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Methanol as a Reaction Medium and Reagent in Substrate Reactions of Rhodium Porphyrins

Shan Li,[†] Sounak Sarkar,[†] and Bradford B. Wayland*[,‡]

[†]*Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, and* [‡]*Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122*

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Methanol solutions of rhodium(III) tetra(*p*-sulfonatophenyl) porphyrin [(TSPP)Rh^{III}] have a hydrogen ion dependent equilibrium between bis-methanol, monomethoxy monomethanol, and bis-methoxy complexes. Reactions of dihydrogen (D_2) with solutions of [(TSPP)Rh^{III}] complexes in methanol produce equilibrium distributions of a rhodium hydride $[(TSPP)Rh^{III}\text{-}D(CD_3OD)]^{-4}$ and rhodium(I) complex $[(TSPP)Rh^{I}(CD_3OD)]^{-5}$. The rhodium hydride complex in methanol functions as a weak acid with an acid dissociation constant of $1.1(0.1) \times 10^{-9}$ at 298 K. Patterns of rhodium hydride substrate reactions in methanol are illustrated by addition with ethene, acetaldehyde, and carbon monoxide to form rhodium alkyl, α-hydroxyethyl, and formyl complexes, respectively. The free energy change for the addition reaction of $[(TSPP)Rh^{III}\text{-}D(CD_3OD)]^{-4}$ with CO in methanol to produce a formyl complex ($\Delta G^\circ_{(298K)} = -4.7(0.1)$ kcal mol^{-1}) is remarkably close to $\Delta G^\circ_{(298K)}$ values for analogous reactions in water and benzene. Addition reactions of the rhodium hydride ($[(TSPP)Rh^{III}\text{-}D(CD_3OD)]^{-4}$) with vinyl olefins invariably yield the anti-Markovnikov product which places the rhodium porphyrin on the less hindered terminal primary carbon center. Addition of the rhodium−methoxide unit in $[(TSPP)Rh^{III}\text{-}OCD_3(CD_3OD)]^{-4}$ with olefins to form β-methoxyalkyl complexes places rhodium on the terminal carbon for alkene hydrocarbons and vinyl acetate, but vinyl olefins that have π-electron withdrawing substituents have a thermodynamic preference for placing rhodium on the interior carbon where negative charge is better accommodated. Equilibrium thermodynamic values for addition of the Rh-OCD_3 unit to olefins in methanol are evaluated and compared with values for Rh−OH addition to olefins in water.

Introduction

Selection of a reaction medium is an important parameter that can be varied to influence both the mechanism and the thermodynamics for organometallic processes.[1−13] Comparative studies of organometallic reactions of rhodium porphyrins in benzene and water have revealed that analogous reactions often occur with similar thermodynamics because of compensating solvation terms but that different types of solvent media can often direct reactions to occur by substantially different mechanisms.[14−19] Substrate reactions in water generally occur much faster and utilize ionic pathways that are not available in benzene. Rhodium porphyrin substrate reactions that are distinctly different

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*To whom correspondence should be addressed. E-mail:bwayland@temple.edu.

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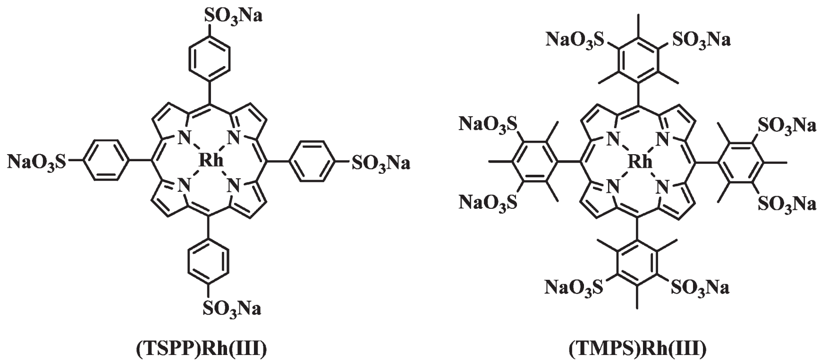

Figure 1. Tetra(*p*-sulfonatophenyl) rhodium(III) porphyrin ((TSPP)Rh(III)) and tetrakis(3,5-disulfonatomesityl)rhodium(III) porphyrin ((TMPS)-Rh(III)) are representative methanol soluble porphyrins.

in water compared to benzene are observed to occur only when water functions as a reactant. Dirhodium ketone (Rh−C(O)−Rh) and dirhodium diketone (Rh−C(O)−C(O)−Rh) complexes[14,15] which are prominent stable species in benzene[20−23] are observed to react by water gas shift type processes in water.[14,15] Formation of β-hydroxyalkyl complexes from reactions of olefins and rhodium(III) porphyrin species in aqueous media also illustrate water functioning as a reagent.[17]

This article reports on the reactivity patterns for rhodium porphyrin species that occur in methanol solvent media and on the evaluation of equilibrium thermodynamics for rhodium hydride and rhodium methoxide reactions with substrates. Regioselectivity for reactions of olefins that produce rhodium alkyl and β-methoxyalkyl derivatives is compared with related reactions in water.[14,15]

Results and Discussion

Methanol and Methoxide Complexes of (TSPP)Rh(III) in Methanol. Sulfonated tetraphenyl porphyrin derivatives provide a convenient set of rhodium porphyrin complexes for reactivity studies in methanol (CD_3OD) solutions (Figure 1).

Rhodium(III) species ($[(TSPP)Rh^{III}]$) in methanol (CD_3OD) occur as an equilibrium mixture of a bis-methanol $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**), monomethanol monomethoxide $[(TSPP)Rh^{III}(OCD_3)(CD_3OD)]^{-4}$ (**2**), and bismethoxide $[(TSPP)Rh^{III}(OCD_3)_2]^{-5}$ (**3**) complexes with the equilibrium distribution of **1**, **2**, and **3** dependent on the deuterium ion concentration (eqs 1 and 2).

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} \rightleftharpoons [(TSPP)Rh^{III}(OCD_3)(CD_3OD)]^{-4} + D^+ \qquad (1)$$

$$[(TSPP)Rh^{III}(OCD_3)(CD_3OD)]^{-4} \rightleftharpoons [(TSPP)Rh^{III}(OCD_3)_2]^{-5} + D^+ \qquad (2)$$

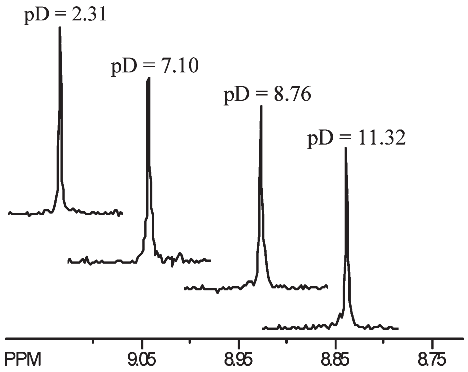

Figure 2. ^1H NMR resonance for porphyrin pyrrole hydrogens at a series of deuterium ion concentrations.

