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Comparative Studies of Preferential Binding of Group Nine Metalloporphyrins (M = Co, Rh, Ir) with Methoxide/Methanol in Competition with Hydroxide/Water in Aqueous Solution

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Aqueous solutions of iridium(III) tetra-(*p*-sulfonatophenyl)porphyrin [(TSPP)Ir^{III}] form a hydrogen ion dependent equilibrium distribution of bisaquo ([(TSPP)$Ir^{III}(OD_2)_2]^{3-}$), monoaquo/monohydroxo ([(TSPP)$Ir^{III}(OD_2)(OD)]^{4-}$) and bishydroxo ([(TSPP)$Ir^{III}(OD)_2]^{5-}$) complexes. Comparison of acid dissociation constants of group nine ([(TSPP)M^{III}-$(OD_2)_2]^{3-}$) (M = Co, Rh, Ir) complexes show that the extent of proton dissociation in water increases regularly on moving down the group from cobalt to iridium consistent with increasing metal ligand bond strength. Addition of small quantities of methanol to aqueous solutions of [(TSPP)Ir^{III}] results in the formation of methanol and methoxide complexes in equilibria with aquo and hydroxo complexes that are observed by ^1H NMR. Direct quantitative evaluation of competitive equilibria of [(TSPP)Ir^{III}] complexes reveals a remarkable thermodynamic preference for methanol binding over that of water ($\Delta G°$ (298 K) = -5.2 kcal mol^{-1}) and methoxide binding over that of hydroxide ($\Delta G°$ (298 K) = -6.1 kcal mol^{-1}) in aqueous media. A comparison of equilibrium thermodynamic values for displacement of hydroxide by methoxide for group nine (TSPP)M^{III} (M = Co, Rh, Ir) complexes in aqueous media are also reported.

Introduction

Environmental and energy issues have stimulated renewed interest in utilizing water as both a reagent and a reaction medium.[1−21] Our effort in this area has been directed toward developing water-soluble metalloporphyrins as platforms for diverse organometallic transformations in aqueous media.[17−21] Aqueous solutions of rhodium porphyrin complexes manifest an exceptional range of substrate reactions that are being incorporated into catalytic processes such as olefin oxidation reactions.[15,16] Complexes of tetra(*p*-sulfonatophenyl) porphyrin rhodium [(TSPP)Rh] react with H_2/D_2, D_2O, CO, aldehydes, and olefins to form hydride, hydroxide, formyl, α- and β-hydroxyalkyl, and alkyl complexes in water.[11,12,22] 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.[12,13] The reaction chemistries of the group nine cobalt and iridium metalloporphyrin derivatives in water are much less developed than the rhodium porphyrin systems, but recent structural characterization of ([(TSPP)$Ir^{III}(OH_2)_2]^{3-}$) is an important advance.[23]

This article lays the foundation for comparative thermodynamic studies of group nine porphyrins [(TSPP)M^{III}] (M = Co, Rh, Ir) by evaluating the acid dissociation constants for

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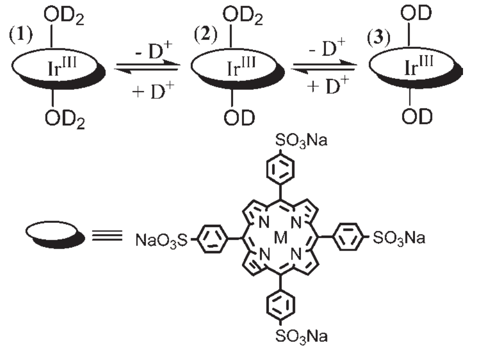

Figure 1. Water and hydroxide complexes of (TSPP) Ir^{III} in water.

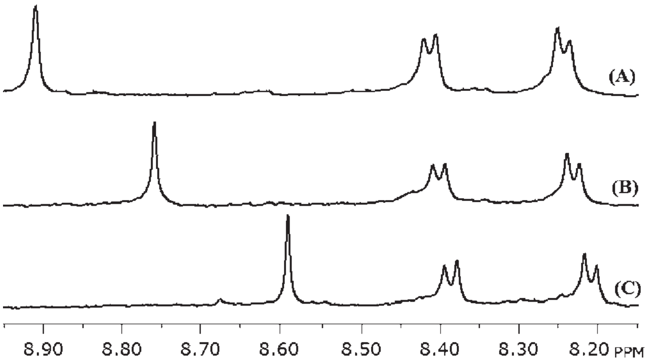

Figure 2. Mole fraction averaged ^1H HMR (500 MHz) porphyrin pyrrole singlet and phenyl AB pattern for **1**, **2**, and **3** in D_2O (T = 293 K) pD of (A) 5, (B) 8.5, and (C) 11.5.

water (H_2O, D_2O) complexes of $[(TSPP)M^{III}]$ (M = Co, Rh, Ir) in water. Equilibrium constants for competitive binding in water–methanol mixtures show thermodynamic preference for methanol and methoxide compared to water and hydroxide respectively. Observations of large thermodynamic preferences for (TSPP)Ir^{III} to bind methanol compared to water ($\Delta G°$(298 K) = -5.2 kcal mol^{-1}) and methoxide versus hydroxide ($\Delta G°$(298 K) = -6.1 kcal mol^{-1}) are particularly remarkable results that establish the capability of iridium complexes to activate low concentrations of alcohols in water.[24–26]

