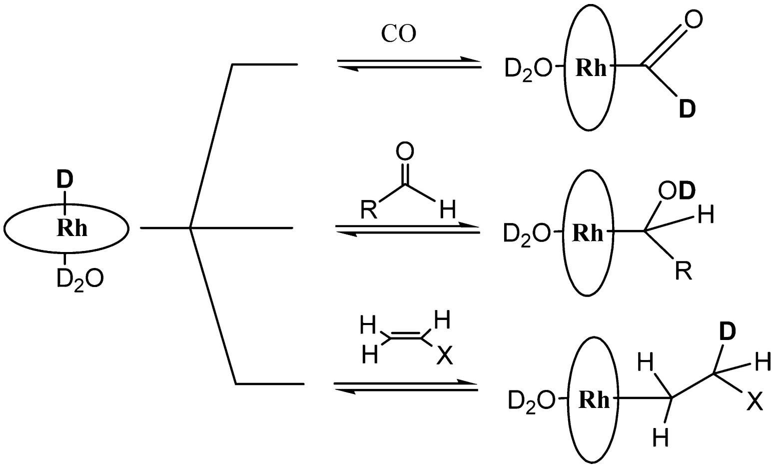
Article

Thermodynamics of Rhodium Hydride Reactions with CO, Aldehydes, and Olefins in Water: Organo-Rhodium Porphyrin Bond Dissociation Free Energies

Xuefeng Fu, and Bradford B. Wayland

J. Am. Chem. Soc., **2005**, 127 (47), 16460-16467• DOI: 10.1021/ja054548n • Publication Date (Web): 04 November 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
ARTICLES
Published on Web 11/04/2005

Thermodynamics of Rhodium Hydride Reactions with CO, Aldehydes, and Olefins in Water: Organo-Rhodium Porphyrin Bond Dissociation Free Energies

Xuefeng Fu and Bradford B. Wayland*

Contribution from the Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received July 8, 2005; E-mail: wayland@sas.upenn.edu

Abstract: Tetra(*p*-sulfonato-phenyl) porphyrin rhodium hydride ($[(TSPP)Rh-D(D_2O)]^{-4}$) (**1**) reacts in water (D_2O) with carbon monoxide, aldehydes, and olefins to produce metallo formyl, α-hydroxyalkyl, and alkyl complexes, respectively. The hydride complex (**1**) functions as a weak acid in D_2O and partially dissociates into a rhodium(I) complex ($[(TSPP)Rh^{I}(D_2O)]^{-5}$) and a proton ($D^+$). Fast substrate reactions of **1** in D_2O compared to reactions of rhodium porphyrin hydride ((por)Rh−H) in benzene are ascribed to aqueous media promoting formation of ions and supporting ionic reaction pathways. The regioselectivity for addition of **1** to olefins is predominantly anti-Markovnikov in acidic D_2O and exclusively anti-Markovnikov in basic D_2O. The range of accessible equilibrium thermodynamic measurements for rhodium hydride substrate reactions is substantially increased in water compared to that in organic media through exploiting the hydrogen ion dependence for the equilibrium distribution of species in aqueous media. Thermodynamic measurements are reported for reactions of a rhodium porphyrin hydride in water with each of the substrates, including CO, H_2CO, CH_3CHO, $CH_2{=}CH_2$, and sets of aldehydes and olefins. Reactions of rhodium porphyrin hydrides with CO and aldehydes have nearly equal free-energy changes in water and benzene, but alkene reactions that form hydrophobic alkyl groups are substantially less favorable in water than in benzene. Bond dissociation free energies in water are derived from thermodynamic results for (TSPP)Rh-organo complexes in aqueous solution for Rh−CDO, Rh−CH(R)OD, and $Rh-CH_2CH(D)R$ units and are compared with related values determined in benzene.

Introduction

Exploring the scope and applications of organo-metallic transformations in water compared to those in more conventional organic media is a major current theme of transition-metal catalysis research.[1−8] One specific objective of this study is to provide a set of experimental equilibrium thermodynamic values for reactions of a rhodium porphyrin hydride ((por)Rh−H) with carbon monoxide, formaldehyde, and ethene in water for quantitative comparisons with related measurements in benzene and also as thermodynamic bench marks for late transition-metal hydride addition reactions. The reactivity patterns for rhodium porphyrin hydrides ((por)Rh−H) are typical of late transition-metal hydrides but display an exceptional breadth of observable substrate reactions.[7−13] Thermodynamic studies on a common set of processes in organic and aqueous media provide quantitative criteria for comparing substrate reactivity patterns and aid in identifying the origins of the factors contributing to medium effects. These classes of metal hydride reactions with unsaturated substrates play a central role in many of the most important catalytic processes, such as hydrogenations, hydroformylation, and related transformations, yet thermodynamic studies for these types of reactions remain sparse. Thermodynamic studies for rhodium porphyrin reactions with substrates such as H_2, CH_4, CO, olefins, and aldehydes provide one of the most extensive

---

(1) (a) Cornils, B.; Kuntz, E. G. Chapter 6. In *Aqueous-Phase Organometallic Catalysis, Concept and Application*; Cornils, B., Herrmann, A. W., Eds.; Wiley-VCH: New York, 1998. (b) Lucey, D. W.; Helfer, D. S.; Atwood, J. D. *Organometallics* **2003**, *22*, 826. (c) Lucey, D. W.; Atwood, J. D. *Organometallics* **2002**, *21*, 2481.

(2) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2181. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961.

(3) (a) Lynn, D. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 3187. (b) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601.

(4) (a) Joo, F. *Acc. Chem. Res.* **2002**, *35*, 738. (b) Joo, F.; Kovacs, J.; Benyei, A. C.; Nadasdi, L.; Laurenczy, G. *Chem.−Eur. J.* **2001**, *7*, 193. (c) Joo, F.; Kovacs, J.; Benyei, A. C.; Katho, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 969. (d) Csabai, P.; Joo, F. *Organometallics* **2004**, *23*, 5640.

(5) (a) Kovacs, J.; Todd, T. D.; Reibenspies, J. H.; Joo, F.; Darensbourg, D. J. *Organometallics* **2000**, *19*, 3963. (b) Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* **1994**, *33*, 200. (c) Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H. *Organometallics* **1992**, *11*, 1990. (d) Parkins, A. W. In *Aqueous Organometallic Chemistry and Catalysis*; Horvath, I. T., Joo, F., Eds.; Kluwer Academic Publisher: Dordrecht, 1997; Vol. 11.

(6) (a) Frost, B. J.; Mebi, C. A. *Organometallics* **2004**, *23*, 5317. (b) Vancheesan, S.; Jesudurai, D. *Catalysis* **2002**, 311. (c) Kundu, A.; Buffin, B. P. *Organometallics* **2001**, *20*, 3635.

(7) Fu, X. F.; Basickes, L.; Wayland, B. B. *Chem. Commun.* **2003**, 520.

(8) Fu, X. F.; Wayland, B. B. *J. Am. Chem. Soc.* **2004**, *126*, 2623.

(9) Wayland, B. B.; Duttaahmed, A.; Woods, B. A. *Chem. Commun.* **1983**, 142.

(10) Wayland, B. B.; Woods, B. A.; Minda, V. M. *Chem. Commun.* **1982**, 634.

(11) Wayland, B. B.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302.

(12) Wayland, B. B.; VanVoorhees, S. L.; Wilker, C. *Inorg. Chem.* **1986**, *25*, 4039.

(13) Coffin, V. L.; Brennen, W.; Wayland, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 6063.

10.1021/ja054548n CCC: $30.25

sets of organo-transition-metal bond energies in organic media.[13−19] Sulfonation of the phenyl groups of tetraphenyl porphyrin derivatives provides water-soluble rhodium porphyrin complexes for thermodynamic studies in aqueous media that are closely related to the benzene-soluble analogues.

Each of the (por)Rh−H reactions with unsaturated substrates, including carbon monoxide, that were first observed in organic media has an analogous process in water.[7] Prior equilibrium thermodynamic studies for reactions of (por)Rh−H complexes with unsaturated substrates in organic media have been limited to carbon monoxide[12,19] and four-carbon or larger aldehydes[12] because smaller aldehydes and vinyl olefins have equilibrium constants that are too large for convenient direct determination by ^{1}H NMR. This restriction is largely overcome in aqueous media where the equilibrium distribution of species in solution can be tuned by the pH dependence. Evaluation of equilibrium constants for reactions of dihydrogen with rhodium(III) porphyrin complexes in water has established a solid foundation for equilibrium thermodynamic studies for a wide range of additional substrate reactions in aqueous media.[8] This article reports on the reactivity and equilibrium thermodynamic studies in water for CO, H_2CO, $CH_2{=}CH_2$, and sets of aldehydes and olefins with tetra(*p*-sulfonato-phenyl) porphyrin rhodium hydride ($[(TSPP)Rh{-}D(D_2O)]^{-4}$) (**1**) and the rhodium(I) derivative ($[(TSPP)Rh^I(D_2O)]^{-5}$) (**2**).

