Delta G°$ (kcal mol^{-1})
1	$[Rh^{III}(D_2O)_2]^{-7} \rightleftharpoons [Rh^{III}(OD)(D_2O)]^{-8} + D^+$	$K_1 = 1.0(0.2) \times 10^{-9}$	+12.3(0.1)
2	$[Rh^{III}(OD)(D_2O)]^{-8} \rightleftharpoons [Rh^{III}(OD)_2]^{-9} + D^+$	$K_2 = 9.7(0.3) \times 10^{-13}$	+16.4(0.1)
3	$D_2O \rightleftharpoons OD^- + D^+$	$K_3 = 2.4 \times 10^{-17}$	+22.6[b]
4	$[Rh^{III}(D_2O)_2]^{-7} + D_2 \rightleftharpoons [Rh{-}D(D_2O)]^{-8} + D^+ + D_2O$	$K_4 = 18.2(0.5)$	−1.7(0.1)
5	$[Rh{-}D(D_2O)]^{-8} \rightleftharpoons [Rh^I(D_2O)]^{-9} + D^+$	$K_5 = 4.3(0.5) \times 10^{-8}$	+10.0(0.1)
6	$[Rh{-}D(D_2O)]^{-8} + CO \rightleftharpoons [Rh{-}CDO(D_2O)]^{-8}$	$K_6 = 1.7(0.1) \times 10^3$	−4.4(0.1)
7	$D^+ + D^- \rightleftharpoons D_2$	$K_7 = 5.2 \times 10^{37}$	−53.2[c]
8	8 $[Rh{-}D(D_2O)]^{-8} + CH_3{-}CH{=}CH_2 \rightleftharpoons [Rh{-}CH_2CHDCH_3(D_2O)]^{-8}$	$K_8 = 5.7(0.1) \times 10^3$	−5.1(0.1)

[a] The reported K values correspond to equilibrium constant expressions that contain all constituents given in the chemical equation including water. [b] The −log (ion product) of D_2O (14.869) ($K = 1.35 \times 10^{-15}$) and the D_2O density (1.1044) were used to determine the $K_3 = 2.44 \times 10^{-17}$ at 298 K. [c] $E°(2H^+ + 2e^- \rightleftharpoons H_2) = 0.00$ V and $E°(2H^- \rightleftharpoons H_2 + 2e^-) = +2.23$ V were used to evaluate $\Delta G°(H^+ + H^- \rightleftharpoons H_2) = -51.4$ kcal mol^{-1} and $\Delta G°(D^+ + D^- \rightleftharpoons D_2) = -53.2$ kcal mol^{-1} (*CRC Handbook of Chemistry and Physics,* 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990−1991; pp 8−38, 6−11, and 8−17).

Table 3. Equilibrium Constants (298 K) and the $\Delta G°$(298 K) (kcal mol^{-1}) for (TMPS)Rh Reactions Derived from Reactions in Table 2

	derived (TMPS)Rh reactions	K_n[a]	$\Delta G°$ (kcal mol^{-1})
9	$[Rh^{III}(OD)(D_2O)]^{-8} + D_2 \rightleftharpoons [Rh{-}D(D_2O)]^{-8} + D_2O$	$K_9 = K_4/K_1 = 1.8 \times 10^{10}$	−14.0(0.1)
10	$[Rh^{III}(OD)_2]^{-9} + D_2 \rightleftharpoons [Rh^I(D_2O)]^{-9} + D_2O$	$K_{10} = K_4K_5/(K_1K_2) = 8.1 \times 10^{14}$	−20.4(0.1)
11	$[Rh^{III}(D_2O)_2]^{-7} + OD^- \rightleftharpoons [Rh(OD)(D_2O)]^{-8} + D_2O$	$K_{11} = K_1/K_3 = 4.1 \times 10^7$	−10.4(0.1)
12	$[Rh^{III}(D_2O)_2]^{-7} + D^- \rightleftharpoons [Rh{-}D(D_2O)]^{-8} + D_2O$	$K_{12} = K_4K_7 = 1.8 \times 10^{40}$	−54.9
13	$[Rh^{III}(OD)(D_2O)]^{-8} + D_2 + CO \rightleftharpoons [Rh{-}CDO(D_2O)]^{-8} + D_2O$	$K_{13} = K_4K_6/K_1 = 3.1 \times 10^{13}$	−18.4(0.1)
14	$[Rh^I(D_2O)]^{-9} + D_2O + CO \rightleftharpoons [Rh{-}CDO(D_2O)]^{-8} + OD^-$	$K_{14} = K_3K_6/K_5 = 9.6 \times 10^{-7}$	8.2(0.1)
15	$[Rh^{III}(D_2O)_2]^{-7} + [Rh^I(D_2O)]^{-9} \rightleftharpoons [Rh(OD)(D_2O)]^{-8} + [Rh\text{-}D(D_2O)]^{-8}$	$K_{15} = K_1/K_5 = 2.3 \times 10^{-2}$	2.2(0.1)
16	$[Rh^{III}(D_2O)_2]^{-7} + [Rh^I(D_2O)]^{-9} + D_2 \rightleftharpoons 2\,[Rh\text{-}D(D_2O)]^{-8} + D_2O$	$K_{16} = K_4/K_5 = 4.2 \times 10^8$	−11.7