Results and Discussion

Aquo and Hydroxo Complexes of (TSPP)Ir^{III} in D_2O. Dissolution of iridium(III) tetra-*p*-sulfanatophenyl porphyrin ($Na_3[(TSPP)Ir^{III}(OD_2)_2]\cdot 18D_2O$) in D_2O results in a pH dependent equilibrium distribution of the bis-aquo $[(TSPP)Ir^{III}(OD_2)_2]^{3-}$ (**1**) with mono and bis-hydroxo complexes $[(TSPP)Ir^{III}(OD)(OD_2)]^{4-}$ (**2**), $[(TSPP)Ir^{III}(OD)_2]^{5-}$ (**3**) (eq 1,2) (Figure1). The axially coordinated water and hydroxide ligands for **1**, **2**, and **3** in water rapidly interchange protons with the bulk water (298 K) (Figure 2) which results in a single mole fraction averaged pyrrole ^1H NMR resonances for **1**, **2**, and **3** (Figure 2). The ^1H NMR of the bis-aquo **1** and bis-hydroxo **3** complexes can be directly observed at limiting low and high pD respectively. The mole fraction averaged pyrrole ^1H NMR resonances for equilibrium distribution of **1**, **2**, and **3** as a function of $[D^+]$ were used in determining the acid dissociation constants by nonlinear least-squares curve fitting to the expression $\delta_{2,3,4(obs)}(pyr) = (K_1K_2\delta_3(pyr) + K_1[D^+]\delta_2(pyr) + [D^+]^2\,\delta_1(pyr))/(K_1K_2 + K_1[D^+] + [D^+]^2)$[13,27] giving K_1(298 K) = 4.8×10^{-8}, K_2(298 K) = 2.6×10^{-11} and $\delta_2(pyr) = 8.75$ ppm; **1** $[(TSPP)Ir^{III}(OD_2)_2]^{3-}$ is $\delta_1(pyr)$ = 8.93 ppm, and **3** $[(TSPP)Ir^{III}(OD)_2]^{5-}$ is $\delta_3(pyr) = 8.57$ ppm.[28] The equilibrium constants agree well with the recent report of Kanemitsu.[23] Equilibrium distribution of **1**, **2**, and **3** in D_2O as a function of the hydrogen ion concentration is illustrated in Figure 3.

$$[(TSPP)Ir^{III}(OD_2)_2]^{3-} \rightleftharpoons [(TSPP)Ir^{III}(OD)(OD_2)]^{4-} + D^+ \tag{1}$$

$$[(TSPP)Ir^{III}(OD)(OD_2)]^{4-} \rightleftharpoons [(TSPP)Ir^{III}(OD)_2]^{5-} + D^+ \tag{2}$$

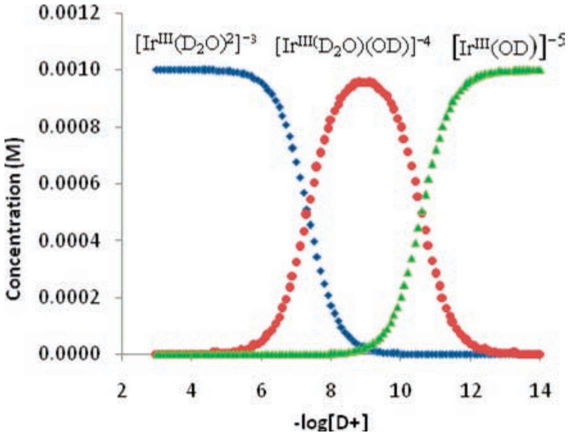

Figure 3. Equilibrium distributions of $[(TSPP)Ir^{III}(OD_2)_2]^{3-}$ (**1**), $[(TSPP)Ir^{III}(OD)(OD_2)]^{4-}$ (**2**), and $[(TSPP)Ir^{III}(OD)_2]^{5-}$ (**3**) as a function of the hydrogen ion concentration in D_2O at 298 K calculated for K_1(298 K) = 4.6×10^{-8} and K_2(298 K) = 2.6×10^{-11} and a total $[(TSPP)Ir^{III}] = 1.0 \times 10^{-3}$ M.

Parallel studies of $Na_3[(TSPP)Co(OD_2)_2]\cdot 18D_2O$ in D_2O similarly result in a pD dependent equilibrium distribution of hydroxo and aquo complexes of $[(TSPP)Co^{III}]$.[28] The acid dissociation constants and chemical shifts were determined as K_1(298 K) = 8.75×10^{-9}, K_2(298 K) = 7.12×10^{-13} and ($[(TSPP)Co^{III}(OD_2)(OD)]^{4-}$) $\delta_2(pyr)$ = 9.22 ppm; ($[(TSPP)Co^{III}(OD_2)_2]^{3-}$) $\delta_1(pyr)$ = 9.38 ppm; ($[(TSPP)Co^{III}(OD)_2]^{5-}$) $\delta_3(pyr)$ = 9.10 ppm.