Rapid proton exchange processes result in a single set of mole fraction averaged porphyrin ^1H NMR resonances for the equilibrium distribution of **1**, **2**, and **3** in methanol at 298 K. Changes in the ^1H NMR chemical shift for the porphyrin pyrrole hydrogens for an equilibrium distribution of **1**, **2**, and **3** as a function of the deuterium ion concentration are illustrated in Figure 2. The mole fraction averaged pyrrole hydrogen resonances as a function of $-\log[D^+]$ were used in determining the acid dissociation constants for $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**) ($K_{1(298K)} = 6.9(0.2) \times 10^{-8}$) and **2** ($K_{2(298K)} = 5.8(0.3) \times 10^{-13}$) (Figure 3) by nonlinear least-squares fitting to the expression $[\delta_{\mathbf{1,2,3}} = (K_1K_2\delta_{\mathbf{3}} + K_1[D^+]\delta_{\mathbf{2}} + [D^+]^2\delta_{\mathbf{1}})/(K_1K_2 + K_1[D^+] + [D^+]^2)]$[15] (Figure 3). The distribution of $[(TSPP)Rh^{III}]$ species **1**, **2**, and **3** in a sample with a total rhodium porphyrin concentration of 1.0×10^{-3} M in CD_3OD is displayed at a series of D^+ concentrations in Figure 4. This plot provides a convenient means for establishing the hydrogen ion concentration conditions needed to obtain the desired distribution of **1**, **2**, and **3**. For example, the monomethoxide $[(TSPP)Rh^{III}(OCD_3)(CD_3OD)]^{-4}$ is found to be the dominant species present in methanol when the pD is in the range of 9−11 (Figure 4).

The first acid dissociation constant for the bis-methanol complex $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**) in CD_3OD ($K_{1(298K)} = 6.9(0.2) \times 10^{-8}$; $\Delta G°_{1(298K)} = 9.8$ (0.1) kcal mol^{-1}) is five times larger than the dissociation constant for the bis-aquo complex $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$ in D_2O ($K = 1.4(0.2) \times 10^{-8}$; $\Delta G°_{(298K)} = 10.7$ (0.1) kcal mol^{-1}).[15] This is a reversal from the order of acid dissociation constants for pure liquid CD_3OD and D_2O where pure CD_3OD(l) (eq 3) ($K_{3(298K)} = 1.0(0.3) \times 10^{-18}$; $\Delta G°_{3(298K)} = 24.5$ (0.1) kcal mol^{-1}) is substantially less acidic than pure D_2O(l) ($K_{(298K)} = 2.44 \times 10^{-17}$;

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Scheme 1. Thermodynamic Comparison (at 298 K) for the Substitution of Methoxide for Methanol in CD_3OD and Hydroxide for Water in D_2O[15] for $(TSPP)Rh^{III}$ Complexes

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} + OCD_3^- \rightleftharpoons [(TSPP)Rh^{III}(OCD_3)(CD_3OD)]^{-4} + CD_3OD \quad \Delta G^o = -14.8(0.1)\ \text{kcal mol}^{-1}$$

$$[(TSPP)Rh^{III}(D_2O)_2]^{-3} + OD^- \rightleftharpoons [(TSPP)Rh^{III}(OD)(D_2O)]^{-4} + D_2O \quad \Delta G^o = -11.9(0.1)\ \text{kcal mol}^{-1}$$

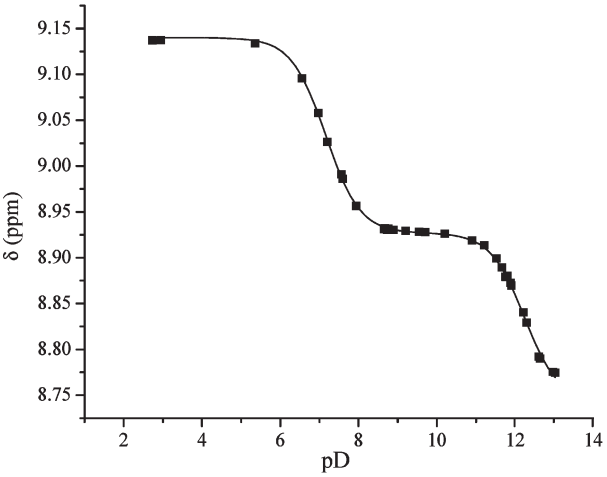


Figure 3. Observed limiting fast-exchange mole fraction-averaged pyrrole ^1H NMR chemical shifts for **1**, **2**, and **3** in CD_3OD as a function of $-\log[D^+]$. The solid line is the nonlinear least-squares best-fit line giving $K_{1(298K)} = 6.9(0.2) \times 10^{-8}$ and $K_{2(298K)} = 5.8(0.3) \times 10^{-13}$. $\delta_1(pyr) = 9.14$ ppm, $\delta_2(pyr) = 8.93$ ppm, $\delta_3(pyr) = 8.74$ ppm.

Scheme 2. Proposed Pathway for Stoichiometric and Catalytic Oxidation of Methanol by Rhodium(III) Porphyrin

$$[(TSPP)Rh^{III}(OCD_3)_2]^{-5} \longrightarrow [(TSPP)Rh^{I}(CD_3OD)]^{-5} + CD_2O$$

$$[(TSPP)Rh^{I}(CD_3OD)]^{-5} + O_2 + CD_3OD \longrightarrow [(TSPP)Rh^{III}(OCD_3)_2]^{-5} + D_2O_2$$

$$D_2O_2 \rightleftharpoons D_2O + 1/2\, O_2$$

$\Delta G°_{(298K)} = 22.6$ (0.1) kcal mol^{-1}). Combining reaction 1 and the reverse of reaction 3 gives an expression

$$CD_3OD \rightleftharpoons CD_3O^- + D^+ \qquad (3)$$

for the substitution of methoxide for methanol (Scheme 1). Displacement of a neutral methanol ligand by the methoxide anion is highly thermodynamically favorable ($\Delta G°_{(298K)} = -14.8$ (0.1) kcal mol^{-1}). The corresponding free energy change for substitution of hydroxide for coordinated water in aqueous solution is $\Delta G°_{(298K)} = -11.9$ (0.1) kcal mol^{-1} (Scheme 1).[15]

Stoichiometric and Catalytic Oxidation of Methanol by Rhodium(III) Porphyrins. Rhodium(III) porphyrin species in CD_3OD at strongly basic conditions (pD > 11) are reduced to rhodium(I) porphyrin, and methanol is oxidized to formaldehyde (Scheme 2). One distinct difference between methanol and water as solvent media is that the alcohol at strongly basic condition functions as a reducing agent for rhodium(III) and thus rhodium(III) porphyrins are not viable reagents for substrate reactions in strongly basic methanol. Oxidation of methanol becomes catalytic through rapid quantitative oxidation of $(TSPP)Rh^I$ to $(TSPP)Rh^{III}$ by dioxygen (Scheme 2), and the formaldehyde product oxidizes further to formate. The methanol oxidation to formaldehyde is currently viewed as occurring by an intermolecular β C$-$H deprotonation of coordinated methoxide in the relatively high dielectric and highly basic medium. The fast quantitative air oxidation of rhodium(I) to rhodium(III) is an important feature of the rhodium porphyrin system that permits rhodium(III) porphyrins to function as oxidation catalysts by directly using O_2 without the need for cocatalysts.[19]

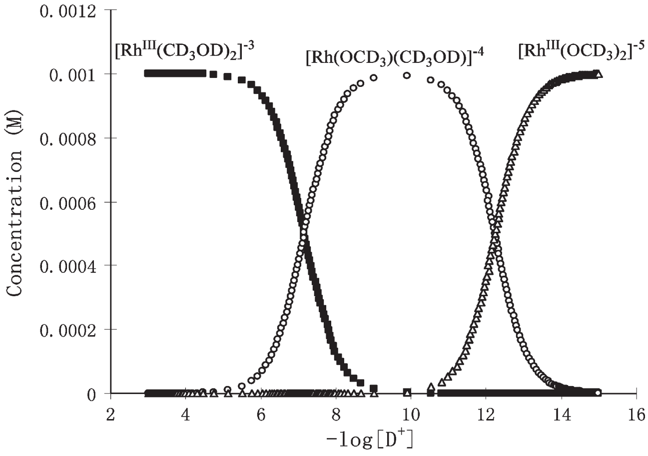


Figure 4. Equilibrium distributions of $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**), $[(TSPP)Rh^{III}(OCD_3)(CD_3OD)]^{-4}$ (**2**), and $[(TSPP)Rh^{III}(OCD_3)_2]^{-5}$ (**3**) for a CD_3OD solution with a total rhodium porphyrin concentration of 1.0×10^{-3} M as a function of the equilibrium deuterium ion concentration ($[D^+]$).