Results and Discussion

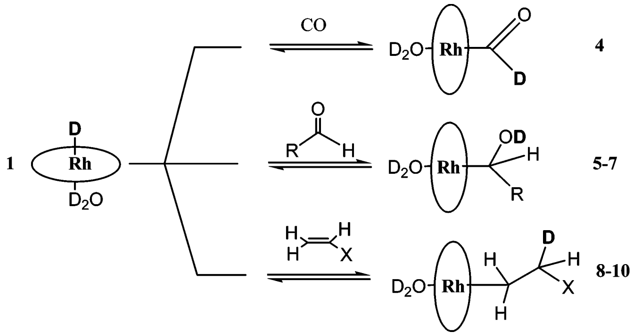
The primary focus of this study was to evaluate equilibrium thermodynamic values for reactions of CO, H_2CO, $CH_2{=}CH_2$, and related substrates with a rhodium porphyrin hydride in aqueous solution. The hydride complex ($[(TSPP)Rh{-}D(D_2O)]^{-4}$) (**1**) is formed in D_2O by reaction of dihydrogen (H_2/D_2) with $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$ (**3**) (eq 1).[8] The hydride (**1**) is a weak acid in D_2O (eq 2) (K_2 (298 K) = 8.0(0.5) × 10^{-8}).[8]

$$1)\quad [(TSPP)Rh^{III}(D_2O)_2]^{-3} + D_2 \rightleftarrows [(TSPP)Rh{-}D(D_2O)]^{-4} + D^+ + D_2O$$

$$2)\quad [(TSPP)Rh{-}D(D_2O)]^{-4} \rightleftarrows [(TSPP)Rh^I(D_2O)]^{-5} + D^+$$

Acid dissociation equilibria for **1** and D_2O[20] provide a convenient means for tuning the equilibrium distribution of rhodium porphyrin species in D_2O through varying the hydrogen ion concentration (Table 1, eqs 2 and 3). This strategy is used to evaluate equilibrium constants for substrate reactions of the hydride (**1**) and the rhodium(I) complex (**2**) that fall outside the range accessible for direct measurement by ^{1}H NMR integration.

Scheme 1. Reactivity Patterns for a Rhodium Porphyrin Hydride in D_2O



Reactions of the rhodium hydride ($[(TSPP)Rh{-}D(D_2O)]^{-4}$) (**1**) with carbon monoxide, aldehydes, and vinyl olefins in D_2O, respectively, produce formyl (Rh−CDO), α-hydroxyalkyl (Rh−CH(OD)R), and alkyl ($Rh{-}CH_2CH(D)X$) complexes (Scheme 1).

Aqueous solutions of the rhodium hydride (**1**) in D_2O react with CO (P_{CO} = 0.2−0.7 atm) to produce equilibrium distributions with a formyl complex $[(TSPP)Rh{-}CDO(D_2O)]^{-4}$ (**4**) (Table 1, eq 4). The formyl complex is clearly identified by ^{13}C NMR of **4** prepared by reaction of **1** with ^{13}CO. The ^{13}C NMR for the formyl group of $[(TSPP)Rh{-}^{13}CDO(D_2O)]^{-4}$ in D_2O ($\delta_{^{13}CHO}$ = 218.7 ppm) appears as an approximate 1:2:2:1 quartet that results from the near equal coupling of D and ^{103}Rh with ^{13}C ($2J_{^{13}C-D} + J_{^{103}Rh-^{13}C} = 78$ Hz). When the ^{1}H derivative of **4** ($[(TSPP)Rh{-}^{13}CHO]^{-4}$) is formed in H_2O, the ^{13}C NMR of the $Rh{-}^{13}CHO$ unit manifests a ^{13}C−H coupling constant of 166 Hz which gives a calculated value for $J_{^{13}C-D}$ of 25.5 Hz (($J_{^{13}C-H}/J_{^{13}C-D}$) = 6.51 Hz), and thus, a value of 27 Hz is derived for $J_{^{103}Rh-^{13}C}$. Reduction of the ^{13}C−H coupling constant from 200 Hz for the $(por)Rh{-}^{13}CHO$ unit in benzene[9,11,12] to 166 Hz in water is an indication that the carbonyl carbon has become more like an sp^3 hybridized center. Water interacting with the formyl group is clearly producing a significant perturbation on the carbonyl unit.

Aldehydes (RCHO) invariably react with **1** and **2** in D_2O with regioselectivity to form α-hydroxyalkyl complexes ($[(TSPP)Rh{-}CH(OD)R(D_2O)]^{-4}$) exclusively in preference to alkoxides ($[(TSPP)Rh{-}OCH_2R(D_2O)]^{-4}$). Olefin substrates ($CH_2{=}CH(X)$) usually react with **1** in acidic D_2O to give anti-Markovnikov addition to form $[(TSPP)Rh{-}CH_2CH(D)X(D_2O)]^{-4}$ as the only ^{1}H NMR observed product, but reaction of the hydride **1** in acidic D_2O with $CH_2{=}CHC_6H_4SO_3Na$ is exceptional in producing comparable quantities of two isomers associated with both anti-Markovnikov ($[(TSPP)Rh{-}CH_2CH(D)X(D_2O)]^{-4}$) and Markovnikov ($[(TSPP)Rh{-}CH(CH_2D)X(D_2O)]^{-4}$) addition products. The olefins in contact with **1** in acidic D_2O are sequentially deuterated at the secondary and then the primary alkene carbon positions. Solutions of **1** in basic D_2O predominantly contain the rhodium(I) complex (**2**) and react rapidly with electrophilically activated olefins ($CH_2{=}CHCO_2CH_3$ and $CH_2{=}CHC_6H_4SO_3Na$) to form, exclusively, the anti-Markovnikov addition products ($Rh{-}CH_2CH(D)X$). These basic D_2O solutions of **2** produce selective deuteration of the secondary olefin carbon to form $CH_2{=}CD(X)$.

Equilibrium Thermodynamic Studies for Reactions of $[(TSPP)Rh{-}D(D_2O)]^{-4}$ and $[(TSPP)Rh^I(D_2O)]^{-5}$ with CO, Aldehydes, and Olefins in Water. Effective equilibrium constants for reactions of $[(TSPP)Rh{-}D(D_2O)]^{-4}$ (**1**) and $[(TSPP)Rh^I(D_2O)]^{-5}$ (**2**) with CO, aldehydes, and olefins in D_2O

---

(14) Cui, W. H.; Wayland, B. B. *J. Am. Chem. Soc.* **2004**, *126*, 8266.
(15) Cui, W. H.; Zhang, X. P.; Wayland, B. B. *J. Am. Chem. Soc.* **2003**, *125*, 4994.
(16) (a) Wayland, B. B. *NATO ASI Ser., Ser. C* **1992**, *367*, 69. (b) Wayland, B. B.; Coffin, V. L.; Sherry, A. E.; Brennen, W. R. ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990; 148.
(17) Wayland, B. B. *Polyhedron* **1988**, *7*, 1545.
(18) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1989**, *111*, 5010.
(19) Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.
(20) Values obtained from: *J. Phys. Chem. Ref. Data*, **1982**, *11* (Suppl. 2). Standard state used: 298.15 K, 0.1 MPa.

Table 1. Equilibrium Constants (K_n) and $\Delta G°_n$ (kcal mol^{-1}) Measured for Reactions of $[(TSPP)Rh{-}D(D_2O)]^{-4}$ (**1**) with CO and Aldehydes in D_2O (298 K)

$[(TSPP)Rh{-}D(D_2O)]^{-4}$ (**1**) reactions	K_n	$\Delta G°_n$
2) $[Rh{-}D]^{-4}$ (**1**) $\rightleftarrows [Rh^I]^{-5}$ (**2**) $+ D^+$	$K_2 = 8.0\ (0.5) \times 10^{-8}$	$+9.7$ (0.1)
3) $D_2O \rightleftarrows OD^- + D^+$ (**3**)	$K_3 = 2.44 \times 10^{-17}$	$+22.6$
4) $[Rh{-}D]^{-4} + CO \rightleftarrows [Rh{-}CDO]^{-4}$ (**4**)	$K_4 = 3.0\ (0.3) \times 10^3$	-4.7 (0.1)
5) $[Rh{-}D]^{-4} + H_2CO \rightleftarrows [Rh{-}CH_2(OD)]^{-4}$ (**5**)	$K_5 = 4.6\ (0.4) \times 10^5$	-7.7 (0.1)
6) $[Rh{-}D]^{-4} + HC(O)CH_3 \rightleftarrows [Rh{-}CH(OD)CH_3]^{-4}$ (**6**)	$K_6 = 1.3\ (0.3) \times 10^3$	-4.3 (0.1)
7) $[Rh{-}D]^{-4} + HC(O)CH_2CH_2CH_2CH_3 \rightleftarrows [Rh{-}CH(OD)CH_2CH_2CH_3]^{-4}$ (**7**)	$K_7 = 4.9\ (0.9) \times 10^2$	-3.7 (0.1)

Table 2. Equilibrium Constants (K_n) and $\Delta G°_n$ (kcal mol^{-1}) Derived for Reactions of $[(TSPP)Rh^I(D_2O)]^{-5}$ (**2**) with CO and Aldehydes in D_2O (298 K)

$[(TSPP)Rh^I(D_2O)]^{-5}$ (**2**) reactions	K_n	$\Delta G°_n$
8) $[Rh^I]^{-5} + CO + D_2O \rightleftarrows [Rh{-}CDO]^{-4}$ (**4**) $+ OD^-$	$K_8 = K_4K_3/K_2 = 9.1\ (0.3) \times 10^{-7}$	$+8.2$ (0.1)
9) $[Rh^I]^{-5} + H_2CO + D_2O \rightleftarrows [Rh{-}CH_2(OD)]^{-4}$ (**5**) $+ OD^-$	$K_9 = K_5K_3/K_2 = 1.4\ (0.4) \times 10^{-4}$	$+5.3$ (0.1)
10) $[Rh^I]^{-5} + HC(O)CH_3 + D_2O \rightleftarrows [Rh{-}CH(OD)CH_3]^{-4}$ (**6**) $+ OD^-$	$K_9 = K_6K_3/K_2 = 4.0\ (0.3) \times 10^{-7}$	$+8.7$ (0.1)
11) $[Rh^I]^{-5} + HC(O)CH_2CH_2CH_3 + D_2O \rightleftarrows [Rh{-}CH(OD)(CH_2)_2CH_3]^{-4}$ (**7**) $+ OD^-$	$K_{10} = K_7K_3/K_2 = 1.5\ (0.9) \times 10^{-7}$	$+9.3$ (0.1)