Aquo and Hydroxo Complexes of (TSPP)Ir^{III} in H_2O. Equations 3 and 4 describe the equilibria between the bis-aquo complex ($[(TSPP)Ir^{III}(OH_2)_2]^{3-}$) (**4**) and the mono and bis-hydroxo complexes ($[(TSPP)Ir^{III}(OH)(OH_2)]^{4-}$) (**5**) and ($[(TSPP)Ir^{III}(OH)_2]^{5-}$) (**6**) in H_2O.

$$[(TSPP)Ir^{III}(OH_2)_2]^{3-} \rightleftharpoons [(TSPP)Ir^{III}(OH)(OH_2)]^{4-} + H^+ \tag{1a}$$

$$[(TSPP)Ir^{III}(OH)(OH_2)]^{4-} \rightleftharpoons [(TSPP)Ir^{III}(OH)_2]^{5-} + H^+ \tag{2a}$$

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Non-linear least-squares curves fitting of the pH dependence of the pyrrole ^{1}H NMR resonances for equilibrium distribution of **4**, **5**, and **6** were used to evaluate the acid dissociation constants[13,29] for compounds **4** and **5**, ($K_{1a} = 1.1 \times 10^{-7}$) ($K_{2b} = 5.3 \times 10^{-11}$). Plots of the observed pyrrole ^{1}H NMR shifts as a function of the hydrogen ion concentration ([D^+]; [H^+]) for the H_2O and D_2O complexes of [(TSPP)Ir^{III}] and the calculated best fit lines are shown in Figure 4. The H_2O complexes are more acidic those of D_2O as a result of the smaller zero-point energy of D_2O[30] (Figure 4).

Results from determining acid dissociation constants for aquo and hydroxo complexes of [(TSPP)M^{III}] (M = Co, Rh, Ir) in D_2O by application of the same ^{1}H NMR method are given in Table 1.[13,31−33]

The relative acidities of the $[(TSPP)M^{III}(OH_2)_2]^{3-}$ (M = Co, Rh, Ir) complexes increase regularly in proceeding down group nine from cobalt to iridium which reflects the trend of increasing metal−ligand bond strengths.[34−36] The free energy changes for displacement of water by hydroxide derived for $[(TSPP)M^{III}(OH_2)_2]^{3-}$ (M = Co, Rh, Ir) complexes (eqs 3, 4; $\Delta G_3° = \Delta G_1° + \Delta G_5°$, $\Delta G_4° = \Delta G_2° + \Delta G_5°$) (Table1). The binding of hydroxide is substantially more favorable than water in all cases and the difference increases when moving down group nine from cobalt to iridium. Preference for the hydroxide anion over water decreases substantially as the effective metal site positive charge is attenuated in going from the diaquo complex ($[(TSPP)M^{III}(OD_2)_2]^{3-}$) to the mono hydroxo monoaquo complexes ($[(TSPP)M^{III}(OD_2)(OD)]^{4-}$) (Table 1).

$$[(TSPP)M^{III}(OD_2)_2]^{3-} + OD^- \rightleftharpoons [(TSPP)M^{III}(OD)(OD_2)]^{4-} + D_2O \qquad (3)$$

$$[(TSPP)M^{III}(OD)(OD_2)]^{4-} + OD^- \rightleftharpoons [(TSPP)M^{III}(OD)_2]^{5-} + D_2O \qquad (4)$$

$$D^+ + OD^- \rightleftharpoons D_2O \qquad (5)$$

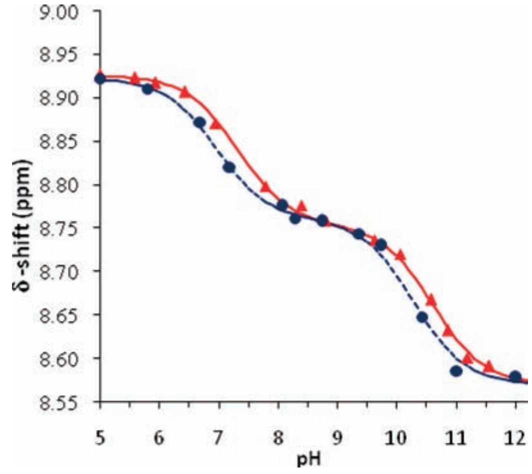

Figure 4. Observed limiting fast exchange mole fraction averaged pyrrole ^{1}H NMR chemical shifts for compounds **1**, **2**, and **3** in D_2O and **4**, **5**, and **6** in H_2O. The points are experimentally determined values, and the lines are calculated for K_{1a} (298 K) = 1.1×10^{-7} and K_{2b} (298 K) = 5.3×10^{-11}.

Free Energy Changes in the Replacement of Water in $[(TSPP)Ir^{III}(OH_2)_2]^{3-}$ by Methanol in Acidic D_2O. Addition of a small quantity of CH_3OH ($1.0-0.1 \times 10^{-3}$ M) to an acidic (pH = 4) D_2O solution of [(TSPP)Ir^{III} (5×10^{-4} M) resulted in observation of three distinct pyrrole resonances that are assigned to the three possible water and methanol complexes $[(TSPP)Ir^{III}(OD_2)(CH_3OD)]^{3-}$ (**7**), $[(TSPP)Ir^{III}(CH_3OH)_2]^{3-}$ (**8**), and $[(TSPP)Ir^{III}(OD_2)_2]^{3-}$ (**1**) (Figure 5). The high field resonance at −2.44 ppm that is not present in deuterated methanol samples is assigned to the coordinated methanol in **7** (Figure 5). Dissolution of [(TSPP)Ir^{III} in pure CD_3OD and observing the ^{1}H NMR allowed the assignment of the pyrrole resonance at 8.74 ppm to $[(TSPP)Ir^{III}(CH_3OH)_2]^{3-}$ (**8**) which also identifies the CH_3 resonance for the coordinated methanol at −2.34 ppm (Figure 5). The remaining pyrrole resonance is assigned to $[(TSPP)Ir^{III}(OD_2)(CH_3OD)]^{3-}$ (**7**). Equilibria corresponding to sequential substitution of water by methanol are described by eqs 6 and 7. Characteristic ^{1}H NMR resonances for compounds **1−3** and **7−10** are found in Table 2.