Reaction of $[TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ with Hydrogen in Methanol. The bis-methanol complex $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**) reacts slowly with H_2/D_2 ($P_{H_2} \sim 0.5$ atm) in acidic CD_3OD media ($[D^+] > 10^{-5}$ M) to form the hydride complex $[(TSPP)Rh\text{-}D\ (CD_3OD)]^{-4}$ (**4**) (eq 4), which occurs in equilibrium with the rhodium(I) derivative $[(TSPP)Rh^I(CD_3OD)]^{-5}$ (**5**) (eq 5).

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} + D_2 \rightleftharpoons [(TSPP)Rh^{III}-D(CD_3OD)]^{-4} + D^+ + CD_3OD \qquad (4)$$

$$[(TSPP)Rh^{III}-D(CD_3OD)]^{-4} \rightleftharpoons [(TSPP)Rh^{I}(CD_3OD)]^{-5} + D^+ \qquad (5)$$

The equilibrium distribution of **4** and **5** depends on the D^+ concentration in solution. The deuterium ion exchange between **4** and **5** in methanol is sufficiently slow to permit direct observation of individual sets of porphyrin hydrogen NMR resonances when pD is between 8 and 10 (Figure 5). This contrasts with aqueous media where proton exchange between water and the rhodium hydride

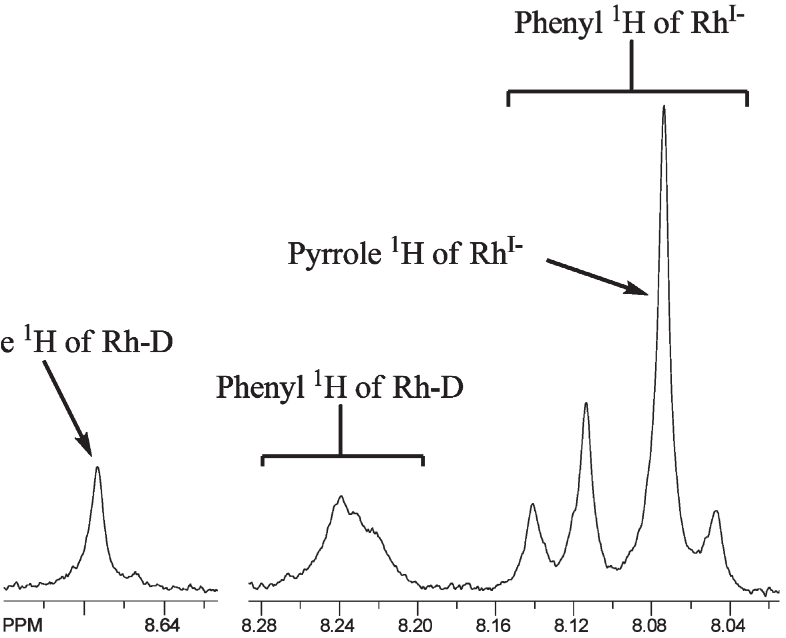


Figure 5. ^{1}H NMR resonances for the pyrrole and phenyl hydrogens of an equilibrium distribution of $[(TSPP)Rh\text{-}D(CD_3OD)_2]^{-4}$ (**4**) and $[(TSPP)Rh^I(CD_3OD)]^{-4}$ (**5**) in CD_3OD at pD = 9.21 (T = 298 K), ($K_{5(298K)}$ = 1.1 (0.1) × 10^{-9}).

Table 1. Equilibrium Constants (K_n) and $\Delta G°_{(298K)}$ (kcal mol^{-1}) for (TSPP)Rh reactions in CD_3OD[a]

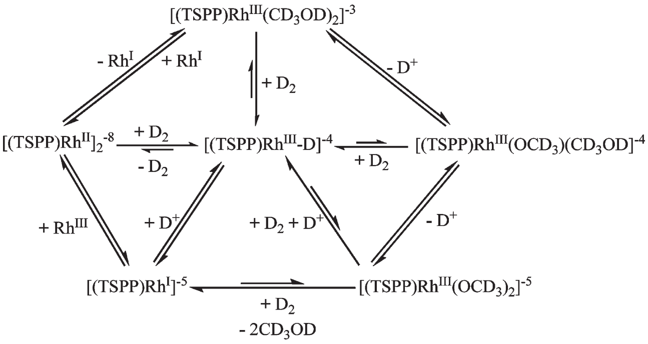
	$K_{n(298K)}$	$\Delta G°_{(298K)}$ (kcal mol^{-1})
(1) $[Rh^{III}(CD_3OD)_2]^{-3} \rightleftharpoons [Rh^{III}(OCD_3)(CD_3OD)]^{-4} + D^+$	$K_1 = 6.9(0.2) \times 10^{-8}$	+9.8(0.1)
(2) $[Rh^{III}(OCD_3)(CD_3OD)]^{-4} \rightleftharpoons [Rh^{III}(OCD_3)_2]^{-5} + D^+$	$K_2 = 5.8(0.3) \times 10^{-13}$	+16.7(0.1)
(3) $CD_3OD \rightleftharpoons OCD_3^- + D^+$	$K_3 = 1.0(0.3) \times 10^{-18}$	+24.5(0.1)[b]
(4) $[Rh^{III}(CD_3OD)_2]^{-3} + D_2 \rightleftharpoons [Rh\text{-}D(CD_3OD)]^{-4} + D^+ + CD_3OD$	$K_4 = 1.0(0.1) \times 10^3$	−4.1(0.1)
(5) $[Rh\text{-}D(CD_3OD)]^{-4} \rightleftharpoons [Rh^I(CD_3OD)]^{-5} + D^+$	$K_5 = 1.1(0.1) \times 10^{-9}$	+12.2(0.1)
(6) $[Rh\text{-}D(CD_3OD)]^{-4} + CO \rightleftharpoons [Rh\text{-}CDO(CD_3OD)]^{-4}$	$K_6 = 3.0(0.1) \times 10^3$	−4.7(0.1)

[a] The reported K values correspond to equilibrium constant expressions that contain all constituents given in the chemical equation including methanol. [b] The pK_a (298 K) of pure CH_3OH ($K_{a\,(298K)} = 2.5 \times 10^{-17}$) was used in deriving the K_a for CD_3OD ($K_{3(298K)} = 1.0\ (0.3) \times 10^{-18}$).

is fast on the NMR time scale.[15] The equilibrium constant for reaction 4 was evaluated in methanol from ^{1}H NMR shift positions and intensities in conjunction with the D^+ concentration (Table 1). The free energy change at 298 K for reaction of the bis-methanol complex $[(TSPP)Rh(CD_3OD)_2]^{-3}$ with hydrogen (D_2) in methanol (eq 4) ($\Delta G°_{4(298K)} = -4.1$ kcal mol^{-1}) is about 2.4 kcal mol^{-1} more favorable than the analogous reaction of $[(TSPP)Rh(D_2O)_2]^{-3}$ with D_2 in water ($[(TSPP)Rh(D_2O)_2]^{-3} + D_2 \rightleftharpoons [(TSPP)Rh\text{-}D(D_2O)]^{-4} + D^+ + D_2O$; $\Delta G°_{(298K)} = -1.7\ (0.1)$ kcal mol^{-1}).[15]