Table 3. Equilibrium Constants (K_n) and $\Delta G°_n$ (kcal mol^{-1}) Measured for Reactions of $[(TSPP)Rh^I(D_2O)]^{-5}$ (**2**) with Olefins in D_2O (298 K)

$[(TSPP)Rh^I(D_2O)]^{-5}$ (**2**) reactions	K_n	$\Delta G°_n$
12) $[Rh^I]^{-5} + CH_2{=}CH_2 + D_2O \rightleftarrows [Rh{-}CH_2CH_2(D)]^{-4}$ (**8**) $+ OD^-$	$K_{12} = 1.1\ (0.7) \times 10^{-3}$	$+4.0$ (0.1)
13) $[Rh^I]^{-5} + CH_2{=}CH(CH_2)_3CH_3 + D_2O \rightleftarrows [Rh{-}CH_2CH(D)(CH_2)_3CH_3]^{-4}$ (**9**) $+ OD^-$	$K_{13} = 3.3\ (0.5) \times 10^{-5}$	$+6.1$ (0.1)
14) $[Rh^I]^{-5} + CH_2{=}CHCO_2CH_3 + D_2O \rightleftarrows [Rh{-}CH_2CH(D)CO_2CH_3]^{-4}$ (**10**) $+ OD^-$	$K_{14} = 8.6\ (0.5) \times 10^{-2}$	$+1.5$ (0.1)
15) $[Rh^I]^{-5} + CH_2{=}CHC_6H_4SO_3Na + D_2O \rightleftarrows [Rh{-}CH_2CH(D)C_6H_4SO_3Na]^{-4}$ (**11**) $+ OD^-$	$K_{15} = 2.7\ (0.3) \times 10^{-4}$	$+4.9$ (0.1)

Table 4. Equilibrium Constants (K_n) and $\Delta G°_n$ (kcal mol^{-1}) Derived for Reactions of $[(TSPP)Rh{-}D(D_2O)]^{-4}$ (**1**) with Olefins in D_2O (298 K)

$[TSPP)Rh{-}D(D_2O)]^{-4}$ (**1**) with olefins	K_n	$\Delta G°_n$
16) $[Rh{-}D]^{-4} + CH_2{=}CH_2 \rightleftarrows [Rh{-}CH_2CH_2(D)]^{-4}$ (**8**)	$K_{16} = K_2K_{12}/K_3 = 3.6\ (0.7) \times 10^6$	-8.9 (0.1)
17) $[Rh{-}D]^{-4} + CH_2{=}CH(CH_2)_3CH_3 \rightleftarrows [Rh{-}CH_2CH(D)(CH_2)_3CH_3]^{-4}$ (**9**)	$K_{17} = K_2K_{13}/K_3 = 1.1\ (0.5) \times 10^5$	-6.9 (0.1)
18) $[Rh{-}D]^{-4} + CH_2{=}CHCO_2CH_3 \rightleftarrows [Rh{-}CH_2CH(D)CO_2CH_3]^{-4}$ (**10**)	$K_{18} = K_2K_{14}/K_3 = 2.8\ (0.8) \times 10^8$	-11.5 (0.1)
19) $[Rh{-}D]^{-4} + CH_2{=}CHC_6H_4SO_3Na \rightleftarrows [Rh{-}CH_2CH(D)C_6H_4SO_3Na]^{-4}$ (**11**)	$K_{19} = K_2K_{15}/K_3 = 8.8\ (0.3) \times 10^5$	-8.1 (0.1)

Table 5. Derived Proton Donor Abilities for $[(TSPP)Rh{-}R(D_2O)]^{-4}$ in D_2O (298 K)

proton donor process	K_n	$\Delta G°_n$
2) $[Rh{-}D]^{-4} \rightleftarrows [Rh^I]^{-5} + D^+$	$K_2 = 8.0 \times 10^{-8}$	$+9.7$ (0.1)
20) $[Rh{-}CDO]^{-4} \rightleftarrows [Rh^I]^{-5} + CO + D^+$	$K_{20} = K_2/K_4 = 2.7 \times 10^{-11}$	$+14.4$ (0.1)
21) $[Rh{-}CH_2(OD)]^{-4} \rightleftarrows [Rh^I]^{-5} + H_2CO + D^+$	$K_{21} = K_2/K_5 = 1.7 \times 10^{-13}$	$+17.4$ (0.1)
22) $[Rh{-}CH(OD)CH_3]^{-4} \rightleftarrows [Rh^I]^{-5} + HC(O)CH_3 + D^+$	$K_{22} = K_2/K_6 = 6.2 \times 10^{-11}$	$+13.9$ (0.1)
23) $[Rh{-}CH_2CH_2(D)]^{-4} \rightleftarrows [Rh^I]^{-5} + CH_2{=}CH_2 + D^+$	$K_{23} = K_2/K_{16} = 2.2 \times 10^{-14}$	$+18.6$ (0.1)

[a] R = D, CDO, CH_2OD, $CH(OD)CH_3$, $CH_2CH_2(D)$.

are given in Tables 1−4 (eqs 4−19). Thermodynamic parameters relevant to the hydride **1** and organo-rhodium complexes functioning as a proton (H^+), a hydrogen atom ($H^•$), and a hydride (H^-) source in water are derived from the data in Tables 1−4 and are listed in Tables 5 and 6, respectively.

Equilibrium constants at 298 K in D_2O were directly measured for reactions of the rhodium hydride $[(TSPP)Rh{-}D(D_2O)]^{-4}$ (**1**) with CO and aldehydes (eq 4−7, Table 1) and for reactions of olefins with the rhodium(I) complex ($[(TSPP)Rh^I(D_2O)]^{-5}$) (**2**) (eq 8−11, Table 2). Evaluation of the relatively large equilibrium constant for the reaction of formaldehyde with **1** (K_5 (298 K) = 4.6 (0.4) × 10^5) in D_2O is aided by the hydrolysis of formaldehyde ($H_2CO + H_2O \rightleftarrows CH_2(OH)_2$; K (298 K) = 36.2)[21] which results in only small equilibrium concentrations of H_2CO. Tuning the distribution of **1** and **2** by changing the hydrogen ion concentration provides an effective approach to expand the range of equilibrium constant values that can be determined by integration of ^1H NMR spectra.

The equilibrium constant for reaction 4 ($[(TSPP)Rh{-}D(D_2O)]^{-4} + CO \rightleftarrows [(TSPP)Rh{-}CDO(D_2O)]^{-4}$) was evaluated in D_2O by the integration of the porphyrin pyrrole ^1H NMR for **1** and **4** and by the assumption that the solubility of CO in D_2O is the same as that in H_2O.[22] The hydride **1** and the rhodium(I) complex **2** are in dynamic equilibrium in aqueous solutions where the concentration of D^+ is less than 10^{-5} M. The mole fraction averaged pyrrole chemical shifts for aqueous solutions of **1** and **2** were used to determine the concentration of the hydride (**1**) for evaluation of K_4 (K_4 (298 K) = 3.0 (0.3) × 10^3, $\Delta G_4°$ (298 K) = −4.7 kcal mol^{-1}) (Table 1).Equilibrium constants for reactions of $[(TSPP)Rh^I(D_2O)]^{-5}$ (**2**) with CO and aldehydes are too small to be directly measured by the ^1H NMR integration method but can be derived from thermodynamic cycles using the data in Table 1. The equilibrium constant for the reaction of $[(TSPP)Rh^I(D_2O)]^{-5}$ (**2**) with CO in D_2O (eq 8), K_8 (298 K) = K_4K_3/K_2 = 9.1 × 10^{-7}, is derived from the

---

(21) Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1.

(22) Fog, P. G. T.; Gerrard, W. *Solubility of Gases In Liquids: A Critical Evaluation of Gas/Liquid Systems in Theory and Practice*; Wiley: Chichester, NY, 1991.

Table 6. Derived Hydride and Hydrogen Atom Donor Abilities for $[(TSPP)Rh{-}R(D_2O)]^{-4}$ Complexes in D_2O (298 K)[a]

hydride donor process	K_n	$\Delta G°_n$
1) $[Rh^{III}(D_2O)_2]^{-3} + D_2 \rightleftarrows [Rh{-}D(D_2O)]^{-4} + D^+ + D_2O$	$K_1 = 18.2 \pm 0.5$	-1.7 ± 0.1
24) $D_2 \rightleftarrows D^+ + D^-$	$K_{24} = 9.6 \times 10^{-40}$	$+53.2$
25) $[Rh{-}D(D_2O)]^{-4} + D_2O \rightleftarrows [Rh^{III}(D_2O)_2]^{-3} + D^-$	$K_{25} = K_{24}/K_1 = 5.3 \times 10^{-41}$	$+54.9$ (0.1)
26) $[Rh{-}CDO(D_2O)]^{-4} + D_2O \rightleftarrows [Rh^{III}(D_2O)_2]^{-3} + CO + D^-$	$K_{26} = K_{25}/K_4 = 1.8 \times 10^{-44}$	$+59.6$ (0.1)
27) $[Rh{-}CH_2(OD)(D_2O)]^{-4} + D_2O \rightleftarrows [Rh^{III}(D_2O)_2]^{-3} + H_2CO + D^-$	$K_{27} = K_{25}/K_5 = 1.2 \times 10^{-46}$	$+62.6$ (0.1)
28) $[Rh{-}CH(OD)CH_3(D_2O)]^{-4} + D_2O \rightleftarrows [Rh^{III}(D_2O)_2]^{-3} + HC(O)CH_3 + D^-$	$K_{28} = K_{25}/K_6 = 4.1 \times 10^{-44}$	$+59.2$ (0.1)
29) $[Rh{-}CH_2CH_2(D)(D_2O)]^{-4} + D_2O \rightleftarrows [Rh^{III}(D_2O)_2]^{-3} + CH_2{=}CH_2 + D^-$	$K_{29} = K_{25}/K_{16} = 1.5 \times 10^{-47}$	$+63.8$ (0.1)
30) $[Rh{-}D(D_2O)]^{-4} \rightleftarrows [Rh^{II}(D_2O)]^{-4\bullet} + D^\bullet$	$K_{30} \cong 9.8 \times 10^{-45}$	$\cong 60$
31) $[Rh{-}CDO(D_2O)]^{-4} \rightleftarrows [Rh^{II}(D_2O)]^{-4\bullet} + CO + D^\bullet$	$K_{31} = K_{30}/K_4 \cong 3.3 \times 10^{-48}$	$\cong 65$
32) $[Rh{-}CH_2CH_2(D)(D_2O)]^{-4} \rightleftarrows [Rh^{II}(D_2O)]^{-4\bullet} + CH_2{=}CH_2 + D^\bullet$	$K_{32} = K_{30}/K_{16} \cong 2.7 \times 10^{-51}$	$\cong 69$