$$[(TSPP)Ir^{III}(OD_2)_2]^{3-} + CH_3OD \rightleftharpoons [(TSPP)Ir^{III}(OD_2)(CH_3OD)]^{3-} + D_2O \qquad (6)$$

$$[(TSPP)Ir^{III}(OD_2)(CH_3OD)]^{3-} + CH_3OD \rightleftharpoons [(TSPP)Ir^{III}(CH_3OD)_2]^{3-} + D_2O \qquad (7)$$

Equilibrium constants for reactions 6 and 7 were evaluated from the integrated intensities of the porphyrin and methanol ^{1}H NMR resonances and the D_2O concentration (55.2 M), (K_6 (298 K) = 6.3×10^3, $\Delta G°_6$ (298 K) = −5.2 kcal mol^{-1} and K_7 (298 K) = 2.5×10^3, $\Delta G°_7$ (298 K) = −4.6 kcal mol^{-1})[28] (Table 3).

Addition of methanol to aqueous solutions of (TSPP)M^{III} (M = Co, Rh) results in a single mole fraction averaged pyrrole resonances and the absence of high field resonances for coordinated methanol which are indicative of fast interchange of methanol and water complexes which contrasts with the limiting slow exchange observed for (TSPP)Ir^{III} complexes.

Free Energy Changes in the Replacement of Hydroxide by Methoxide in Basic D_2O. Basic D_2O solutions (pD = 11−13) of [(TSPP)Ir^{III} (5×10^{-4} M) with a small addition of CH_3OH ($0.1-1.0 \times 10^{-3}$ M) resulted in observation of equilibrium distributions of hydroxo and methoxide complexes $[(TSPP)Ir^{III}(OD)_2]^{5-}$ (**3**), $[(TSPP)Ir^{III}(OD)(OCH_3^-)]^{5-}$ (**9**), and $[(TSPP)Ir^{III}(OCH_3^-)_2]^{5-}$ (**10**) (Figure 6, eqs 8, 9). Assignments of the ^{1}H NMR for **3**, **9**, and **10** are based on the changes in the observed

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Table 1. First and Second Acid Dissociation Constants and Free Energy Changes (K_1, K_2, $\Delta G_1°$, $\Delta G_2°$) (298 K) and Free Energy Changes for Reactions That Substitute Hydroxide for Water ($\Delta G_3°$, $\Delta G_4°$) (298 K) in $[(\mathrm{TSPP})\mathrm{M^{III}}(\mathrm{OD_2})_2]^{3-}$ (M = Co, Rh, Ir) Complexes in Aqueous Solutions

group 9 (TSPP)M^{III}	K_1	K_2	$\Delta G_1°$ (kcal mol^{-1})	$\Delta G_2°$ (kcal mol^{-1})	$\Delta G_3°$ (kcal mol^{-1})	$\Delta G_4°$ (kcal mol^{-1})
Co (D_2O)[a]	8.8×10^{-9}	7.1×10^{-13}	+10.9	+16.4	−11.7	−6.1
Rh (D_2O)[b]	1.4×10^{-8}	2.8×10^{-12}	+10.6	+15.6	−12.0	−6.8
Ir (D_2O)	4.8×10^{-8}	2.6×10^{-11}	+9.90	+14.3	−13.7	−8.2
Ir (H_2O)	1.1×10^{-7}	5.3×10^{-11}	+9.41	+13.9	−14.5	−10.0

[a] see Supporting Information. [b] Reference 13.

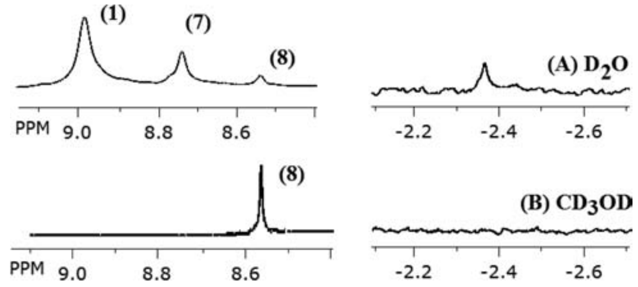

Figure 5. [TSPP]Ir^{III} complexes in (A) D_2O with a small concentration of methanol and (B) in pure CD_3OD.

Table 2. Characteristic ^{1}H HMR (500 MHz) Resonance for the Porphyrin Pyrrole and Methyl of Coordinated CH_3OH/CH_3O^- for [(TSPP)Ir^{III}] Methanol/Water Species in D_2O

(TSPP)Ir^{III} species	pyrole	MeOH/OMe
$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OD_2})_2]^{3-}$ (**1**)	8.93	
$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OD})(\mathrm{OD_2})]^{4-}$ (**2**)	8.75	
$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OD})_2]^{5-}$ (**3**)	8.588	
$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OD_2})(\mathrm{CH_3OD})]^{3-}$ (**7**)	8.84	−2.44[a]
$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{CH_3OD})_2]^{3-}$ (**8**)	8.76	−2.34[a]
$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OCH_3})(\mathrm{OD})]^{5-}$ (**9**)	8.585	−2.51[b]
$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OCH_3})_2]^{5-}$ (**10**)	8.45	−2.55[b]

[a] CH_3OH. [b] OCH_3^-.

