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Published in issue 2, 2010 of *Dalton Transactions*

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# Reactivity and kinetic–mechanistic studies of regioselective reactions of rhodium porphyrins with unactivated olefins in water that form β-hydroxyalkyl complexes and conversion to ketones and epoxides†

**Jiadi Zhang,[a] Bradford B. Wayland,[b] Lin Yun,[a] Shan Li[b] and Xuefeng Fu*[a]**

***Received 22nd June 2009, Accepted 19th September 2009***
***First published as an Advance Article on the web 22nd October 2009***
**DOI: 10.1039/b912219b**



This article reports on the selective oxidation of unactivated alkenes to ketones and epoxides through the intermediacy of β-hydroxyalkyl rhodium porphyrin complexes which are formed by reactions of terminal alkenes with tetra(*p*-sulfonatophenyl)porphyrin rhodium(III) complex. The β-hydroxyalkyl rhodium porphyrin complexes in water undergo β-C–H elimination to produce ketones in aqueous pH 9.0 solutions and O–H deprotonation in KOH/DMSO solutions resulting in the rapid and quantitative intramolecular nucleophilic displacement to form 1,2-epoxyalkanes.

## Introduction

The activation of alkenes by coordination to metal centers is one of the most widely exploited synthetic methodologies in the functionalization of organic molecules,[1-5] and has contributed significantly to advances in selective organic transformations.[6-10]

Catalytic air oxidation of ethene to acetaldehyde by an aqueous Pd(II)/Cu(II) catalyst system is known as the Wacker process. Mechanistic studies for the Wacker reaction and closely related processes have shown that alkene binding with palladium(II) activates reactions of olefins with nucleophiles including water, alcohols, and amines to form β-substituted alkyl complexes.[11] Subsequent C–H and O–H elimination reactions of the β-substituted alkyl complexes produce organic carbonyls, epoxides, heterocyclic molecules, and hydrofunctionalized alkenes.[12-15] Several rhodium and iridium complexes have also been reported to mediate oxidation of olefins in hydrocarbon media,[16-19] but relatively little attention has been given to complexes of transition metals other than palladium(II). The importance of olefin transformations and objectives of green chemistry justify the continuing search for new classes of catalyst materials that give oxidations in water and use dioxygen as the oxidant. This article reports on the observed stepwise reactions of rhodium porphyrins with olefins in water to form β-hydroxyalkyl complexes that react on to give stoichiometric oxidation of alkenes to ketones in aqueous media and epoxides in DMSO. Several objectives in olefin activation and oxidation have been advanced in this study through observation of product inhibited catalytic oxidation of olefins to organic carbonyls in water using dioxygen as the oxidant.

## Results and discussion

### Formation of β-hydroxyalkyl rhodium complexes in water

Tetra(*p*-sulfonatophenyl)porphyrin rhodium(III) diaquo complex $[(TSPP)Rh^{III}(D_2O)_2]^{3-}$ (**1**) is a convenient entry point for aqueous ($D_2O$) solution reactivity studies of rhodium porphyrins. The rhodium(III) diaquo complex occurs in $D_2O$ solution as a pH dependent equilibrium distribution with the mono- and bis-hydroxo complexes ($[(TSPP)Rh^{III}(OD)(D_2O)]^{4-}$ (**2**) and $[(TSPP)Rh^{III}(OD)_2]^{5-}$ (**3**)) where $K_1 = 1.4 \pm 0.2 \times 10^{-8}$ and $K_2 = 2.8 \pm 0.3 \times 10^{-12}$ (eqn (1) and (2)).[20]

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

$$[(TSPP)Rh^{III}(OD)(D_2O)]^{4-} \rightleftharpoons [(TSPP)Rh^{III}(OD)_2]^{5-} + D^+ \quad (2)$$

Reactions of $(TSPP)Rh^{III}$ complexes with a series of olefins produce β-hydroxyalkyl complexes in water.‡

**Reaction of $(TSPP)Rh^{III}$ with 2-substituted olefins.** Ethene and larger terminal alkene hydrocarbons ($CH_2$=CHR) react regioselectively with $(TSPP)Rh^{III}$ in $D_2O$ to form β-hydroxy alkyl rhodium complexes ($[(TSPP)Rh–CH_2CH(OD)R(D_2O)]^{4-}$) where rhodium is attached to the terminal primary $CH_2$ unit (eqn (3)).[21]

$$[(TSPP)Rh–OD(D_2O)]^{4-} + CH_2{=}CHR \rightleftharpoons [(TSPP)Rh–CH_2CH(OD)R(D_2O)]^{4-} \quad (3)$$