[a] R = D, CDO, CH_2OD, $CH(OD)CH_3$, $CH_2CH_2(D)$.

following cycle by adding the reverse eq 2 (eq −2) with eqs 3 and 4.

$$-2)\quad [(TSPP)Rh^{I}(D_2O)]^{-5} + D^+ \rightleftarrows [(TSPP)Rh{-}D(D_2O)]^{-4}$$

$$3)\quad D_2O \rightleftarrows D^+ + OD^-$$

$$4)\quad [(TSPP)Rh{-}D(D_2O)]^{-4} + CO \rightleftarrows [(TSPP)Rh{-}CDO(D_2O)]^{-4}$$

$$8)\quad [(TSPP)Rh^{I}(D_2O)]^{-5} + CO + D_2O \rightleftarrows [(TSPP)Rh{-}CDO(D_2O)]^{-4} + OD^-$$

Equilibrium constants derived for reactions of $[(TSPP)Rh^{I}(D_2O)]^{-5}$ with CO, formaldehyde, acetaldehyde, and butyraldehyde in D_2O are listed in Table 2.

Equilibrium constants for reactions of the hydride (**1**) ($[(TSPP)Rh{-}D(D_2O)]^{-4}$) with olefins are too large for direct evaluation but can be derived from measurement of the equilibrium constants for reactions of the rhodium(I) complex ($[(TSPP)Rh^{I}(D_2O)]^{-5}$) with olefins combined with acid dissociation constants for D_2O[20] and the hydride **1**, as illustrated in the cycle below ($K_{16} = K_2K_{12}/K_3$).

$$12)\quad [(TSPP)Rh^{I}(D_2O)]^{-5} + CH_2{=}CH_2 + D_2O \rightleftarrows [(TSPP)Rh{-}CH_2CH_2(D)(D_2O)]^{-4} + OD^-$$

$$2)\quad [(TSPP)Rh{-}D(D_2O)]^{-4} \rightleftarrows [(TSPP)Rh^{I}(D_2O)]^{-5} + D^+$$

$$-3)\quad D^+ + OD^- \rightleftarrows D_2O$$

$$16)\quad [(TSPP)Rh{-}D(D_2O)]^{-4} + CH_2{=}CH_2 \rightleftarrows [(TSPP)Rh{-}CH_2CH_2(D)(D_2O)]^{-4}$$

The range of equilibrium constants determined by varying the hydrogen ion concentration in water ($3.3 \times 10^{-5} - 2.8 \times 10^{8}$; $\Delta(\Delta G°) = 17.6$ kcal mol^{-1}) far exceeds the accessible range for K and $\Delta G°$ values that could be measured in organic media. Directly measured equilibrium constants for substrate reactions of the hydride **1** are found in Table 1, and the measured values for reactions of the rhodium(I) complex **2** are found in Table 3. Tables 2 and 4 contain K and $\Delta G°$ values for substrate reactions of **1** and **2** that are derived from the measured values in Tables 1 and 3.

Relative Rates and Mechanistic Inferences for Porphyrin Rhodium Hydride Substrate Reactions in Benzene and Water. Concerted reactions of rhodium porphyrin hydrides with unsaturated substrates including CO, aldehydes, and olefins occur very slowly because all of the coordination sites adjacent to the hydride position are occupied by the relatively rigid porphyrin pyrrole nitrogen donors. The conventional organometallic mechanism which involves substrate addition cis to the hydride position followed by hydrogen migration to the substrate is blocked in metallo-porphyrin complexes. Addition reactions of porphyrin rhodium hydrides with olefins and CO in organic media are catalyzed by $(por)Rh^{II}$ metallo radicals which provide a pathway for substrate binding and activation at the reactive metal center.[23] Reaction of the substrate with a porphyrin rhodium(II) metallo radical followed by hydrogen atom transfer from a rhodium hydride gives a radical chain process (eqs 33 and 34).[23−26] Sequential addition of the radical components of the Rh−H unit circumvents the restrictions for concerted processes.

$$33)\quad (por)Rh^{II\bullet} + S \rightleftarrows [(por)RhS]^\bullet$$

$$34)\quad [(por)RhS]^\bullet + H{-}Rh(por) \rightleftarrows (por)Rh{-}SH + (por)Rh^{II\bullet}$$

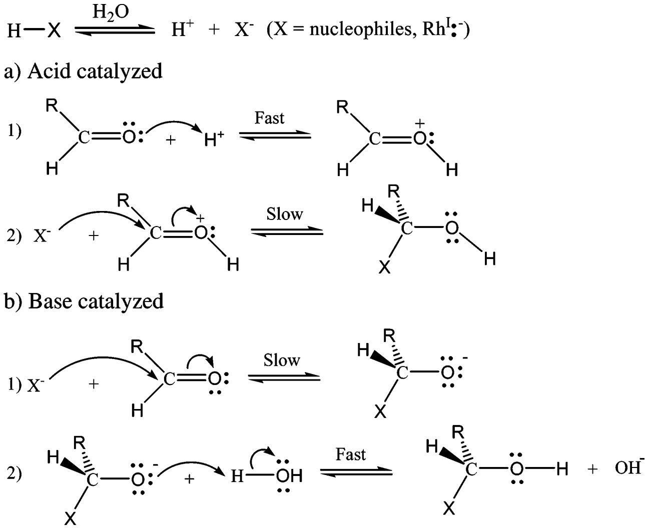
Substrate reactions of **1** in D_2O are typically much faster than uncatalyzed reactions of (por)Rh−H in benzene. This is ascribed to a greater variety of reaction pathways in water and, in particular, to the ability of water to support ionic species and heterolytic processes. In aqueous solution, the rhodium hydride (**1**) partially dissociates into rhodium(I) and proton fragments ($Rh^{I}{:}^-$, D^+). The rhodium(I) complex (**2**) is an effective nucleophile even in donor media such as water because the monohydrate $[(TSPP)Rh^{I}(D_2O)]^{-5}$ is a 5-coordinate 18-electron complex which retains a site that provides facile access to the metal center for substrate molecules. Heterolytic dissociation of the Rh−D unit in **1** into $Rh^{I}{:}^-$ and D^+ has a much smaller free-energy change ($\Delta G° = 9.7$ kcal mol^{-1}) than either formation of hydride (Rh^+, D^-) ($\Delta G° = 54.9$ kcal mol^{-1}) or homolysis to $D^\bullet$ and $Rh^{II\bullet}$ ($\Delta G° \cong 60$ kcal mol^{-1}) and provides a facile pathway to generate an open reactive metal center for substrate reactions in water (Table 6, eqs 25 and 30).

Addition of the Rh−D unit in $[(TSPP)Rh{-}D(D_2O)]^{-4}$ to unsaturated substrates in D_2O is envisioned to occur by mechanisms that are related to acid- and base-catalyzed addition reactions of aldehydes and olefins. General pathways for reactions of **1** with unsaturated substrates ($CH_2{=}CHX$, RCHO, and CO) are proposed to parallel the established mechanisms for reactions of HX with aldehydes in water (Scheme 2).

---

(23) Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.
(24) Wayland, B. B.; Coffin, V. L.; Farnos, M. D. *Inorg. Chem.* **1988**, *27*, 2745.
(25) Wayland, B. B.; DelRossi, K. J. *J. Organomet. Chem.* **1984**, *276*, C27.
(26) Wayland, B. B.; Sherry, A. E.; Coffin, V. L. *Chem. Commun.* **1989**, 662.

Scheme 2. Pathways for Addition of HX to an Aldehyde in Water



In acidic media ($[D^+] \sim 10^{-3}-10^{-7}$), the hydride **1** adds rapidly with both activated and unactivated olefins as well as aldehydes. All of the substrate reactions of **1** in acidic media are too fast to be followed by ^1H NMR at 298 K. In acidic media where the concentration of the rhodium(I) complex (**2**) is very small, the addition of the rhodium hydride with aldehydes and olefins probably occurs by initial protonation of the substrate followed by reaction with either the rhodium hydride (**1**) or the rhodium(I) complex (**2**) (Scheme 2a). Protonation of the alkene π-bond activates both alkene carbon centers so that a thermodynamically controlled distribution of regioisomers is expected. Addition of **1** to most olefins resulted in observation of only the anti-Markovnikov product ($Rh-CH_2CH(D)X$) by ^1H NMR, but 4-styrenesulfonic acid sodium salt produced nearly equal quantities of regioisomers. Olefins in contact with acidic D_2O solutions of **1** are sequentially deuterated at the secondary and then the primary alkene carbons which are consistent with the formation of both regioisomers.