intensities for the pyrrole and methoxide resonances as the methanol concentration is varied.

$$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OD})_2]^{5-} + \mathrm{OCH_3}^- \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OD})(\mathrm{OCH_3})]^{5-} + \mathrm{OD}^- \quad (8)$$

$$[(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OD})(\mathrm{OCH_3})]^{5-} + \mathrm{OCH_3}^- \rightleftharpoons [(\mathrm{TSPP})\mathrm{Ir^{III}}(\mathrm{OCH_3})_2]^{5-} + \mathrm{OD}^- \quad (9)$$

Reactions 8 and 9 describe processes where hydroxide is displaced by methoxide in water which provide a direct comparison of the hydroxide and methoxide binding with [(TSPP)Ir^{III}] in water. Equilibrium constants for reactions 8 and 9 were evaluated by ^{1}H NMR integrated intensities for the [(TSPP)Ir^{III}] species, pD measurements, and the equilibrium concentrations of OD^- and OCH_3^- from reaction 10 (K_{10} (298 K) = 0.3)[37,38] in water. Equilibrium constants K_8 and K_9 evaluated at 298 K, Table , (K_8 (298 K) = 3.2×10^4, $\Delta G°_8$ (298 K) = −6.1 kcal mol^{-1} and K_9(298 K) = 8.6×10^3, $\Delta G°_9$(298 K) = −5.4 kcal mol^{-1}).

$$\mathrm{CH_3OH} + \mathrm{OH}^- \rightleftharpoons \mathrm{H_2O} + \mathrm{CH_3O}^- \quad (10)$$

Analogous studies of [(TSPP)Rh^{III}] and [(TSPP)Co^{III}] in highly basic D_2O (pD = 11−13) with addition of known quantities of methanol result in observing sets of hydroxide and methoxide complexes that exhibit characteristic porphyrin pyrrole and high field ^{1}H NMR resonances paralleling the observations for [(TSPP)Ir^{III}] complexes of hydroxide and methoxide.[28]

Equilibrium constants for reactions corresponding to displacement of hydroxide by methoxide for the group nine [(TSPP)M^{III}] (M = Co, Rh, Ir) complexes are summarized in Table 4. All of the [(TSPP)M^{III}] (M = Co, Rh, Ir) reactions where methoxide substitutes for hydroxide in water are thermodynamically favorable (Table 4). The thermodynamic preference for complexing with methoxide compared to hydroxide increases slightly from Co^{III} ($\Delta G°$ = −1.5 kcal mol^{-1}), to Rh^{III} ($\Delta G°$ = −1.9 kcal mol^{-1}) and becomes remarkably large for Ir^{III} ($\Delta G°$ = −6.1 kcal mol^{-1}) (Table 4).

Trends in ^{1}H NMR Parameters for ($[(\mathrm{TSPP})\mathrm{M^{III}}(\mathrm{OCH_3})(\mathrm{OH})]^{5-}$). The porphyrin pyrrole and coordinated methoxide methyl ^{1}H NMR resonances for $[(\mathrm{TSPP})\mathrm{M^{III}}(\mathrm{OCH_3})(\mathrm{OD})]^{5-}$ (M = Co, Rh, Ir) are summarized in Table 5. Porphyrin ring current ^{1}H NMR reasonances have a $(1 - 3\cos^2\theta)/r^3$ dependence which results in downfield shifts for the in-plane pyrrole hydrogens and upfield shifts for the M-OCH_3 group near the center of the π orbitals.[39,40] The ring current shifts also scale with the π electron population, and the regular decrease in the downfield pyrrole hydrogen shifts in going from the Co^{III} to the Ir^{III} derivatives is consistent with decreasing π electron population resulting from increased M-porphyrin π mixing. Decreasing high field shifts for the M-OCH_3 group for M = Co, Rh, Ir is also consistent with this model (Table 5).

Comparison of the Free Energy Changes for Replacement of D_2O by OD^- and OCH_3^- from ($[(\mathrm{TSPP})\mathrm{M^{III}}(\mathrm{D_2O})(\mathrm{OD})]^{4-}$) (M = Co, Rh, Ir) in Water. Reactions that substitute methoxide and hydroxide for water in (TSPP)M^{III} complexes are depicted by eqs 4 and 11 and the equilibrium thermodynamic values given in Table 6. Reactions 4 and 11 provide the best opportunity to compare the interactions of methoxide and hydroxide with a set of group nine (Co, Rh, Ir) complexes.

$$[(\mathrm{TSPP})\mathrm{M^{III}}(\mathrm{OD})(\mathrm{OD_2})]^{4-} + \mathrm{OCH_3}^- \rightleftharpoons [(\mathrm{TSPP})\mathrm{M^{III}}(\mathrm{OD})(\mathrm{OCH_3})]^{5-} + \mathrm{D_2O} \quad (11)$$

The free energy change for displacement of D_2O by OD^- ($\Delta G_4°$(298 K) becomes steadily more favorable in passing