The β-hydroxyalkyl complexes are easily identified by the porphyrin ring current induced high-field $^1H$ NMR resonances of the organic group bonded to the rhodium center. The $^1H$ NMR resonances for the diastereotopic α-$CH_2$ group in $(TSPP)Rh–CH_2CH(OD)CH_2CH_2CH_3$ in $D_2O$ are centered at −5.93 and −5.74 ppm. Isolating ($(TSPP)Rh–CH_2CH(OH)CH_2CH_2CH_3$) formed in water and dissolving in anhydrous DMSO-$d_6$ permitted observing the doublet hydroxyl proton resonance ($(TSPP)RhCH_2CH(OH)CH_2CH_2CH_3$) at 0.01 ppm

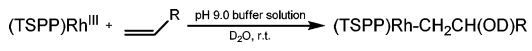
[a]*Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications, Peking University, Beijing, 100871, China. E-mail: fuxf@pku.edu.cn; Fax: +86 10 6275 1708; Tel: +86 10 6275 6035*

[b]*Department of Chemistry, Temple University, Philadelphia, PA, 19122, USA. E-mail: BWayland@Temple.edu; Fax: +1 215 204 1532; Tel: +1 215 204 7875*

† Electronic supplementary information (ESI) available: Experimental procedures and NMR spectra. See DOI: 10.1039/b912219b

‡ Tetra(*p*-sulfonatophenyl)porphyrin rhodium(III) monohydroxide complex ($[(TSPP)Rh^{III}(D_2O)(OD)]^{4-}$) and its alkyl derivatives $[(TSPP)Rh^{III}–R(D_2O)]^{4-}$ are 4– charged complexes and abbreviated as (TSPP)Rh–OD and (TSPP)Rh–R, respectively.

**Table 1** Formation of β-hydroxyalkyl rhodium porphyrin complexes in borate buffer aqueous solution (pH = 9.0) at 298 K[a]

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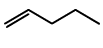
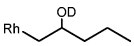
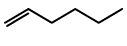
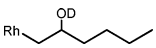
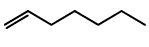
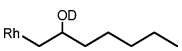
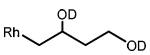
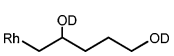
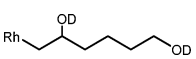
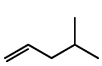
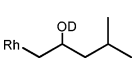
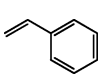
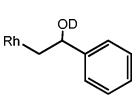
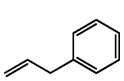
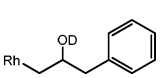
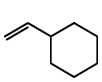
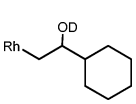
| 1 |  | 3 h |  | 92 (3)[c] |
| 2 |  | 6.7 h |  | 80 (6)[c] |
| 3 |  | 1.5 h[b] |  | 84 (2)[c] |
| 4 |  | <5 min |  | >95 |
| 5 |  | <5 min |  | >95 |
| 6 |  | <5 min |  | >95 |
| 7 |  | 82 h |  | >95 |
| 8 |  | 1.4 h[b] |  | 94 |
| 9 |  | 34 h[b] |  | 89 |
| 10 |  | 34 h[b] |  | 91 |

[a] The initial concentration of (TSPP)Rh$^{III}$ was $1.9 \times 10^{-3}$ M. The yield of the reaction was measured by $^1$H NMR spectroscopy. [b] The reaction was run in a mixed-solvent composed of 1,4-dioxane-$d_8$ and $D_2O$ (1/4 v/v). [c] The values in parentheses are the overall percentage of the formed (TSPP)Rh–$CH_2C(O)R$ as by-product.

(d, $^3J_{HH}$ = 5.6 Hz). Reactions of (TSPP)Rh$^{III}$ with a series of terminal alkenes in a borate buffer with pH 9.0 produce β-hydroxyalkyl complexes [(TSPP)Rh–$CH_2CH(OD)R(D_2O)]^{4-}$ (**4**) that reach equilibrium in time periods of several minutes to hours depending inversely on the olefin solubility (Table 1). Highly soluble alkenes (Table 1, entries 4–6) cleanly react to completion within minutes but poorly soluble alkenes (Table 1, entries 1–3) react much slower which allows time to produce some β-carbonyl organometallic derivatives ([(TSPP)Rh–$CH_2C(O)R)(D_2O)]^{4-}$) by β-C–H elimination of **4**.[22]

**Reaction of (TSPP)Rh$^{III}$ with 2,2-disubstituted alkenes in water.** Reaction of (TSPP)Rh$^{III}$ with a 2,2-disubstituted alkene (2-methyl-1-butene) also forms a β-hydroxyalkyl complex [(TSPP)Rh–$CH_2C(OD)(CH_3)(CH_2CH_3)(D_2O)]^{4-}$ (**5**) (eqn (4)).

$$[(TSPP)Rh–OD(D_2O)]^{4-} + CH_2{=}C(CH_3)CH_2CH_3 \rightleftharpoons [(TSPP)Rh–CH_2C(OD)(CH_3)(CH_2CH_3)(D_2O)]^{4-} \quad (4)$$