In basic D_2O ($[D^+] \sim 10^{-9}-10^{-12}$), the rhodium hydride is deprotonated to form the rhodium(I) complex **2** ($[(TSPP)Rh^I(D_2O)]^{-5}$). The rhodium(I) complex (**2**) in D_2O ($[D^+] < 10^{-9}$) reacts rapidly with aldehydes and electrophilic olefins such as methyl acrylate and 4-styrenesulfonic acid sodium salt to produce alkyl derivatives (eqs 9, 10, 14, and 15). These reactions probably proceed through initial attack by the rhodium(I) nucleophile at the electrophilic carbon center followed by protonation from water (Scheme 2b). The net addition of **1** to the activated olefins exclusively places the Rh^I: nucleophile at the activated CH_2 site to form the anti-Markovnikov products ($Rh-CH_2CH(D)X$). In basic D_2O media, the activated olefins become selectively deuterated ($CH_2{=}CDX$) through rhodium hydride mediated exchange with D_2O. Alkenes such as ethene and propene which do not have a site that is activated for interaction with a nucleophile are observed to react only very slowly with **2** in basic D_2O.

Addition of the rhodium hydride unit in **1** to CO in both acidic and basic D_2O ($[D^+] = 10^{-3}-10^{-9}$) produces a rhodium formyl complex ($[(TSPP)Rh-CDO(D_2O)]^{-4}$) (eqs 4 and 8) at a moderate rate. Our working hypothesis is that reactions 4 and 8 proceed through the same type of transition state ($[Rh{:}^{-}\cdots C(O)\cdots H^+]$) as reactions of **1** with aldehyde and olefins (Scheme 2). The CO reaction, in contrast with the pathways outlined in Scheme 2, most probably occurs by concerted addition of the $Rh^I{:}^-$ and H^+ units without an intermediate. The interaction of Rh(I) with CO is proposed to assist in the rehybridization of the carbon center in CO from sp to sp^2 in the transition state. Interaction of the rhodium(I) nucleophile with CO does not result in a stable complex or an observable intermediate, but this type of interaction could provide a pathway that stabilizes the transition state ($[Rh{:}^{-}\cdots C(O)\cdots H^+]$) for a concerted addition of Rh^{I-} and H^+ fragments to CO.

Organo-Rhodium Porphyrins as Sources of Proton, Hydride, and Hydrogen Atoms. Dissociation of a proton from $[(TSPP)Rh-D(D_2O)]^{-4}$ in water ($\Delta G° = +9.7$ kcal mol^{-1}) is greatly preferred to either Rh−D homolysis (60 kcal mol^{-1}) or heterolysis to form hydride (54.9 kcal mol^{-1}) (Table 6). The hydride donor ability of **1** ($\Delta G° \cong 54.9$ kcal mol^{-1}) places (TSPP)Rh−D near the average position on the hydricity scale that was recently established by DuBois.[27,28] Similarly, dissociation of protons from the α-carbon of Rh−CDO (**4**), the β-O−D of $Rh-CH_2OD$ (**5**), and the β-C−D/H of $Rh-CH_2CH_2D$ (**8**) occurs with a much smaller free-energy increase (13.8−18.6 kcal mol^{-1}) than that for either heterolysis to hydride or homolysis to hydrogen atoms which require $\Delta G°$ values from 59 to 69 kcal mol^{-1} (Table 6).

Comparison of $\Delta G°$ (298 K) Values for Porphyrin Rhodium Hydride Substrate Reactions of CO, Aldehydes, and Olefins in Water and Benzene. Estimates of the differences in the solvation free-energy changes in water and benzene ($(\Delta G°_{hyd}) - (\Delta G°_{C_6H_6})$) for (TSPP)Rh species that are found in Table 8 are derived from hydration free energies for substrates (Table 7) in conjunction with measured free-energy changes for substrate reactions (Tables 1 and 4). Determination of equilibrium constants for reactions of CO, H_2CO, and $CH_2{=}CH_2$ with the hydride $[(TSPP)Rh-D(D_2O)]^{-4}$ (**1**) in water provides the first opportunity to compare experimental thermodynamic values for reactions of a metal hydride with this entire series of substrates. The observed $\Delta G°$ (298 K) values change from −4.7 kcal mol^{-1} for the CO reaction to −7.7 kcal mol^{-1} for H_2CO and −8.9 kcal mol^{-1} for ethene (Table 1). A change in the equilibrium constants by a factor of 10^3 and a free-energy change $\Delta(\Delta G°)$ of 4.2 kcal mol^{-1} for this series of substrate reactions are not very large considering that transition-metal hydride reactions with olefins to form alkyl complexes are commonly observed, but reactions of metal hydrides with CO that produce observable quantities of a metallo-formyl species are extremely rare.

Free-energy changes ($\Delta G°$ (298 K)) for substrate reactions of (OEP)Rh−H in benzene have been measured for the reaction with CO (−4.8 kcal mol^{-1})[19] and estimated for reactions of H_2CO (−7.0 (0.5) kcal mol^{-1}) and $CH_2{=}CH_2$ (−18 (3) kcal mol^{-1}), respectively. Close similarity of the $\Delta G°$ values for the CO and H_2CO reactions with (por)Rh−D species in water and benzene indicates that the aqueous solvation free-energy changes ($\Delta G°_{hyd}$) for reactants and products must nearly cancel for CO and aldehyde substrate reactions in water and benzene, but the

---

(27) Ellis, W. W.; Ciancanelli, R.; Miller, S. M.; Raebiger, J. W.; DuBois, M. R.; DuBois, D. L. *J. Am. Chem. Soc.* **2003**, *125*, 12230.

(28) Ellis, W. W.; Raebiger, J. W.; Curtis, C. J.; Bruno, J. W.; DuBois, D. L. *J. Am. Chem. Soc* **2004**, *126*, 2738.

ethene reaction with **1** in water is substantially less favorable ($\Delta(\Delta G_{16}^\circ) \cong +9$ kcal mol^{-1}) than the parallel type of process in benzene.

The difference in the free energies of hydration for the substrate complexes (Rh−CDO and Rh−CH$_2$OD) and the rhodium hydride (**1**) (Rh−D) are nearly equal but opposite in sign to the hydration free energy for the substrates. For these cases, the ΔG° values for the substrate reactions in benzene and water are comparable within less than 1 kcal mol^{-1}. The large difference in the hydration free energy (∼11 kcal mol^{-1}) between Rh−CH$_2$CH$_2$D (**8**) and Rh−D (**1**) is identified as the reason the reaction to produce the ethyl complex ([(TSPP)Rh−CH$_2$CH$_2$D(D$_2$O)]$^{-4}$) (eq 11) in water is ∼9 kcal mol^{-1} less favorable than the analogous substrate reaction in benzene.

Effective Organo-Rh(TSPP) Bond Dissociation Free Energies (BDFEs) in D$_2$O. Bond dissociation enthalpy (BDE) is the thermodynamic parameter most often used by chemists to compare the energetics associated with homolysis of a two-centered bond unit. BDE values are particularly useful for comparison of the gas-phase processes where the species present are well defined. In aqueous media where each type of solution species is comprised of several hydrated subspecies, the enthalpy/entropy compensation[29−31] makes the bond dissociation free energy (BDFE) a better thermodynamic parameter for comparison of bond homolysis energetics.

Free-energy changes (ΔG° (298 K)) observed for the addition reactions of the rhodium hydride **1** with CO and sets of aldehyde and olefin substrates in aqueous media in conjunction with free-energy changes in hydration (ΔG°_{hyd}) (Tables 1−7) are used in deriving effective BDFEs in D$_2$O at 298 K. Representative thermodynamic cycles given below are used to illustrate the derivation of the Rh−CDO, Rh−CH$_2$OD, and Rh−CH$_2$CH$_2$D BDFE values compiled in Table 9.

(TSPP)Rh−CDO BDFE. Production of the rhodium formyl complex (**4**) by reaction of the hydride (**1**) with CO (eq 4) occurs with a ΔG°_4 (298 K) of −4.7 kcal mol^{-1}. A thermodynamic cycle gives 44 kcal mol^{-1} for the Rh−CDO BDFE in (TSPP)-Rh−CDO.

$$\begin{tikzcd}
D_g^{\bullet} \arrow[d, "\Delta G^o_{hyd}=+4.5"'] & + & CO_g \arrow[r] \arrow[d, "\Delta G^o_{hyd}=+4.1"] & {\cdot CDO_g} \arrow[d, "\Delta G^o_{hyd}=-2"] & \Delta G_g^o = -10\ \text{kcal mol}^{-1} \\
D_{aq}^{\bullet} & + & CO_{aq} \arrow[r] & {\cdot CDO_{aq}} & \Delta G_{aq}^o = -20.6\ \text{kcalmol}^{-1}
\end{tikzcd}$$

$$\begin{array}{ll}
[Rh\text{-}CDO]^{-4}_{aq} \rightleftharpoons [Rh\text{-}D]^{-4}_{aq} + CO_{aq} & \Delta G^\circ = +\ 4.7\ \text{kcalmol}^{-1} \\
[Rh\text{-}D]^{-4}_{aq} \rightleftharpoons [Rh^{II}]^{-4}\bullet_{aq} + D\bullet_{aq} & \Delta G^\circ = +60\ \text{kcalmol}^{-1} \\
D\bullet_{aq} + CO_{aq} \rightleftharpoons \bullet CDO_{aq} & \Delta G^\circ = -20.6\ \text{kcalmol}^{-1} \\
\cline{2-2}
[Rh\text{-}CDO]^{-4}_{aq} \rightleftharpoons [Rh^{II}]^{-4}\bullet_{aq} + \bullet CDO_{aq} & \Delta G^\circ = 44\ \text{kcalmol}^{-1}
\end{array}$$