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Table 3. Measured K_n and $\Delta G°_n$ Values for the Reactions of [(TSPP)Ir^{III}] in D_2O with Methanol Described by eqs 6, 7 at Acidic Conditions and eqs 8, 9 at Basic Conditions

	measured [(TSPP)Ir^{III}] reactions	K_n (298 K)	$\Delta G°_n$ (kcal mol^{-1})
6	$[(TSPP)Ir^{III}(OD_2)_2]^{3-} + CH_3OD \rightleftharpoons [(TSPP)Ir^{III}(OD_2)(CH_3OD)]^{3-} + D_2O$	6.3(0.3) × 10^3	−5.2(0.1)
7	$[(TSPP)Ir^{III}(OD_2)(CH_3OD)]^{3-} + CH_3OD \rightleftharpoons [(TSPP)Ir^{III}(CH_3OD)_2]^{3-} + D_2O$	2.5(0.2) × 10^3	−4.6(0.1)
8	$[(TSPP)Ir^{III}(OD)_2]^{5-} + OCH_3^- \rightleftharpoons [(TSPP)Ir^{III}(OD)(OCH_3)]^{5-} + OD^-$	32 (3) × 10^3	−6.1(0.2)
9	$[(TSPP)Ir^{III}(OD)(OCH_3)]^{5-} + OCH_3^- \rightleftharpoons [(TSPP)Ir^{III}(OCH_3)_2]^{5-} + OD^-$	8.6(0.3) × 10^3	−5.4(0.2)

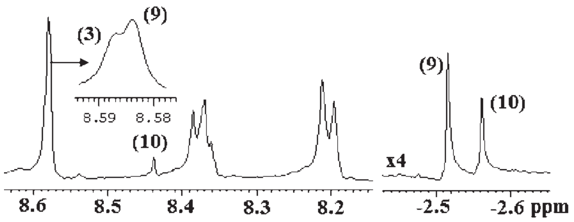

Figure 6. ^{1}H NMR (500 MHz) of observed equilibrium species in D_2O with addition of 1 × 10^{-4} M CH_3OH at pH = 11.75. The pyrrole resonances of compounds **3**, **9**, and **10** and corresponding upfield peaks (magnified × 4) are shown.

Table 4. Equilibrium Constants (K_n) and $\Delta G°_n$ (kcal mol^{-1}) for Substitution of Methoxide for Hydroxide on $[(TSPP)M^{III}(OD)_2]^{5-}$;($K_8$, $\Delta G°_8$) and $[(TSPP)M^{III}(OD)(OCH_3)]^{5-}$; ($K_9$, $\Delta G°_9$) (M = Co^{III}, Rh^{III}, Ir^{III}) at pH 12

	K_8 (298 K)	$\Delta G°_8$ (kcal mol^{-1})	K_9 (298 K)	$\Delta G°_9$ (kcal mol^{-1})
Co^{III}	12(3)	−1.5(0.2)	3.0(2)	−0.6(0.04)
Rh^{III}	26(5)	−1.9(0.1)	10(3)	−1.4(0.1)
Ir^{III}	32(3) × 10^3	−6.1(0.2)	8.6(0.2)x10^3	−5.4(0.2)

Table 5. Porphyrin Pyrrole Resonances and Methoxide Methyl ^{1}H NMR (500 MHz) Resonances of Group Nine Metal $[(TSPP)M^{III}(OCH_3)(OD)]^{5-}$

Group 9 Species	pyrrole	OMe
$[(TSPP)Co^{III}(OCH_3)(OD)]^{5-}$	9.01	−3.59
$[(TSPP)Rh^{III}(OCH_3)(OD)]^{5-}$	8.92	−2.80
$[(TSPP)Ir^{III}(OCH_3)(OD)]^{5-}$	8.59	−2.51

Table 6. Derived Free Energy Changes ($\Delta G_n°$ (kcal mol^{-1}) (298 K)) for Reactions That Displace Water by X (X = OD^-/OCH_3^-) [(TSPP)M^{III}] (M = Co, Rh, Ir) in Aqueous Media: $[(L)M^{III}(OD_2)(OD)]^{4-} + X^- \rightleftharpoons [(L)M^{III}(OD)(X)]^{5-} + D_2O$

$[(TSPP)M^{III}(OD_2)(OD)]^{4-}$	OD^-	OCH_3^-
$[(TSPP)Co^{III}(OD_2)(OD)]^{4-}$	−6.1	−7.7
$[(TSPP)Rh^{III}(OD_2)(OD)]^{4-}$	−6.8	−8.9
$[(TSPP)Ir^{III}(OD_2)(OD)]^{4-}$	−8.2	−14.4

from cobalt (−6.1 kcal mol^{-1}) to rhodium (−6.8 kcal mol^{-1}) to iridium (−8.2 kcal mol^{-1}) (Table 6). The ($\Delta G_{11}°$(298 K)) for substitution of D_2O by OCH_3^- also becomes more favorable in moving down group nine (Co(−7.7), Rh(−8.9), Ir(−14.4) kcal mol^{-1}), but there is a substantially larger change between rhodium (−8.9 kcal mol^{-1}) and iridium (−14.4 kcal mol^{-1}) which is not observed for the OD^- reactions (Rh(−6.8), Ir(−8.2) kcal mol^{-1}). There is thus a specific feature of the binding of methoxide with iridium(III) which is distinguishable from hydroxide interactions. A greater importance of covalent bonding in M-OCH_3 compared to M-OD could be a major contribution to this observation.