Evaluation of the Acid Dissociation Constant for $[(TSPP)Rh^{III}\text{-}D(CD_3OD)]^{-4}$ in Methanol. The acid dissociation constant for the hydride complex $[(TSPP)Rh^{III}\text{-}D(CD_3OD)]^{-4}$ **4** in CD_3OD is substantially smaller ($K_{5(298K)} = 1.1(0.1) \times 10^{-9}$; $\Delta G°_{5(298K)} = 12.2\ (0.1)$ kcal mol^{-1}) than the corresponding aquo complex $[(TSPP)Rh^{III}\text{-}D(D_2O)]^{-4}$ in D_2O ($K_{(298K)} = 8.0 \times 10^{-8}$; $\Delta G°_{(298K)} = 9.7\ (0.1)$ kcal mol^{-1}). The heterolytic dissociation of the Rh-D unit in water is 2.5 kcal mol^{-1} ($\Delta(\Delta G°)_{(298K)} = -2.5$ kcal mol^{-1}) more favorable than in methanol. The difference is effectively same as the difference in proton solvation energies in water and methanol ($\Delta(\Delta G°)_{(298K)} = \Delta G°_{H^+(H_2O)} - \Delta G°_{H^+(CH_3OH)} =$ −2.4 kcal mol^{-1}, where $\Delta G°_{H^+(H_2O)}$ and $\Delta G°_{H^+(CH_3OH)}$ are the free energies for solvation of the proton in water and methanol, respectively).[24] The smaller extent of heterolytic dissociation and thus acidity of the rhodium hydride in methanol compared to water is an important difference between water and methanol media.

Scheme 3. Simultaneous Equilibria that Occur in the (TSPP)Rh(III)/D_2 System in CD_3OD



Reactivity Patterns for $[(TSPP)Rh^{III}\text{-}D(CD_3OD)]^{-4}$ in Methanol with CO, Aldehydes, and Olefins. Carbon monoxide, acetaldehyde, and ethene react with the hydride

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

	$K_n{}^a$	$\Delta G°$
(12) $[Rh^{III}(OCD_3)(CD_3OD)]^{-4} + D_2 \rightleftharpoons [Rh\text{-}D(CD_3OD)]^{-4} + CD_3OD$	$K_{12} = K_4/K_1 = 1.4 \times 10^{10}$	−13.8(0.1)
(13) $[Rh^{III}(OCD_3)_2]^{-5} + D_2 \rightleftharpoons [Rh^{I}(CD_3OD)]^{-5} + CD_3OD$	$K_{13} = K_4K_5/(K_1K_2) = 2.7 \times 10^{13}$	−18.3(0.1)
(14) $[Rh^{III}(CD_3OD)_2]^{-3} + OCD_3{}^{-} \rightleftharpoons [Rh(OCD_3)(CD_3OD)]^{-4} + CD_3OD$	$K_{14} = K_1/K_3 = 6.9 \times 10^{10}$	−14.8(0.1)
(15) $[Rh^{III}(CD_3OD)_2]^{-3} + D^{-} \rightleftharpoons [Rh\text{-}D(CD_3OD)]^{-4} + CD_3OD$	$K_{15} = K_4K_{20} = 5.2 \times 10^{40}$	−55.5(0.1)
(16) $[Rh^{III}(OCD_3)(CD_3OD)]^{-4} + D_2 + CO \rightleftharpoons [Rh\text{-}CDO(CD_3OD)]^{-4} + CD_3OD$	$K_{16} = K_4K_6/K_1 = 4.3 \times 10^{13}$	−18.6(0.1)
(17) $[Rh^{I}(CD_3OD)]^{-5} + CD_3OD + CO \rightleftharpoons [Rh\text{-}CDO(CD_3OD)]^{-4} + OCD_3{}^{-}$	$K_{17} = K_3K_6/K_5 = 2.7 \times 10^{-6}$	7.6(0.1)
(18) $[Rh^{III}(CD_3OD)_2]^{-3} + [Rh^{I}(CD_3OD)]^{-5} \rightleftharpoons [Rh(OCD_3)(CD_3OD)]^{-4} + [Rh\text{-}D(CD_3OD)]^{-4}$	$K_{18} = K_1/K_5 = 63$	−2.5(0.1)
(19) $[Rh^{III}(CD_3OD)_2]^{-3} + [Rh^{I}(CD_3OD)]^{-5} + D_2 \rightleftharpoons 2[Rh\text{-}D(CD_3OD)]^{-4} + CD_3OD$	$K_{19} = K_4/K_5 = 9.1 \times 10^{11}$	−16.3(0.1)
(20) $D^{+} + D^{-} \rightleftharpoons D_2$	$K_{20} = 5.2 \times 10^{37}$	-53.2^{b}

[a] The reported K values correspond to equilibrium constant expressions that contain all constituents given in the chemical equation including water ($T = 298$ K). [b] $E°(2H^{+} + 2e^{-} \rightleftharpoons H_2) = 0.00$ 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.

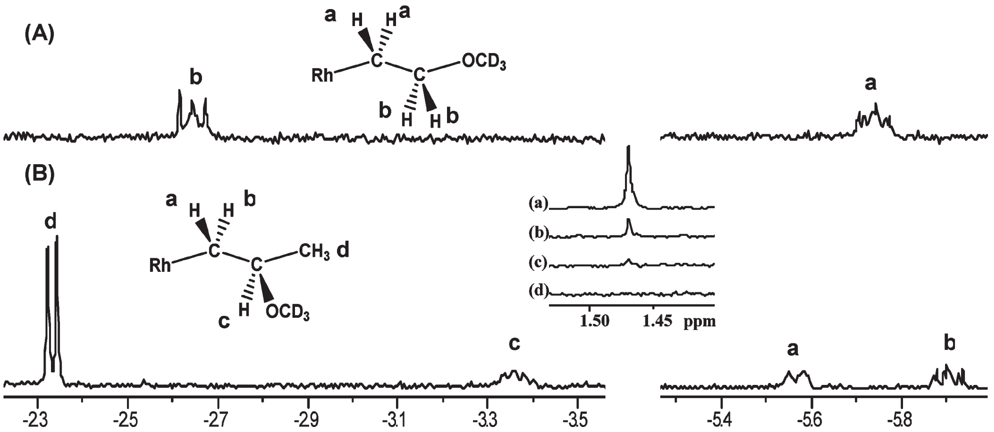


Figure 6. High-field ^1H NMR resonances for (A) (TSPP)Rh-CH_2-CH_2-OCD_3 and (B) [(TSPP)Rh-CH_2-$CH(OCD_3)$-CH_3. (Inset: Observation of the β-OCH_3 group in (TSPP)Rh-$CH(CO_2CH_3)$-CH_2-OCH_3 and very slow exchange of the $-OCD_3$ group in CD_3OD. (a) $t = 0$, (b) $t = 1$ month, (c) $t = 2$ months, and (d) $t = 3$ months.)

complex $[(TSPP)Rh\text{-}D(CD_3OD)]^{-4}$ (**4**) (pD = 6 − 8, 298 K) in methanol to produce rhodium formyl $[(TSPPRh^{III}\text{-}CDO(CD_3OD)]^{-4}$ (**6**) (eq 6), α-hydroxyethyl $[(TSPP)\text{-}Rh^{III}\text{-}CH(OD)CH_3(CD_3OD)]^{-4}$ (**7**) (eq 7), and ethyl $[(TSPP)Rh^{III}\text{-}CH_2CH_2D(CD_3OD)]^{-4}$ (**8**) (eq 8) complexes respectively.