(TSPP)Rh−CH$_2$OD BDFE. Estimation of the (TSPP)Rh−CH(R)OD BDFE in water can be obtained from standard free-energy changes for reactions 5−7 in conjunction with the (TSPP)Rh−D$_{aq}$ BDFE and the O−D BDFE for hydroxyalkyl radicals ($^\bullet$CH(R)O−D)$_{aq}$ in water. A thermodynamic cycle to derive the ((TSPP)Rh−CH$_2$OD)$_{aq}$ BDFE in D$_2$O using reaction 5 gives 39 kcal mol^{-1} ((Rh−CH$_2$OD)$_{aq}$ = 39 kcal mol^{-1}).

$$\begin{tikzcd}
D_g^{\bullet} \arrow[d, "\Delta G^o_{hyd}=+4.5"'] & + & H_2CO_g \arrow[r] \arrow[d, "\Delta G^o_{hyd}=-3.5"] & {\cdot CH_2(OD)_g} \arrow[d, "\Delta G^o_{hyd}=-5.0"] & \Delta G_g^o = -22.2\ \text{kcalmol}^{-1} \\
D_{aq}^{\bullet} & + & H_2CO_{aq} \arrow[r] & {\cdot CH_2(OD)_{aq}} & \Delta G_{aq}^o = -28.3\ \text{kcalmol}^{-1}
\end{tikzcd}$$

$$\begin{array}{ll}
D\bullet_{aq} + H_2CO_{aq} \rightleftharpoons \bullet CH_2(OD)_{aq} & \Delta G_{aq}^\circ = -28.3\ \text{kcalmol}^{-1} \\
[Rh\text{-}CH_2(OD)]^{-4}_{aq} \rightleftharpoons [Rh\text{-}D]^{-4}_{aq} + H_2CO_{aq} & \Delta G^\circ = +\ 7.7\ \text{kcalmol}^{-1} \\
[Rh\text{-}D]^{-4}_{aq} \rightleftharpoons [Rh^{II}]^{-4}\bullet_{aq} + D\bullet_{aq} & \Delta G^\circ = +\ 60.0\ \text{kcalmol}^{-1} \\
\cline{2-2}
[Rh\text{-}CH_2(OD)]^{-4}_{aq} \rightleftharpoons [Rh^{II}]^{-4}\bullet_{aq} + \bullet CH_2(OD)_{aq} & \Delta G^\circ = +\ 39.4\ \text{kcalmol}^{-1}
\end{array}$$

(TSPP)Rh−CH$_2$CH$_2$(D) BDFE. The free-energy change (ΔG°) for the process of rhodium ethyl bond homolysis is expressed by the following thermodynamic cycle which yields a Rh−CH$_2$CH$_2$D BDFE of 36 kcal mol^{-1}.

$$\begin{tikzcd}
D_g^{\bullet} \arrow[d, "\Delta G^o_{hyd}=+4.5"'] & + & CH_2{=}CH_{2\,g} \arrow[r] \arrow[d, "\Delta G^o_{hyd}=+1.3"] & {\cdot CH_2CH_2D_{(g)}} \arrow[d, "\Delta G^o_{hyd}=+1.8"] & \Delta G_g^o = -29\ \text{kcalmol}^{-1} \\
D_{aq}^{\bullet} & + & CH_2{=}CH_{2\,aq} \arrow[r] & {\cdot CH_2CH_2D_{aq}} & \Delta G_{aq}^o = -33.0\ \text{kcalmol}^{-1}
\end{tikzcd}$$

$$\begin{array}{ll}
D\bullet_{aq} + CH_2{=}CH_{2aq} \rightleftharpoons \bullet CH_2CH_2D_{aq} & \Delta G^\circ = -33.0\ \text{kcalmol}^{-1} \\
[Rh\text{-}CH_2CH_2D]^{-4}_{aq} \rightleftharpoons [Rh\text{-}D]^{-4}_{aq} + (CH_2{=}CH_2)_{aq} & \Delta G^\circ = +8.9\ \text{kcalmol}^{-1} \\
[Rh\text{-}D]^{-4}_{aq} \rightleftharpoons [Rh^{II}]^{-4}\bullet_{aq} + D\bullet_{aq} & \Delta G^\circ = +\ 60.0\ \text{kcalmol}^{-1} \\
\cline{2-2}
[Rh\text{-}CH_2CH_2D]^{-4}_{aq} \rightleftharpoons [Rh^{II}]^{-4}\bullet_{aq} + (\bullet CH_2CH_2D)_{aq} & \Delta G^\circ = +35.9\ \text{kcalmol}^{-1}
\end{array}$$

Effective Rh−X BDFEs in water can vary substantially from the values in benzene depending on the component solvation free energies. The effective Rh−D BDFE is 6 kcal mol^{-1} larger, the Rh−CH$_2$OD BDFE is equal, and the Rh−CH$_2$CH$_2$D BDFE is 8 kcal mol^{-1} smaller in water than the corresponding BDFE in benzene. The Rh−D BDFE is larger in water because of the positive hydration free energy (ΔG°_{hyd}) for H$^\bullet$ (ΔG°_{hyd}(H$^\bullet$) = +4.5 kcal mol^{-1}), and the ΔG°_{hyd} of Rh−D (**1**) is more negative than that of Rh$^{II\bullet}$. The Rh−OD BDFE is larger in water even though the ΔG°_{hyd} of $^\bullet$OH is negative because the ΔG°_{hyd}(Rh−OD) is substantially more negative (≅ −7 kcal mol^{-1}) than that for Rh$^{II\bullet}$. The largest difference in Rh−X BDFE values occurs for the alkyl complexes where the Rh−CH$_2$CH$_2$D BDFE is ≅8 kcal mol^{-1} less favorable in water than in benzene. The ΔG°_{hyd} of Rh−CH$_2$CH$_2$D is ≅10−11 kcal mol^{-1} less negative than that of Rh$^{II\bullet}$ as a consequence of the hydrophobicity of the alkyl hydrocarbon chain which substantially reduces the effective BDFE of Rh−CH$_2$CH$_2$D in water.

Conclusions

Reactions of rhodium porphyrin hydrides with unsaturated substrates previously reported in hydrocarbon media are observed to have analogous types of substrate transformations in aqueous media. Tetra(*p*-sulfonato-phenyl) porphyrin rhodium hydride ([(TSPP)Rh−D(D$_2$O)]$^{-4}$ (**1**)) is a weak acid in D$_2$O (K_a (298 K) = 8.0 × 10^{-8}) and reacts with carbon monoxide, aldehydes, and olefins to produce metallo formyl (Rh−CDO), α-hydroxyalkyl (Rh−CH(OD)R), and alkyl complexes (Rh−CH$_2$CHDX), respectively. All of the substrate reactions of the hydride (**1**) in acidic D$_2$O are orders of magnitude faster than the corresponding processes in benzene which is ascribed to water promoting and supporting ionic pathways. Aldehydes react rapidly and regioselectively with the rhodium hydride (**1**) in both acidic and basic D$_2$O to form α-hydroxyalkyl complexes (Rh−CH(OD)R) rather than alkoxides (Rh−OCH(D)R). Elec-

---

(29) Liu, L.; Guo, Q. X. *Chem. Rev.* **2001**, *101*, 673.

(30) (a) Grunwald, E.; Steel, C. *Pure Appl. Chem.* **1993**, *65*, 2543. (b) Grunwald, E.; Steel, C. *J. Phys. Chem.* **1993**, *97*, 13326. (c) Grunwald, E.; Steel, C. *J. Phys. Org. Chem.* **1994**, *7*, 734.

(31) (a) Linert, W.; Han, L. F.; Lukovits, I. *Chem. Phys.* **1989**, *139*, 441. (b) Mallardi, A.; Giustini, M.; Palazzo, G. *J. Phys. Chem. B* **1998**, *102*, 9168. (c) Fang, Y.; Fan, J. M.; Liu, L.; Li, X. S.; Guo, Q. X. *Chem. Lett.* **2002**, 116.

Table 7. ΔH°_f, ΔG°_f, and ΔG°_{hyd} (298 K, kcal mol^{-1}) for Substrates and Radicals

compound	ΔH°_f	ΔG°_f	ΔG°_{hyd}
CO	-26.4^{a}	-32.8^{a}	4.1^{a}
H_2	0^{a}	0^{a}	$+4.2^{k}$
H_2O	-57.8^{a}	-54.6^{a}	-2.1^{l}
H_2CO	-25.9^{a}	$-26.3-24.5^{a}$	-4.5^{i}
CH_3CHO	-39.7^{a}	-30.8^{a}	-3.5^{j}
$CH_3CH_2CH_2CHO$	-49.0^{b}	-27.4^{b}	-3.18^{j}
$CH_2{=}CH_2$	12.5^{a}	16.3^{a}	1.27^{j}
$CH_2{=}CH(CH_2)_3CH_3$	-9.96^{b}	20.9^{b}	1.68^{j}
$H^{\bullet}$	52.1^{a}	48.6^{a}	$+4.5^{k}$
$^{\bullet}OH$	$+9.3^{a}$	$+8.2^{a}$	-2.4^{l}
$^{\bullet}CHO$	10.3^{a}	6.7^{a}	-4.1^{j}
$^{\bullet}CH_2(OH)$	$-4.0^{c}/-4.25^{d}$	0.0^{d}	-5.11^{j}
$^{\bullet}CH(OH)CH_3$	$-14.4^{e}/-15.2^{f}$		-5.02^{j}
$^{\bullet}CH_2CH_3$	28.8^{g}		1.83^{j}
$^{\bullet}CH_2(CH_2)_4CH_3$	6.0^{h}		2.49^{j}

[a] *J. Phys. Chem. Ref. Data* **1982**, *11* (Suppl. 2). Standard state used: 298.15 K, 0.1 MPa. [b] *Chemical thermodynamics of organic compounds*; Stull, D. R., Westrum, E. F., Jr., Sinke, G. C., Eds.; John Wiley & Sons, Inc.: New York, 1969. [c] Ruscic, B.; Berkowitz, J. *J. Phys. Chem.* **1993**, *97*, 11451−11455. [d] Hohnsom, R. D., III; Hudgens, J. W. *J. Phys. Chem.* **1996**, *100*, 19874−19890. [e] Holmes, J. L.; Lossing, F. P.; Mayer, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 9723−9728. [f] Ruscic, B.; Berkowitz, J. *Chem. Phys.* **1994**, *101*, 10936−10946. [g] Lee, J.; Chen, C.-J.; Bozzelli, J. W. *J. Phys. Chem. A* **2002**, *106*, 7155−7170. [h] Lossing, F. P.; Maccoll, A. *Can. J. Chem.* **1976**, *54*, 990−992. [i] Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1. [j] Sandberg, L.; Casemyr, R.; Edholm, O. *J. Phys. Chem. B* **2002**, *106*, 7889−7897. [k] Han, P.; Bartels, D. M. *J. Phys. Chem.* **1990**, *94*. [l] Abraham, M. H.; Whiting, G. S.; Fuchs, R.; Chambers, E. J. *J. Chem. Soc., Perkin Trans.* **1990**, *2*, 291.