Contributing Factors to $\Delta G°$ for Ligand Displacements in Water. Thermodynamics of ligand displacement reactions in water (eq 12) are influenced by contributions from the solvation free energies of both reactants and products along with metal−ligand interactions. Solvation free energies for

$$\text{M-L}_{(aq)} + \text{L}'_{(aq)} \rightleftharpoons \text{M-L}'_{(aq)} + \text{L}_{(aq)} \qquad (12)$$

$CH_3OH_{(g)}$ (−5.1 kcal mol^{-1})[41] and $H_2O_{(g)}$ (−6.3 kcal mol^{-1})[41] in $H_2O_{(l)}$ favor displacement of the water ligand by ∼1 kcal mol^{-1}. The difference in solvation energies of the metal complexes is anticipated to be small and partially compensates for the difference in the aquation free energies for methanol and water. Additionally, repulsive steric interactions of CH_3OH as a ligand are larger than that for H_2O. Thus, the preference of (TSPP)M^{III} binding methanol over water in water must be attributed to M-L bonding interactions.

Methanol displacing water from ($[(TSPP)Ir^{III}(OD_2)_2]^{3-}$) (eq 6) ($K_6$(298 K) = 6.2(0.3) × 10^3, $\Delta G°_6$(298 K) = −5.2(0.1) kcal mol^{-1}) results in a large thermodynamic preference of (TSPP)Ir^{III} binding methanol compared to water, and the dominant contribution to $\Delta G°_6$ must arise from more favorable bonding interaction. When methanol functions as a ligand to bind with metals, the methyl group interaction with the oxygen center attenuates the charge separation at the oxygen donor site and promotes M-CH_3OH covalent bonding relative to the M-H_2O bonding. The M-L interactions within group nine (Co, Rh, Ir) are dominated by increasing importance of covalent bonding acceptor properties from Co to Rh to Ir. Thus, the larger covalent bonding donor affinity of methanol/methoxide compared to water/hydroxide when matched with the larger covalent bonding acceptor properties of (TSPP)Ir^{III} amplifies the difference between (TSPP)Ir^{III} and the Rh^{III} and Co^{III} derivatives.

Reduction of [(TSPP)Ir^{III}] by Methoxide. The capability for accomplishing metal complex promoted and catalyzed alcohol oxidations in water is dependent on substrate coordination and activation and favorable thermodynamics for methanol and methoxide binding with [(TSPP)M^{III}] (M = Co, Rh, Ir) in aqueous solution is a major factor in obtaining processes involving alcohols such as oxidation to aldehydes[42] and amine alkylation[25] in water. The dramatic preferential selectivity of [(TSPP)Ir^{III}] for binding methanol and methoxide in water illustrates how iridium(III) has the potential to be an effective catalyst for alcohol reactions in water. Reduction [(TSPP)Ir^{III}] (5 × 10^{-4} M) to [(TSPP)Ir^{I}] or

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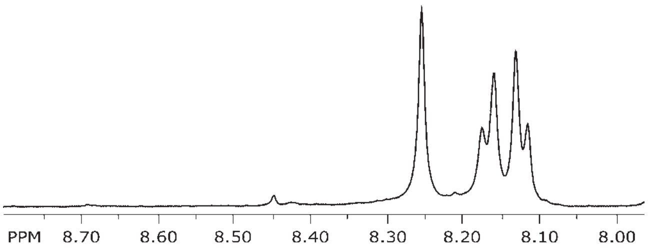

Figure 7. ^{1}H NMR (500 MHz, 298 K) of $[(TSPP)Ir^I]^{5-}$ with pyrrole peak at 8.26 ppm and AA′ BB′ phenyl pattern centered at 8.15 ppm.

[(TSPP)Ir−H] by low concentrations of methanol ((1−5) $\times 10^{-3}$ M) in basic D_2O illustrate the effectiveness of this system (eq 13, 14, Figure 7). The formation of Ir-OCH_3, Ir−H and Ir^I provide an entry point to many substrate transformations.

$$[(TSPP)Ir^{III}(OD)(OCH_3)]^{5-} \rightleftharpoons [(TSPP)Ir\text{-}D(OD)]^{5-} + CH_2O \qquad (13)$$

$$[(TSPP)Ir\text{-}D(OD)]^{5-} \rightleftharpoons [(TSPP)Ir^I(OD)]^{-6} + D^+ \qquad (14)$$

Summary

Acid dissociation constants for ($[(TSPP)M^{III}(OD_2)_2]^{3-}$) (M = Co, Rh, Ir) (Table 1) in conjunction with equilibrium constants for substitution of OCH_3^- and CH_3OH for hydroxide and water are used to identify trends in ligand binding by group nine porphyrin complexes. Equilibrium thermodynamic studies quantitatively describe the preferenial binding of anions (OD^-, OCH_3^-) over that of neutral ligands (D_2O, CH_3OH) for all of the group nine metalloporphyrin complexes. The magnitude of the difference in binding energies for anionic compared to neutral ligands decreases substantially as the effective positive charge of the metal complex decreases. All observations are consistent with a regular increase in the metal ligand binding on moving down group nine (Co, Rh, Ir) porphyrin complexes. The acid dissociation constants and free energy changes in moving down group nin-e (Ir > Rh > Co) demonstrate the general trend. Exceptionally large thermodynamic preferences are observed for $(TSPP)Ir^{III}$ to bind methanol compared to water and methoxide versus hydroxide and indicate the special capability of iridium(III) complexes to activate low concentrations of alcohols in water.