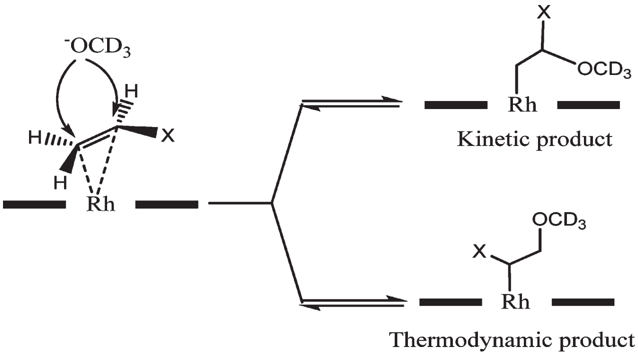
$$[(TSPP)Rh\text{-}D(CD_3OD)]^{-4} + CO \rightleftharpoons [(TSPP)Rh\text{-}CDO(CD_3OD)]^{-4} \qquad (6)$$

$$[(TSPP)Rh\text{-}D(CD_3OD)]^{-4} + CH_3CHO \rightleftharpoons [(TSPP)Rh\text{-}CH(OD)CH_3(CD_3OD)]^{-4} \qquad (7)$$

$$[(TSPP)Rh\text{-}D(CD_3OD)]^{-4} + CH_2 = CH_2 \rightleftharpoons [(TSPP)Rh\text{-}CH_2CH_2D(CD_3OD)]^{-4} \qquad (8)$$

The reaction of CO with **4** to produce the formyl complex (eq 6) achieves a ^1H NMR measurable equilibrium ($K_{6(298K)} = 3.0 \times 10^3$; $\Delta G°_{6(298K)} = -4.7$ (0.1) kcal mol^{-1}) (Table 1) which is the same $\Delta G°$ value as that measured for the addition of rhodium hydride [(TSPP)Rh-D] with CO to give a formyl complex in water.[15,16]

Scheme 4. Reactions of (TSPP)Rh(III) with Styrene or Methyl Acrylate in Methanol

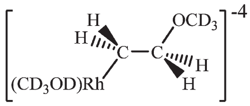
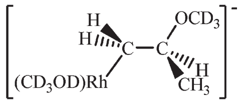
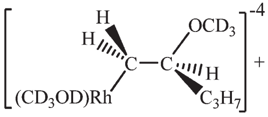
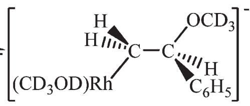
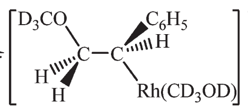
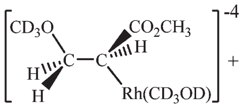


Addition reactions of the rhodium hydride **4** with both unactivated alkene hydrocarbons and activated vinyl olefins like styrene and methyl acrylate exclusively give organo-rhodium complexes corresponding to anti-Markovnikov regioselectivity which places rhodium on the terminal primary carbon (eq 9). The regioselectivities observed for addition of rhodium hydride (Rh-D) with olefins in methanol are identical to those previously observed for the analogous processes in water.[16]

$$[(TSPP)Rh\text{-}D(CD_3OD)]^{-4} + CH_2 = CHY \rightleftharpoons [(TSPP)Rh^{III}\text{-}CH_2CH_2Y(CD_3OD)]^{-4} \qquad (9)$$

$$Y = H, \text{alkyl}, C_6H_5, C(O)OCH_3$$

Table 3. Directly Measured Equilibrium constants (K_n) and $\Delta G°$ (kcal mol^{-1}) Values for the Reactions of $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ with olefins in CD_3OD (T = 298 K)

$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**) Reactions	K_n	$\Delta G°_n$
21) **1**+ $CH_2{=}CH_2 \rightleftharpoons$  + D^+ (**11**)	$K_{21} = 8.2(0.2) \times 10^{-3}$	2.8 (0.1)
22) **1**+ $CH_2{=}CHCH_3 \rightleftharpoons$  + D^+ (**12**)	$K_{22} = 1.6(0.3) \times 10^{-2}$	2.4 (0.1)
23) **1**+ $CH_2{=}CHC_3H_7 \rightleftharpoons$  + D^+ (**13**)	$K_{23} = 9.3(0.9) \times 10^{-4}$	4.1 (0.1)
24) **1**+ $CH_2{=}CHC_6H_5 \rightleftharpoons$  + D^+ (**14**)	$K_{24} = 2.0(0.2) \times 10^{-4}$	5.0 (0.1)
25) **1**+ $CH_2{=}CHC_6H_5 \rightleftharpoons$  + D^+ (**17**)	$K_{25} = 4.3(0.8) \times 10^{-4}$	4.6 (0.1)
26) **1**+ $CH_2{=}CHCO_2CH_3 \rightleftharpoons$  + D^+ (**18**)	$K_{26} = 6.2(0.6) \times 10^{-2}$	1.6 (0.1)

Reaction of $[(TSPP)Rh^{I}(CD_3OD)]^{-5}$ with CH_3I and $[(TSPP)Rh^{III}(CD_3OD)]^{-3}$ in Methanol. The rhodium(I) complex $[(TSPP)Rh^{I}(CD_3OD)]^{-5}$ (**5**) retains the properties of a nucleophile in methanol in spite of the fact that methanol is both a donor and a hydrogen bonding medium. This is illustrated by the immediate reaction of **5** with CH_3I to form a rhodium methyl complex $[(TSPP)Rh^{III}\text{-}CH_3(CD_3OD)]^{-4}$ (**9**) (eq 10). At acidic conditions ($[D^+] > 10^{-6}$ M) where the rhodium hydride is the predominant species, the reaction with CH_3I to form **9** occurs very slowly because of the low level of heterolytic Rh−H dissociation in methanol.

$$[(TSPP)Rh^{I}(CD_3OD)]^{-5} + CH_3I \rightleftharpoons [(TSPP)Rh^{III}\text{-}CH_3(CD_3OD)]^{-4} + I^- \qquad (10)$$

$[(TSPP)Rh^{I}(CD_3OD)]^{-5}$ also reacts with methanol solutions of $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**) to produce an equilibrium distribution with a $Rh^{II}{-}Rh^{II}$ bonded dimer $[(TSPP)Rh^{II}(CD_3OD)]_2^{-8}$ (**10**) (eq 11).

$$[(TSPP)Rh^{I}(CD_3OD)]^{-5} + [(TSPP)Rh^{III}(CD_3OD)_2]^{-3} \rightleftharpoons [(TSPP)Rh^{II}(CD_3OD)]_2^{-8} + CD_3OD \qquad (11)$$

The rhodium(II) dimer(**10**) never becomes the majority species but achieves a ^1H NMR observable concentration in a narrow range of pD (pD 7.8−8.2). The $Rh^{II}{-}Rh^{II}$ bonded dimer **10** is recognized in solution by the set of characteristic widely spread porphyrin phenyl ^1H NMR resonances that have been previously reported for ^1H NMR spectra of $[(por)Rh^{II}]_2$ complexes[17,25] and other metal−metal bonded face to face dimers.[26]

Equilibrium Thermodynamics for Reactions of $[(TSPP)Rh^{III}]$ Complexes with Hydrogen in Methanol. Methanol solutions of rhodium(III) tetra(*p*-sulfonatophenyl) porphyrin $[(TSPP)Rh^{III}]$ complexes with methanol and methoxide axial ligands react with dihydrogen H_2/D_2 to form an equilibrium distribution of six rhodium species including a rhodium hydride, rhodium(I) anion, rhodium(II) dimer, and three rhodium(III) methanol/methoxide complexes (Scheme 3). By adjusting the D^+ and dihydrogen concentrations it is possible to produce ^1H NMR measurable equilibria of [(TSPP)Rh] species in methanol. A series of equilibrium constants for most of the processes in Scheme 3 were measured directly by ^1H NMR and are summarized in Table 1. The measured thermodynamic values found in Table 1 were used to derive additional thermodynamic values for reactions 12−19, which are listed in Table 2.