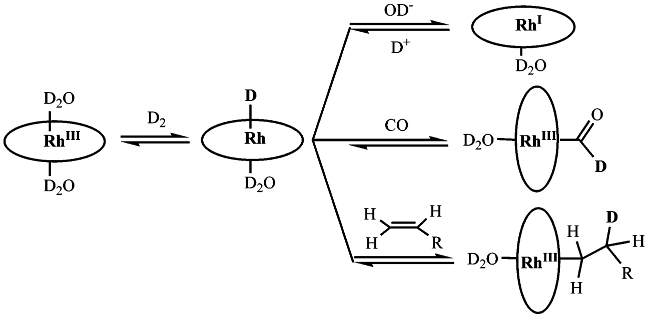
[a] The reported K values correspond to equilibrium constant expressions that contain all constituents given in the chemical equation including water (T = 298 K).

The absence of observable quantities of a (TMPS)Rh^{II} species in D_2O indicates that the average Rh−D and Rh−OD BDFE must be at least 60 kcal mol^{-1}. The capability for a (TSPP)Rh^{II} species to occur at observable concentrations in water is a result of the dimerization by Rh^{II}−Rh^{II} bonding ($\Delta G° \sim -12(2)$ kcal mol^{-1}) to form $[(TSPP)Rh^{II}(D_2O)]_2^{-8}$.

Reactions of $[(TMPS)Rh^I(D_2O)]^{-9}$ and $[(TMPS)Rh{-}D(D_2O)]^{-8}$ with CO and Olefins in Water. Reactions of rhodium(III) porphyrins with hydrogen (H_2/D_2) in water produce a rhodium hydride as part of a more complex set of simultaneous equilibria involving a rhodium(I) complex and several rhodium(III) species. Knowledge of the equilibrium thermodynamic relationships between the solution species in D_2O permitted the establishment of conditions used in this study where either the rhodium hydride (Rh−H) or rhodium(I) complex is the only (TMPS)Rh species present in observable concentrations. The thermodynamic objectives have been advanced by directly measuring the equilibrium distributions of species for each of the substrate reactions in aqueous solution and evaluating the corresponding equilibrium constants.

The hydride complex ($[(TMPS)Rh\text{-}D(D_2O)]^{-8}$) is a weak acid ($K_a$(298 K) = $4.3(0.5) \times 10^{-8}$) and reacts in water with substrates such as CO and olefins to produce rhodium formyl and rhodium alkyl complexes (Scheme 2). The quantitative rates of reactions for $[(TMPS)Rh{-}D(D_2O)]^{-8}$ with CO and olefins are similar to those for the less sterically demanding and more acidic $[(TSPP)Rh{-}D(D_2O)]^{-4}$.[9]

Scheme 2. Reactivity Patterns of $[(TMPS)Rh{-}D(D_2O)]^{-8}$ in Water



Comparisons of Equilibrium Constants (K_n) and $\Delta G_n°$ (kcal mol^{-1}) for Substrate Reactions of (TSPP)Rh and (TMPS)Rh in Water (298 K). The equilibrium constants for reactions of $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ with D_2 and $[(TMPS)Rh{-}D(D_2O)]^{-8}$ with CO and $CH_2{=}CHCH_3$ were directly measured in water by ^{1}H NMR. The reaction of $[(TMPS)Rh^{III}(D_2O)_2]^{-7}$ (298 K) with D_2 has $K_4 = 18.2(0.5)$ ($\Delta G_4° = -1.7(0.1)$ kcal mol^{-1}), which is the same as that previously measured for the reaction of $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$ with D_2.[8] The reaction of $[(TMPS)Rh{-}D(D_2O)]^{-8}$ with CO (298 K) to form $[(TMPS)Rh{-}CDO(D_2O)]^{-8}$ (**6**) has an equilibrium constant ($K_6 = 1.7(0.1) \times 10^3$, $\Delta G_6 = -4.4(0.1)$ kcal mol^{-1}) which is close to the value previously measured for the reaction of $[(TSPP)Rh{-}D(D_2O)]^{-4}$ with CO ($K = 3.0(0.3) \times 10^3$, $\Delta G = -4.7(0.1)$ kcal mol^{-1}, T = 298 K) in water.[9]

Comparisons of equilibrium constants (K_n) and $\Delta G_n°$ (kcal mol^{-1}) (298 K) for reactions of (TSPP)Rh and (TMPS)Rh derivatives in water are listed in Table 4. The acid dissociation constants for the (TMPS)Rh^{III} aquo/hydroxo complexes (**1** and **2**) and the hydride $[(TMPS)Rh{-}D(D_2O)]^{-8}$ (**4**) are

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(20) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255.