Experimental Section

General Considerations. D_2O was purchased from Cambridge Isotope Laboratory Inc. and degassed by three freeze−pump−thaw cycles before use. Proton NMR spectra were obtained on a Bruker Avance^{III} 500 MHz at 293 K. Chemical shifts were referenced to 3-trimethyl silyl-1 propane sulfonic acid sodium salt. Proton NMR spectra was used to identify solution species and to determine the distribution of species at equilibrium. pH measurements are performed on Thermo Scientific XL15 m and Orion 9802 glass electrode[43] precalibrated by Thermo Orion buffer solutions of pH = 4.01, 7.00, and 10.01. Meso-tetraphenylporphyrin was synthesized by the method of Adler.[44] Sulfonation of meso-tetra phenylporphyrin sodium salt was achieved and subsequently purified by the method of Srivastava.[45]

Concentration of Complexes and Ionic Strength of Aqueous Solutions. Thermodynamic studies of (TSPP)Ir complexes in water were carried out at concentrations less than 2×10^{-3} M to minimize molecular and ionic association. Most equilibrium constant measurements were performed at a low ionic strength ($\mu \sim 10^{-3}$) where the ion activity coefficients approach unity.

Synthesis of $Na_3[(TSPP)M^{III}(D_2O)_2]$ (M = Co, Rh, Ir). $Na_3[(TSPP)M^{III}(OD_2)_2]$ (M = Co, Rh, Ir) was synthesized following reported methods by Ashley.[32,33] Dissolution of **1** in D_2O results in solutions of the bis aquo complex $[(TSPP)Ir^{III}(OD_2)_2]^{3-}$ (**1**) in an equilibrium distribution with the mono and bis hydroxo complexes, $[(TSPP)Ir^{III}(OD_2)(OD)]^{4-}$ (**2**), $[(TSPP)Ir^{III}(OD)_2]^{5-}$ (**3**) . $Na_3[(TSPP)Ir^{III}(OD_2)_2]$ ^{1}H NMR (500 MHz, D_2O) δ(ppm): 8.93 (s, 8H, pyrrole), 8.44 (d, 8H, o-phenyl, $J^1{}_{H\text{-}}{}^1{}_H$ = 8 Hz), 8.25 (d, 8H, m-phenyl, $J^1{}_{H\text{-}}{}^1{}_H$ = 8 Hz). $Na_3[(TSPP)Co^{III}(D_2O)_2]$ ^{1}H NMR (500 MHz, D_2O) δ(ppm): 9.38 (s, 8H, pyrrole), 8.41 (d, 8H, *o*-phenyl, $J^1{}_{H\text{-}}{}^1{}_H$ = 8 Hz), 8.23 (d, 8H, m-phenyl, $J^1{}_{H\text{-}}{}^1{}_H$ = 8 Hz). $Na_3[(TSPP)Rh^{III}(D_2O)_2]$ ^{1}H NMR (500 MHz, D_2O) δ(ppm): 9.15 (s, 8H, pyrrole), 8.44 (d, 8H, *o*-phenyl, $J^1{}_{H\text{-}}{}^1{}_H$ = 8 Hz), 8.25 (d, 8H, m-phenyl, $J^1{}_{H\text{-}}{}^1{}_H$ = 8 Hz). UV−vis (CH_3OH) 408 nm, 516 nm.

Acid Dissociation Constant Measurement for $[(TSPP)M^{III}(OD_2)_2]^{3-}$ (M = Co, Ir) in water. Samples of ($[(TSPP)M^{III}(OD)_2]^{5-}$) (M = Co, Ir) (**4**) were prepared by mixing standardized D_2O solution of NaOD with the stock solutions of complex **1** ($0.5-1.0 \times 10^{-3}$ M) in NMR tubes. A series of DCl and NaOD deuterium oxide solutions were used to tune the pH values. A plot of the pyrrole hydrogen ^{1}H NMR chemical shifts to pD value (pD = pH + 0.41) and fit by non-linear least-squares curve fitting to the equation: $\delta_{2,3,4(obs)}(pyr) = (K_1K_2\delta_3(pyr) + K_1[D^+]\delta_2(pyr) + [D^+]^2\,\delta_1(pyr))/(K_1K_2 + K_1[D^+] + [D^+]^2)$.

Equilibrium Constant Measurement for $[(TSPP)M^{III}]$ + Methanol (M = Co, Rh, Ir) in D_2O. To NMR tubes containing basic (pD = 11) solutions of $\sim 10^{-3}$ M ($[(TSPP)M^{III}(OD)_2]^{5-}$) (M = Co, Rh, Ir) various quantities of methanol were added, and the NMR spectra recorded. Similarly, small quantities of methanol were made to NMR tubes containing acidic (pD = 3) solutions of $\sim 10^{-3}$ M ($[(TSPP)M^{III}(OD_2)_2]^{3-}$) (M = Co, Rh, Ir), and the NMR spectra recorded. Integration of upfield resonances against pyrrole resonances allowed the evaluation of equilibrium constants for axially coordinated methoxide and methanol species in equilibrium with hydroxide and water group nine metalloporphyrins.

Synthesis of $[(TSPP)Ir\text{-}D(OD_2)]^{4-}/[(TSPP)Ir^I(OD_2)]^{5-}$. 0.4 mL $[(TSPP)Ir^{III}(OD_2)_2]^{3-}$ D_2O stock solutions ($1.2-1.8 \times 10^{-3}$ M, $[D^+] < 10^{-9}$ M) was added into a vacuum adapted NMR tube. A 10 μL addition of a stock 2.4×10^{-1} M methanol/deuterium oxide solution was added into the NMR tube and degassed. The tube was heated for 2 days at 343 K, and the ^{1}H NMR (500 MHz, D_2O) was obtained at 360 K, shown in Figure 7.

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Supporting Information Available: Calculations of equilibrium constants, tables and representative NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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