Reactions of $(TSPP)Rh^{III}$ Species with Olefins in Methanol. Rhodium methanol/methoxide complexes (**1**, **2**, and **3**) in methanol react with olefins to produce

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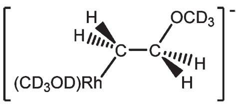
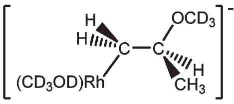
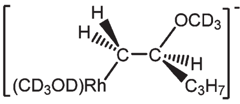
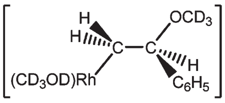
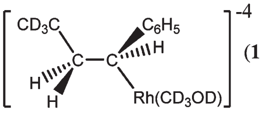
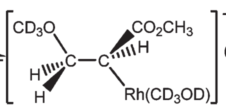
(25) Wayland, B. B.; Van Voorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039–4042.

(26) Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 7030–7032.

Table 4. Equilibrium Constants (K_n) and $\Delta G°$ (kcal mol^{-1}) Values for Reactions of $[(TSPP)Rh^{III}\text{-}OCD_3(CD_3OD)]^{-4}$ with Olefins in CD_3OD Derived from Table 3 (T = 298 K)

$[(TSPP)Rh^{III}\text{-}OCD_3(CD_3OD)]^{-4}$ (**2**) Reactions	K_n	$\Delta G°_n$
27) **2** + $CH_2{=}CH_2$ ⇌  (**11**)	K_{27} = K_{21}/K_1 = $1.2(0.2) \times 10^5$	-6.9
28) **2** + $CH_2{=}CHCH_3$ ⇌  (**12**)	K_{28} = K_{22}/K_1 = $2.3(0.3) \times 10^5$	-7.3
29) **2** + $CH_2{=}CHC_3H_7$ ⇌  (**13**)	K_{29} = K_{23}/K_1 = $2.9(0.3) \times 10^4$	-6.1
30) **2** + $CH_2{=}CHC_6H_5$ ⇌  (**14**)	K_{30} = K_{24}/K_1 = $2.8(0.3) \times 10^3$	-4.7
31) **2** + $CH_2{=}CHC_6H_5$ ⇌  (**17**)	K_{31} = K_{25}/K_1 = $6.2(0.7) \times 10^3$	-5.2
32) **2** + $CH_2{=}CHCO_2CH_3$ ⇌  (**18**)	K_{32} = K_{26}/K_1 = $9.0(0.9) \times 10^5$	-8.1

rhodium β-methoxyalkyl complexes. Formation of the β-alkoxyalkyl rhodium complexes ($[(TSPP)Rh^{III}\text{-}CH_2CH(R)(OCD_3)(CD_3OD)]^{-4}$) in CD_3OD is followed by the appearance of characteristic high field ^1H NMR resonances that result from porphyrin ring current effects on the hydrogens in groups bonded to the rhodium center (Figure 6). Formation of the β-alkoxyalkyl species in CH_3OH and then dissolution in CD_3OD permits observation of the $-OCH_3$ protons by ^1H NMR (δ = 1.47 ppm) which very slowly decline in intensity by exchange of methoxide groups with CD_3OD (Figure 6, inset). Reactions of alkenes including ethene, propene,and pentene with $[(TSPP)Rh^{III}\text{-} OCD_3(CD_3OD)]^{-4}$ produce regiospecific products with rhodium attached exclusively to the terminal primary carbon $[(TSPP)Rh^{III}\text{-}CH_2\text{-} CH_2(OCD_3)(CD_3OD)]^{-4}$ (**11**), $[(TSPP)Rh^{III}\text{-}CH_2CH(OCD_3)CH_3(CD_3OD)]^{-4}$ (**12**), and $[(TSPP)Rh^{III}\text{-}CH_2-CH(OCD_3)C_3H_7(CD_3OD)]^{-4}$ (**13**), (eqs 21−23). Vinyl acetate which has a π-donor methoxide substituent also reacts with **1** to give the regioselectivity observed for alkenes $[(TSPP)Rh\text{-}CH_2CH(OCD_3)(OC(O)CH_3)(CD_3OD)]$ (**15**). Reactions of **1** with olefins activated by π-electron withdrawing groups such as styrene and methyl acrylate initially produce a kinetic product where rhodium adds to the terminal carbon, but then slowly convert to an equilibrium distribution with the thermodynamically preferred products where rhodium is attached to the internal carbon and methoxide is on the terminal primary carbon center (eqs 24−26; Scheme 4). The kinetically preferred initial product (eq 24) places the bulky rhodium porphyrin at the least sterically encumbered terminal carbon, but the thermodynamically preferred isomer places rhodium at the internal carbon center (eq 25).

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} + CH_2{=}CH_2 \rightleftharpoons [(TSPP)Rh^{III}\text{-}CH_2CH_2(OCD_3)(CD_3OD)]^{-4} + D^+ \quad (21)$$

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} + CH_2{=}CHCH_3 \rightleftharpoons [(TSPP)Rh^{III}\text{-}CH_2CHCH_3(OCD_3)(CD_3OD)]^{-4} + D^+ \quad (22)$$

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} + CH_2{=}CHC_3H_7 \rightleftharpoons [(TSPP)Rh^{III}\text{-}CH_2CHC_3H_7(OCD_3)(CD_3OD)]^{-4} + D^+ \quad (23)$$

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} + CH_2{=}CHC_6H_5 \rightleftharpoons [(TSPP)Rh^{III}\text{-}CH_2CH(OCD_3)C_6H_5(CD_3OD)]^{-4} + D^+ \quad (24)$$

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} + CH_2{=}CHC_6H_5 \rightleftharpoons [(TSPP)Rh^{III}\text{-}CH(C_6H_5)CH_2(OCD_3)(CD_3OD)]^{-4} + D^+ \quad (25)$$

$$[(TSPP)Rh^{III}(CD_3OD)_2]^{-3} + CH_2{=}CHCO_2CH_3 \rightleftharpoons [(TSPP)Rh^{III}\text{-}CH(CO_2CH_3)\text{-}CH_2(OCD_3)(CD_3OD)]^{-4} + D^+ \quad (26)$$

Thermodynamic preference for rhodium bonding to the internal carbon results from better stabilization of negative charge, and this electronic effect more than compensates for the larger destabilizing steric effect for this isomer.[27] The kinetic and thermodynamic regioselectivities for addition of the Rh−OH unit in water[17] and Rh-OCD_3 unit in methanol are the same for all olefins studied.

Equilibrium Thermodynamics for Rhodium(III) Reactions with Olefins in CD_3OD. Equilibrium constants for reactions of $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**) with olefins in CD_3OD were directly evaluated by ^1H NMR along with measurement of the D^+ concentration (pD = 4−6, 298 K). The equilibrium constants and free energy changes for reactions of **1** with olefins (reactions 21−26) are summarized in Table 3, and values derived for reactions of $[(TSPP)Rh^{III}(ODC_3)(CD_3OD)]^{-4}$ are in Table 4.