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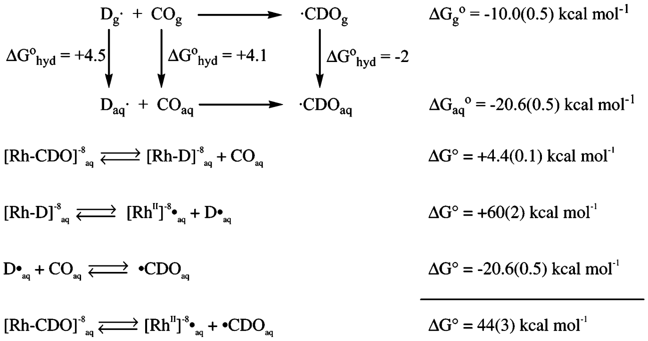
Table 4. Equilibrium Constants (K_n) and $\Delta G_n°$ (kcal mol^{-1}) for Substrate Reactions of (TSPP)Rh and (TMPS)Rh in Water (298 K)

	(TSPP)Rh		(TMPS)Rh	
(por)Rh reactions[a]	K_n	$\Delta G_n°$	K_n	$\Delta G_n°$
$[Rh^{III}(D_2O)_2]^{-n} \rightleftharpoons [Rh^{III}(OD)(D_2O)]^{-(n+1)} + D^+$	1.4×10^{-8}	+10.7	1.0×10^{-9}	+12.3
$[Rh^{III}(OD)(D_2O)]^{-(n+1)} \rightleftharpoons [Rh^{III}(OD)_2]^{-(n+2)} + D^+$	2.8×10^{-12}	+15.8	9.7×10^{-13}	+16.4
$[Rh^{III}(D_2O)_2]^{-n} + D_2 \rightleftharpoons [Rh\text{-}D(D_2O)]^{-(n+1)} + D^+ + D_2O$	18.2	−1.7	18.2	−1.7
$[Rh{-}D(D_2O)]^{-(n+1)} \rightleftharpoons [Rh^{I}(D_2O)]^{-(n+2)} + D^+$	8.0×10^{-8}	+9.7	4.3×10^{-8}	+10.0
$[Rh{-}D(D_2O)]^{-(n+1)} + CO \rightleftharpoons [Rh{-}CDO(D_2O)]^{-(n+1)}$	3.0×10^{3}	−4.7	1.7×10^{3}	−4.4
$[Rh{-}D(D_2O)]^{-(n+1)} + CH_2{=}CHCH_3 \rightleftharpoons [Rh{-}CH_2CHDCH_3(D_2O)]^{-(n+1)}$	3.7×10^{4}	−6.2	5.7×10^{3}	−5.1

[a] $n = 3$ (TSPP); $n = 7$ (TMPS).

all smaller than the values for the (TSPP)Rh system.[8,9] The reduced capability of (TMPS)Rh to stabilize negative charge compared to (TSPP)Rh is consistent with the electron-releasing character of the *o*,*p*-methyl groups and placement of the sulfonate groups in the meta positions in the TMPS ligand.

(TMPS)Rh−CDO BDFE. Reaction of the hydride **4** with CO (eq 6) produces the rhodium formyl complex **6** with a $\Delta G_6°$ (298K) of −4.4(0.1) kcal mol^{-1}. The thermodynamic cycle gives 44(3) kcal mol^{-1} for the Rh−CDO BDFE in (TMPS)Rh−CDO which is indistinguishable from the value previously determined for (TSPP)Rh−CDO (Rh−CDO BDFE = 44(3) kcal mol^{-1}).[9]



Conclusions

Aqueous (D_2O) solutions of tetrakis(3,5-disulfonatomesityl)porphyrin rhodium(III) aquo/hydroxo complexes ((TMPS)-$Rh^{III}{}_{aq}$) react with dihydrogen to produce equilibrium distributions of rhodium hydride and rhodium(I) complexes. Acid dissociation constants for the (TMPS)Rh aquo and hydride complexes are somewhat smaller than the corresponding values for the (TSPP)Rh derivatives which indicates that TSPP can stabilize negative charge better than the TMPS ligand. The Steric demands of the TMPS porphyrin ligand prohibit formation of a Rh(II)−Rh(II)-bonded dimer species, related rhodium(I) complexes with rhodium(III) species, and intermolecular association of alkyl complexes which are prominent features of the rhodium tetra(*p*-sulfonatophenyl)-porphyrin ((TSPP)Rh) system. Reactions of the hydride complex $[(TMPS)Rh{-}D(D_2O)]^{-8}$ in water with CO and olefins produce rhodium formyl and alkyl complexes. Equilibrium thermodynamic values for substrate reactions of (TMPS)Rh−D in water are comparable to the values for the reactions of (TSPP)Rh−D. A (TMPS)Rh^{II} complex is not observed in D_2O because of the thermodynamically favorable reaction with D_2O which is anticipated from bond dissociation free-energy (BDFE) values for (TMPS)Rh−D (60 kcal mol^{-1}), (TMPS)Rh−OD (60 kcal mol^{-1}), and D−OD (117 kcal mol^{-1}).[8] The difference in the (TMPS)-Rh−OD and (TMPS)Rh−D bond dissociation free energies (BDFE) is negligible (∼0.2 kcal mol^{-1}) and slightly smaller than the difference of ∼1.8 kcal mol^{-1} measured for the (TSPP)Rh system.

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