Table 8. Estimated Difference in the Free Energy of Solvation $\Delta(\Delta G^\circ)$ (kcal mol^{-1}, 298 K) for (TSPP)Rh Species

(TSPP)Rh species	$\Delta(\Delta G^\circ_{hyd})^{a}$	$\Delta(\Delta G^\circ_{sol})^{b}$
$(Rh-D)-(Rh^{II\bullet})$	−2.4	−4.0
$(Rh-D)-(Rh-CDO)$	−4.2	−3.2
$(Rh-D)-(Rh-CH_2OD)$	+5.2	+3.7
$(Rh-D)-(Rh-CH(OD)CH_2CH_2CH_3)$	+5.6	+3.9
$(Rh-D)-(Rh-CH_2CH_3)$	−10	−11

[a] $\Delta(\Delta G^\circ_{hyd})$ is defined as the difference in the hydration free energies for the (TSPP)Rh species. [b] $\Delta(\Delta G^\circ_{sol})$ is defined as the difference in the solvation free energies (ΔG°_{hyd}) in water and benzene (ΔG°_{C6H6}).

Table 9. Rh−X Bond Dissociation Free Energies for (por)Rh−X^{a} Complexes in D_2O and C_6D_6 (kcal mol^{-1})^{b,c}

Rh–X	BDFE(D_2O)	BDFE(C_6D_6)
Rh−D	60	54
Rh−H	59	53
Rh−OH	62	(<57)
Rh−CDO	44	49
$Rh-CH_2OD$	39	39
$Rh-CH(OD)CH_3$	37	37
$Rh-CH_2CH_2D$	36	44
$Rh-CH_2CHD(CH_2)_3CH_3$	34	(42)
$Rh-CH_3$	(41)	49

[a] The porphyrin (por) is TSPP in water and a TPP derivative in benzene (ref 14, 18, and 12). [b] BDFE of Rh−X is defined as the change in free energy (ΔG° (298 K)) for homolytic dissociation of Rh−X into $Rh^{II\bullet}$ and $X^{\bullet}$ units in the designated medium. [c] Values in parentheses are estimated.

trophilic olefins such as methyl acrylate react quickly with rhodium(I) ($[(TSPP)Rh^{I}(D_2O)]^{-5}$ (**2**)) in D_2O to form the anti-Markovnikov addition products ($Rh-CH_2CH(D)X$), but unactivated alkenes such as ethene react very slowly. Anti-Markovnikov addition also occurs in acidic media for **1** with most of the olefins studied, with the exception of 4-styrenesulfonic acid sodium salt, which gives a mixture of isomers.

Equilibrium constants (298 K) were evaluated for each of the substrate reactions in water (Tables 1−4). The pH dependence for the distribution of solution species in water has permitted a substantial increase in the scope of thermodynamic studies compared to those accessible in benzene. Direct measurement of the equilibrium constants for reactions of the rhodium(I) complex (**2**) with olefins ($CH_2{=}CH(X)$) in D_2O to form alkyl complexes ($Rh-CH_2CH(D)X$) along with the acid dissociation constant of **1** permit evaluation of equilibrium constants as large as 2.8×10^{8} for reactions of the hydride **1** with olefins and equilibrium constants as small as 2.5×10^{-7} for substrate reactions of **2**.

Reactions of rhodium hydrides with CO and aldehydes have a cancellation of relatively large solvation energies to produce nearly equal free-energy changes in water and benzene, but the formation of hydrophobic alkyl groups from alkene reactions with **1** is substantially less favorable in water compared with that in benzene. Compensation of enthalpy and entropy is an important characteristic of aqueous media that makes the free-energy change the best thermodynamic parameter for comparative studies. Measured free-energy changes for the substrate reactions of the hydride (**1**) (eqs 4−7, Table 1) in conjunction with aqueous solvation free energies (Table 7) are used in deriving bond dissociation free-energy (BDFE) values for organo-rhodium porphyrin complexes in water (Table 9). BDFE values for the metal complexes and substrate processes provide a systematic method to anticipate new reactivity and to identify the origins of medium-dependent behavior.

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 just before use. Tetra(*p*-sulfonato-phenyl) porphyrin sodium salt was purchased from Mid-Century Chemicals. Research grade hydrogen and carbon monoxide were purchased from Matheson Gas Products and used without further purification. Carbon-13 labeled carbon monoxide was purchased from Cambridge Isotope Laboratories, Inc.

Proton NMR was obtained on a Bruker AC-360 interfaced to an Aspect 300 computer at ambient temperature. Chemical shifts were referenced to 3-trimethylsilyl-1-propanesulfonic acid sodium salt. Carbon-13 NMR spectra were obtained on an AMX-500 instrument.

Synthesis of $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$ (**3**), $[(TSPP)Rh-D(D_2O)]^{-4}$ (**1**), and $[(TSPP)Rh^{I}(D_2O)]^{-5}$ (**2**) were reported in the previously published paper.[7,8] Substrate reactions of $[(TSPP)Rh-D(D_2O)]^{-4}$ (**1**) and $[(TSPP)Rh^{I}(D_2O)]^{-5}$ (**2**) with CO, aldehydes, and olefins in water were carried out by vacuum transfer of the substrate to vacuum-line adapted NMR tubes containing preformed samples of **1** and **2** in D_2O at a defined hydrogen ion ($[D^+]$) concentration, and then dihydrogen was repressurized into the sample to suppress the formation of $(TSPP)Rh^{III}$ species. The total concentration of rhodium complexes is maintained in the range 1×10^{-3}−5×10^{-4} M to ensure that each species is monomeric.

Proton NMR was used to identify solution species and to determine the distribution of each species at equilibrium. Equilibrium constants were evaluated from the intensity integrations of ^{1}H NMR for each species in combination with D^+ concentration measurement and the solubility of the small organic substrate in water.[22] Equilibrium concentrations of $[(TSPP)Rh-D(D_2O)]^{-4}$ for the substrate reactions were determined from the averaged ^{1}H NMR chemical shifts in combination with the D^+ ion concentration which determines the equilibrium distribution of $[(TSPP)Rh^{I}(D_2O)]^{-5}$ and $[(TSPP)Rh-D(D_2O)]^{-4}$.

Reaction of $[(TSPP)Rh-D(D_2O)]^{-4}$ with CO. A solution of **1** (10^{-3} M) was pressurized with a mixture of H_2/CO containing 70% CO (0.6

atm) to form $[(\text{TSPP})\text{Rh}-\text{CDO}(\text{D}_2\text{O})]^{-4}$ (**4**). The equilibrium constant was evaluated from the ^{1}H NMR integrations of rhodium hydride and rhodium formyl porphyrin pyrrole hydrogens at 8.78 and 8.89 ppm, respectively.

^{1}H NMR (360 MHz, D_2O) δ (ppm) ($[(\text{TSPP})\text{Rh}-\text{CDO}\ (\text{D}_2\text{O})]^{-4}$ (**4**)): 8.89 (s, 8H, pyrrole), 8.54 (d, 4H, *o*-phenyl, $J_{^1\text{H}-^1\text{H}} = 8$ Hz), 8.31 (d, 4H, *o*-phenyl, $J_{^1\text{H}-^1\text{H}} = 8$ Hz), 8.20 (d, 8H, *m*-phenyl, $J_{^1\text{H}-^1\text{H}} = 8$ Hz). ^{13}C NMR (500 MHz, D_2O) δ (ppm): 218 (q, 1C, formyl, $J_{^{103}\text{Rh}-^{13}\text{C}} = 28$ Hz, $J_{^2\text{H}-^{13}\text{C}} = 25$ Hz).

Reactions of $[(\text{TSPP})\text{Rh}^{\text{I}}(\text{D}_2\text{O})]^{-5}$ and $[(\text{TSPP})\text{Rh}-\text{D}(\text{D}_2\text{O})]^{-4}$ with Aldehydes in Water. Aqueous solutions of paraformaldehyde are a source of H_2CO in equilibrium with $\text{CH}_2(\text{OD})_2$ ($\text{H}_2\text{CO} + \text{D}_2\text{O} \rightleftarrows \text{CH}_2(\text{OD})_2$) that reacts with the hydride **1** (10^{-3} M) to form a rhodium hydroxy methyl complex $[(\text{TSPP})\text{Rh}-\text{CH}_2(\text{OD})]^{-4}$ (**5**). The equilibrium concentration of the formaldehyde monomer (H_2CO) in D_2O was determined by integration of the ^{1}H NMR for $\text{H}_2\text{C}(\text{OD})_2$ relative to 3-trimethylsilyl-1-propanesulfonic acid sodium salt as a concentration standard and the reported equilibrium constant for the formaldehyde hydration reaction (K (298 K) = 36.2). The equilibrium constant of the formaldehyde reaction with Rh−D was determined by integration of the ^{1}H NMR for $[(\text{TSPP})\text{Rh}-\text{D}(\text{D}_2\text{O})]^{-4}$ and $[(\text{TSPP})\text{Rh}-\text{CH}_2(\text{OH})(\text{D}_2\text{O})]^{-4}$ and combined with the concentration of $[\text{H}_2\text{CO}]$.