Reactions between $[(TSPP)Rh^{III}\text{-}OCD_3(CD_3OD)]^{-4}$ (**2**) and olefins to form rhodium β-methoxyalkyl complexes are relatively fast and thermodynamically highly favorable. The reactions proceed effectively to completion which prohibits direct evaluation of the equilibrium constants by ^1H NMR. Equilibrium thermodynamics between **2** and olefins however can be evaluated indirectly by using the measured thermodynamic values for reactions of the rhodium bis-methanol complex **1** with olefins and the acid dissociation constant of **1** (K_1). The derived thermodynamic values for addition of Rh-OCD_3 unit to olefins (reactions 27−32) are summarized in Table 4. The free energy changes for adding the Rh-OCD_3 unit to alkene hydrocarbons in methanol are very similar to the previously reported values for addition of the Rh-OD unit to the alkenes in water.[17] The average difference for the $\Delta G°$ values favors the Rh-OCD_3 addition to alkenes by about 1.0 kcal mol^{-1}. One specific example is the addition of the (TSPP)Rh-OCD_3 to ethene in methanol (eq 27; $\Delta G°_{27} = -6.9(0.1)$ kcal mol^{-1}) which compares to a $\Delta G°_{(298K)}$ of − 5.9(0.1) kcal mol^{-1} for the addition of the (TSPP)Rh-OD unit to ethene in water.[17]

Summary and Conclusions

The broad conclusion from reactivity and thermodynamic studies is that the general behavior of rhodium porphyrins is remarkably similar in methanol and water but that differences in ligand binding and solvation energies have a significant impact on the thermodynamic parameters. Methanol soluble rhodium(III) porphyrins $[(TSPP)Rh^{III}]$ in methanol establish equilibria between bis-methanol (**1**), monomethoxide monomethanol (**2**), and bis-methoxide (**3**) complexes, which parallel the analogous mono- and bis-hydroxide complexes in water.[15] The methanol complexes are more acidic than the water complexes which is a manifestation of larger free energy change for CD_3O^- substituting for coordinated CD_3OD ($\Delta G°_{(298K)} = -14.8$ kcal mol^{-1}) when compared to OD^- substituting for coordinated water ($\Delta G°_{(298K)} = -11.7$ kcal mol^{-1}) (Scheme 1). In strongly basic methanol (CD_3OD) (pD > 11), the $(TSPP)Rh^{III}\text{-}OCH_3$ complexes are reduced to a rhodium(I) complex which is a reaction that cannot occur with water or benzene. The rhodium(III) species in methanol (pD < 8) react with hydrogen (D_2) to form a hydride complex $[(TSPP)Rh\text{-}D(CD_3OD)]^{-4}$ that behaves as a weak acid ($K_{(298K)} = 1.1 \times 10^{-9}$; $\Delta G°_{(298K)} = 12.2(0.1)$ kcal mol^{-1}). The larger acid dissociation constant for (TSPP)Rh-D in water ($K_{a(298K)} = 8.0 \times 10^{-8}$) compared to methanol can be explained in terms of the slightly larger solvation energy for protons in water compared to methanol ($\Delta(\Delta G°) = -2.4$ kcal mol^{-1}).[24] The rhodium hydride $[(TSPP)Rh\text{-}D(CD_3OD)]^{-4}$ in methanol reacts with CO, acetaldehyde, and olefins to produce formyl, α-hydroxyethyl, and alkyl complexes respectively which are also prominent substrate reactions in water[16] and benzene.[28] Compensating solvation energies for reactants and products yields equal thermodynamics to produce a rhodium formyl complex from reactions of the rhodium hydride with CO in methanol and water ($K_{(298K)} = 3.0 \times 10^3$, $\Delta G°_{(298K)} = -4.7$ kcal mol^{-1}) and very nearly equal thermodynamics for the analogous reaction in benzene.[28] Addition of rhodium hydride $[(TSPP)Rh^{III}\text{-}D(CD_3OD)]^{-4}$ to olefins invariably forms the anti-Markovnikov product which places the rhodium porphyrin unit on the less hindered terminal primary carbon center. The rhodium methoxide unit in $[(TSPP)Rh^{III}\text{-}OCD_3(CD_3OD)]^{-4}$ reacts with alkene hydrocarbons and vinyl acetate to give β-methoxyalkyl complexes where rhodium is attached to the terminal primary carbon, but reaction with olefins that are activated by π-acceptor groups results in placing the rhodium prophyrin at the more sterically hindered interior carbon center (Tables 3 and 4). The regioselectivity and equilibrium thermodynamics for addition of the rhodium methoxide unit in $[(TSPP)Rh^{III}\text{-}OCD_3(CD_3OD)]^{-4}$ to olefins in methanol complexes parallel the reported results for olefin reactions of the analogous hydroxide complex $[(TSPP)Rh^{III}\text{-}OD(D_2O)]^{-4}$ in water.[17] Continuing thermodynamic studies of cobalt, rhodium, and iridium porphyrin substrate reactions are directed toward achieving direct comparisons of bond dissociation free energies (BDFE) for group 9 metalloporphyrins in diverse solvent media.

Experimental Section

Materials and Instruments. The sodium salt of free-base tetra(*p*-sulfonatophenyl)porphyrin $Na_4[(TSPP)H_2]\cdot xH_2O$ was purchased from Sigma Adlrich and used as received without any further purification. The rhodium complex $Na_3[(TSPP)Rh^{III}\text{-}(CH_3OH)_2]$ was synthesized using a literature method.[29] Methanol-d_4 (CD_3OD, 99.8 D%) was purchased from Cambridge Isotope Laboratories, Inc., and used without further purification. Sodium methoxide ($NaOCH_3$) and trifluoromethanesulfonic acid-*d* (CF_3SO_3D) were purchased from Aldrich and dissolved in CD_3OD to make 0.01 M stock solutions. 3-Trimethylsilyl-1-propanesulfonic acid sodium salt $(CH_3)_3SiCH_2\text{-}CH_2CH_2SO_3Na\cdot H_2O$ was purchased from Eastman Kodak Company and used as an internal standard for the calibration of chemical shift and intensity integration of species in CD_3OD. Reagent grade of hydrogen, carbon monoxide, ethene, and propene were purchased from Matheson Gas Products. Pentene, hexene, styrene, methyl acrylate, and vinyl acetate were purchased from Aldrich and used as received. ^1H NMR spectra were obtained on a Bruker AC-300 or AM-500 spectrometer interfaced to an Aspect 300 computer at ambient temperature. pH measurements were performed on a Hanna 212 pH meter connected with a Thermo micro-electrode for NMR cells.

General Procedures. To a 5 mm NMR tube with vacuum adapter, 25 μL of a 5×10^{-3} M aqueous solution of 3-trimethylsilyl-1-propanesulfonic acid sodium salt was added followed by a

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[27] Harvey, J. N. *Organometallics* **2001**, *20*, 4887–4895.

[28] Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659–3663.