^{1}H NMR (360 MHz, D_2O) δ (ppm) ($[(\text{TSPP})\text{Rh}-\text{CH}_2(\text{OH})(\text{D}_2\text{O})]^{-4}$ (**5**)): 8.8 (8H, pyrrole), 8.30−8.00 (16H, phenyl), −2.86 (d, 2H, CH_2).

Solutions of $[(\text{TSPP})\text{Rh}-\text{D}(\text{D}_2\text{O})]^{-4}$ (5×10^{-4} M) react with acetaldehyde to form α-hydroxyalkyl complexes $[(\text{TSPP})\text{Rh}-\text{CH}(\text{OD})\text{CH}_3(\text{D}_2\text{O})]^{-4}$ (**6**). The extent of conversion to the α-hydroxyalkyl complex decreases in basic solution and becomes unobservable when $[\text{D}^+]$ is less than 10^{-10} M. The equilibrium concentrations of the aldehydes in D_2O were determined by ^{1}H NMR relative to a standard 3-trimethylsilyl-1-propanesulfonic acid sodium salt. Equilibrium constants (298 K) were measured by integration of the ^{1}H NMR for $[(\text{TSPP})\text{Rh}-\text{D}(\text{D}_2\text{O})]^{-4}$ and $[(\text{TSPP})\text{Rh}-\text{CH}(\text{OH})\text{CH}_3(\text{D}_2\text{O})]^{-4}$ combined with the concentration of the acetaldehydes.

^{1}H NMR (360 MHz, D_2O) δ (ppm) ($[(\text{TSPP})\text{Rh}-\text{CH}(\text{OD})\text{CH}_3(\text{D}_2\text{O})]^{-4}$ (**6**)): 8.44 (8H, pyrrole), 8.3−8.0 (16H, phenyl), −2.6 (br, 1H, $\text{C}\mathbf{H}(\text{OD})\text{CH}_3$), −4.4 (br, 3H, $\text{CH}(\text{OD})\text{C}\mathbf{H}_3$).

Reaction of $[(\text{TSPP})\text{Rh}^{\text{I}}(\text{D}_2\text{O})]^{-5}$ and $[(\text{TSPP})\text{Rh}-\text{D}(\text{D}_2\text{O})]^{-4}$ with Ethene, Hexene, Methyl Acrylate, and 4-Styrenesulfonic Acid Sodium Salt. A solution of **2** (5×10^{-4} M) reacted with ethene, hexene, methyl acrylate, and 4-styrenesulfonic acid sodium salt to form $[(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}_2\text{D}(\text{D}_2\text{O})]^{-4}$, $[(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{D})(\text{CH}_2)_3\text{CH}_3(\text{D}_2\text{O})]^{-4}$, $[(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{D})\text{CO}_2\text{CH}_3(\text{D}_2\text{O})]^{-4}$, and $[(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{D})\text{C}_6\text{H}_4\text{SO}_3\text{Na}(\text{D}_2\text{O})]^{-4}$, respectively. Reactions of **1** (5×10^{-4} M) with ethene, hexene, and methyl acrylate produce the same products as those of **2**, with the exception of **1** with 4-styrenesulfonic acid sodium salt which produces both $[(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{D})\text{C}_6\text{H}_4\text{SO}_3\text{Na}(\text{D}_2\text{O})]^{-4}$ and $[(\text{TSPP})\text{Rh}-\text{CH}(\text{CH}_2\text{D})\ \text{C}_6\text{H}_4\text{SO}_3\text{Na}(\text{D}_2\text{O})]^{-4}$. The reactions of rhodium hydride with all the substrate olefins go to completion within the time needed to run an ^{1}H NMR, but the reactions of $[(\text{TSPP})\text{Rh}^{\text{I}}(\text{D}_2\text{O})]^{-5}$ with unactivated olefins such as ethene and hexene are much slower and take months to achieve an equilibrium distribution. The thermodynamic equilibrium constants were evaluated from the integration of the ^{1}H NMR for the rhodium alkyl and rhodium(I) complexes in combination with the proton concentration which determines the equilibrium concentration of $[(\text{TSPP})\text{Rh}-\text{D}(\text{D}_2\text{O})]^{-4}$. The substrate olefin hydrogens slowly reduce in ^{1}H NMR intensity compared to the internal reference, which indicates that the olefins are partially deuterated. 4-Styrenesulfonic acid sodium salt becomes almost fully deuterated ($\text{CD}_2{=}\text{CDX}$) indicating that both regioisomers are being formed in acidic D_2O. In basic D_2O media, the activated olefins become selectively deuterated ($\text{CH}_2{=}\text{CDX}$) through rhodium hydride mediated exchange with D_2O.

^{1}H NMR (360 MHz, D_2O) δ (ppm) ($[(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}_2\text{D}]^{-4}$ (**8**)): 8.64 (8H, pyrrole), 8.33−8.14 (16H, phenyl), −4.6 (br, 2H, $\text{CH}_2\text{C}\mathbf{H}_2\text{D}$), −5.7 (br, 2H, $\text{C}\mathbf{H}_2\text{CH}_2\text{D}$).

^{1}HNMR (360 MHz, D_2O) δ (ppm) ($[(\text{TSPP})\text{Rh}-\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{DCH}_3]^{-4}$ (**9**)): 8.71 (8H, pyrrole), 8.39−8.16 (16H, phenyl), 0.02 (3H, $\text{CH}_2\text{CHD}(\text{CH}_2)_3\text{CH}_3$), −0.29 (2H), −0.86 (2H), −1.92 (2H), −4,95 (1H), −6.08 (2H).

^{1}H NMR (360 MHz, D_2O) δ (ppm) ($[(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{D})\text{CO}_2\text{CH}_3]^{-4}$ (**10**)): 8.70 (s, 8H, pyrrole), 8.29 (d, 4H, phenyl, $J_{^1\text{H}-^1\text{H}} = 8$ Hz), 8.25 (d, 4H, phenyl, $J_{^1\text{H}-^1\text{H}} = 8$ Hz), 8.14 (d, 4H, phenyl, $J_{^1\text{H}-^1\text{H}} = 8$ Hz), 8.11 (d, 4H, phenyl, $J_{^1\text{H}-^1\text{H}} = 8$ Hz), −3.26 (t, 1H, $\text{CH}_2\text{C}\mathbf{H}\text{D}(\text{CO}_2\text{CH}_3)$, $J_{^1\text{H}-^1\text{H}} = 6.2$ Hz, $J_{^2\text{H}-^1\text{H}} = 1.0$ Hz), −5.62 (d of d, 2H, $\text{C}\mathbf{H}_2\text{CHD}(\text{CO}_2\text{CH}_3)$, $J_{^1\text{H}-^1\text{H}} = 6.2$ Hz, $J_{^{103}\text{Rh}-^1\text{H}} = 2.8$ Hz).

^{1}H NMR (360 MHz, D_2O) δ (ppm) ($[(\text{TSPP})\text{Rh}-\text{CH}_2\text{CH}(\text{D})\text{C}_6\text{H}_4\text{SO}_3\text{Na}]^{-4}$ (**11**)): 8.62 (8H, pyrrole), 8.41−8.0 (16H, phenyl), −3.2 (t, 1H, $\text{CH}_2\text{C}\mathbf{H}(\text{D})\text{C}_6\text{H}_4\text{SO}_3\text{Na}$), −5.5 (d of d, 2H, $\text{C}\mathbf{H}_2\text{CH}(\text{D})\text{C}_6\text{H}_4\text{SO}_3\text{Na}$). ^{1}H NMR (360 MHz, D_2O) δ (ppm) ($[(\text{TSPP})\text{Rh}-\text{CH}(\text{CH}_2\text{D})\text{C}_6\text{H}_4\text{SO}_3\text{Na}]^{-4}$): 8.59 (8H, pyrrole), 8.41−8.0 (16H, phenyl), −4.17 (t, 1H, $\text{C}\mathbf{H}(\text{CH}_2\text{D})\text{C}_6\text{H}_4\text{SO}_3\text{Na}$), −4.34 (d, 2H, $\text{CH}(\text{C}\mathbf{H}_2\text{D})\text{C}_6\text{H}_4\text{SO}_3\text{Na}$).

Estimation of Bond Dissociation Free Energies (Δ*G*° (298 K)) of D−X from Values of H−X in Water. The BDFEs of $(\text{D}-\text{D})_{\text{aq}}$ and $(\text{D-OD})_{\text{aq}}$ are estimated on the basis of the corresponding H−H and H−OH values and the zero-point energy difference. The difference between H−H and D−D is ≅1.7 kcal mol^{-1}, and the difference between H−OH and D−OD is ≅1.5 kcal mol^{-1} which results from the difference in stretching frequencies. The derived BDFEs for $\text{D}-\text{D}_{\text{aq}}$ and $\text{D}-\text{OD}_{\text{aq}}$ are 103.4 and 117.6 kcal mol^{-1}, respectively.

Acknowledgment. This research was supported by the Department of Energy, Division of Chemical Sciences, Office of Science, through grant DE-FG02-86ER-13615.

JA054548N