[29] Krishnamurthy, M. *Inorg. Chim. Acta* **1977**, *25*, 215–218.

drop of ~5 × 10^{-3} M aqueous solution of $Na_3[(TSPP)Rh^{III}(CH_3OH)_2]$. Water was then removed from the NMR tube followed by addition of 0.4 mL of CD_3OD. To this methanol solution of $(TSPP)Rh^{III}$, portions of 0.01 M $NaOCH_3$ in CD_3OD or 0.01 M CF_3SO_3D in CD_3OD were added to adjust the acidity of the sample. At the desired pH, substrates were introduced to the NMR tube and reactions are followed by ^1H NMR. Resonance for methyl hydrogens of 3-trimethylsilyl-1-propanesulfonic acid sodium salt was set at 0 ppm, and other chemical shifts were referenced to it. Concentration of each species in solution was determined by comparison with the concentration of 3-trimethylsilyl-1-propanesulfonic acid sodium salt. Proton NMR spectra were used to identify solution species and determine the distribution of species at equilibrium. When a reaction reached equilibrium, resonances in the ^1H NMR spectrum were integrated and the deuterium ion concentration was measured. For reaction with gases such as carbon monoxide, solubility data in methanol at various gas pressures were used to determine the gas concentration in CD_3OD.[30]

Measurement of $[D^+]$ in CD_3OD. The glass electrode of a pH meter responds as efficiently to deuterium ions as it does with hydrogen ions, but the magnitude of the response is different.[31] For identical solutions, the $p(\alpha_D)$ values differ from pH readings by a constant of 0.447 (α_D = activity of D^+, $p(\alpha_D) - pH = 0.447$)[32] when α_D was measured in molal concentration. Conversion to molar units yields the relationship between pH readings and actual pD values as $pD = pH_{reading} + 0.41$ at 25 °C.

Acid Dissociation Constants for $(TSPP)Rh^{III}(CD_3OD)_2$ and $(TSPP)Rh^{III}(OCD_3)(CD_3OD)$ in CD_3OD. At a series of $[D^+]$, the chemical shifts of the porphyrin pyrrole hydrogen were recorded. The single resonance at each pD manifests the fast exchange among $[(TSPP)Rh^{III}(CD_3OD)_2]^{-3}$ (**1**), $[(TSPP)Rh^{III}(OCD_3)(CD_3OD)]^{-4}$ (**2**), and $[(TSPP)Rh^{III}(OCD_3)_2]^{-5}$ (**3**). The chemical shift of this single peak is the mole fraction averaged signal of (**1**), (**2**), and (**3**). Fitting into the $\delta_{\mathbf{1,2,3}} = (K_1K_2\delta_{\mathbf{3}} + K_1[D^+]\delta_{\mathbf{2}} + [D^+]^2\delta_{\mathbf{1}})/(K_1K_2 + K_1[D^+] + [D^+]^2)$ gives $K_1 = 6.9(0.2) \times 10^{-8}$ and $K_2 = 5.8(0.3) \times 10^{-13}$.

Reactions of $(TSPP)Rh^{III}$ with Ethene, Propene, and Pentene in Methanol. $[(TSPP)Rh\text{-}CH_2CH(OCD_3)R(CD_3OD)]^{-4}$ was formed right after vacuum transfer of alkyl olefins (R = H, CH_3, and $CH_2CH_2CH_3$) into vacuum adapted NMR tubes containing CD_3OD solutions of $[(TSPP)Rh(OCD_3)(CD_3OD)]^{-4}$.

$[(TSPP)Rh\text{-}CH_2CH_2(OCD_3)(CD_3OD)]^{-4}$ (11). ^1H NMR (300 MHz, CD_3OD) δ (ppm): 8.83 (s, 8H, pyrrole), 8.40 (d, 4H, *o*-phenyl, $J_{^1H-^1H} = 7.2$ Hz), 8.29 (d, 4H, *o*-phenyl, $J_{^1H-^1H} = 7.2$ Hz), 8.24 (d, 4H, *m*-phenyl, $J_{^1H-^1H} = 7.2$ Hz), 8.20 (d, 4H, *m*-phenyl, $J_{^1H-^1H} = 7.2$ Hz), −5.76 (br t, 2H(α)), −2.52, (t, 2H(β), $J_{^1H-^1H} = 6$ Hz).

$[(TSPP)Rh\text{-}CH_2CH(OCD_3)CH_3(CD_3OD)]^{-4}$ (12). ^1H NMR (300 MHz, CD_3OD) δ (ppm): 8.83 (s, 8H, pyrrole), 8.40 (d, 4H, *o*-phenyl, $J_{^1H-^1H} = 7.2$ Hz), 8.29 (d, 4H, *o*-phenyl, $J_{^1H-^1H} = 7.2$ Hz), 8.24 (d, 4H, *m*-phenyl, $J_{^1H-^1H} = 7.2$ Hz), 8.20 (d, 4H, *m*-phenyl, $J_{^1H-^1H} = 7.2$ Hz), −5.70 (m, $1H_A$(α)), −5.76 (m, $1H_B$-(α)), −2.50 (m, 1H(β)), −1.97 (d, 3H(γ), 6 Hz).

$[(TSPP)Rh\text{-}CH_2CH(OCD_3)C_3H_7(D_2O)]^{-4}$ (13). ^1H NMR (300 MHz, CD_3OD) δ (ppm): 8.68 (8H, pyrrole), 8.50−8.10 (16H, phenyl), −5.96 (m, $1H_A$(α)), −5.75 (m, $1H_B$(α)), −3.02 (m, 1H(β)), −2.66 (m, $1H_A$(γ)), −1.77 (m, $1H_B$(γ)), −0.72 (m, 2H(δ)), −0.31 (t, 3H(ε)).

Reactions of $[(TSPP)Rh^{III}]^{-3}$ with Styrene and Methyl Acrylate. Mixing methanol solutions of (**2**) with styrene and methyl acrylate initially produces $[(TSPP)Rh\text{-}CH_2CH(OCD_3)C_6H_5(CD_3OD)]^{-4}$(**14**) and $[(TSPP)RhCH_2CH(OCD_3)CO_2\ CH_3(D_2O)]^{-4}$ (**16**) as the kinetically preferred isomers which subsequently rearrange to produce $[(TSPP)Rh\text{-}CH(C_6H_5)CH_2\text{-}OCD_3(CD_3OD)]^{-4}$ (**17**) and $[(TSPP)Rh\text{-}CH(CO_2CH_3)CH_2\text{-}OCD_3(CD_3OD)]^{-4}$ (**18**) as the thermodynamically preferred products.

$[(TSPP)Rh\text{-}CH(CO_2CH_3)CH_2\text{-}OCD_3(CD_3OD)]^{-4}$ (18). ^1H NMR (250 MHz, CD_3OD) δ (ppm): 8.90 (s, 8H, pyrrole), 8.47−8.20(m, 16H, phenyl), 1.86 (s, 1H, OCH_3), −1.79 (t, 1H, $CH(CO_2CH_3)$, $^3J_{^1H-^1H} = 11.2$ Hz), −3.06 (d of d, 1H, CH_2, $^3J_{^1H-^1H} = 4.1$ Hz, $^2J_{^1H-^1H} = 11.2$ Hz), −4.9 (d of t, 1H, CH_2, $^3J_{^1H-^1H} = 4.1$ Hz, $^2J_{^1H-^1H} = 11.2$ Hz).

$[(TSPP)Rh\text{-}CH_2CH(OCD_3)C_6H_5(CD_3OD)]^{-4}$ (14). ^1H NMR (360 MHz, CD_3OD) δ (ppm): 8.80 (s, 8H, pyrrole), 8.46−8.20(m, 16H, phenyl), −1.95 (m, 1H, CH_2), −5.15 (m, 1H, CH_2), −5.65 (m, 1H, CH). $[(TSPP)Rh\text{-}CH(C_6H_5)CH_2\text{-}OCD_3(CD_3OD)]^{-4}$: ^1H NMR (360 MHz, CD_3OD) δ (ppm): 8.80 (s, 8H, pyrrole), 8.46−8.20 (m, 16H, phenyl), −1.67 (m, 1H, CH_2), −2.97 (m, 1H, CH_2), −4.30 (m, 1H, CH).

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