The $^1$H–$^1$H and $^{103}$Rh–$^1$H coupling patterns that are partially obscured by line broadening in water became clearly resolved when **5** was isolated from water and redissolved in $CD_3OD$ (Fig. 1(b)). The characteristic AB pattern for the α-$CH_2$ unit ($\delta$(ppm): –5.55 ($H_A$), –5.48 ($H_B$), $J_{AB}$ = 9.9 Hz, $J_{RhH}$ = 2.9 Hz) in **5** in $CD_3OD$ is substantially improved from the broad resonance observed in $D_2O$ at –5.72 ppm (Fig. 1(a)). The hydroxyl proton resonance for (TSPP)Rh–$CH_2C(OH)(CH_3)(CH_2CH_3)$ was also identified from the $^1$H NMR spectrum (s, –0.16 ppm) in anhydrous DMSO-$d_6$ by preparation of the sample in $H_2O$ and transferring into DMSO-$d_6$ (Fig. 1(c)).

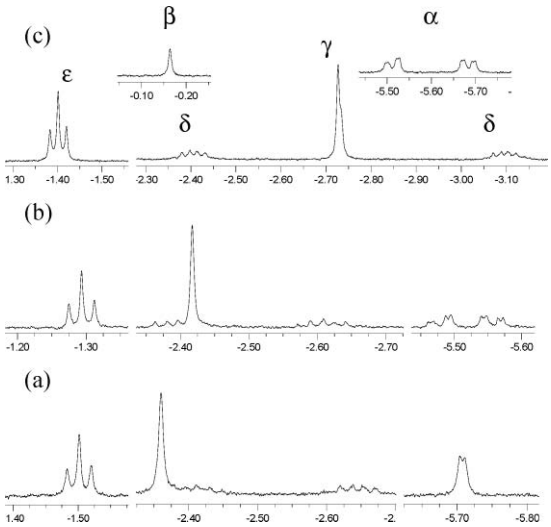



**Fig. 1** High-field $^1$H NMR (400 MHz) for (TSPP)Rh–$CH_{2\alpha}C(OH_\beta)(CH_{3\gamma})(CH_{2\delta}CH_{3\varepsilon})$ (a) in $D_2O$, (b) in $CD_3OD$, and (c) in DMSO-$d_6$.

### Kinetics of alkene reaction with (TSPP)Rh$^{III}$ in water

**Evaluation of rate and equilibrium constants ($k_f$, $k_r$, $K_{eq}$).** Formations of (TSPP)Rh–$CH_2CH(OD)R$ as a function of time from reactions of (TSPP)Rh$^{III}$ species with pentene and hexene in $D_2O$ at 298 K using a pH = 9.0 buffer are illustrated in Fig. 2.

Expressions were derived for several plausible mechanisms. The kinetics for this reaction are potentially complicated by having three different aquo/hydroxo complexes, but the monohydroxo complex is the dominant species (>93%) at pH = 9.0 so that effectively all of the β-hydroxyalkyl products were formed through the monohydroxo complex ([(TSPP)Rh$^{III}$$(D_2O)(OD)]^{4-}$ (**2**)). Thus, the rate of formation of [(TSPP)Rh–$CH_2CH(OD)R(D_2O)]^{4-}$ is derived as d[Rh–$CH_2CH(OD)R$]/d$t$ = $k_f$[**2**][alkene] – $k_r$[Rh–$CH_2CH(OD)R$]. The best fit from nonlinear least squares curve fitting is obtained for the mechanism where effectively all of the product forms from reaction of **2** with alkenes (see Experimental section for detailed derivation). The forward rate constant for the pentene reaction at 298 K ($k_f = (2.3 \pm 0.1) \times 10^{-1}$ L mol$^{-1}$ s$^{-1}$) and the reverse reaction rate constant ($k_r = (10.0 \pm 1.0) \times 10^{-5}$ s$^{-1}$), along with the corresponding values for the hexene reaction (298 K) ($k_f = (8.0 \pm 0.1) \times 10^{-2}$ L mol$^{-1}$ s$^{-1}$, $k_r = (7.8 \pm 1.0) \times 10^{-5}$ s$^{-1}$) are obtained from the kinetic simulation (Fig. 2). The equilibrium constant for pentene $K_{eq}$ ($K_{eq} = k_f/k_r = (2.3 \pm 0.1) \times 10^3$) that is derived from the kinetic analysis is close to the value obtained from direct equilibrium thermodynamic measurement by integration of the $^1$H NMR spectrum ($K_{eq} = (4.1 \pm 0.6) \times 10^3$).

Reaction (3) occurs through formation of π complexes ((TSPP)Rh($CH_2$=CHR)) by alkene substitution for a coordinated water molecule followed by nucleophilic attack on the olefin π complex and a proton transfer.

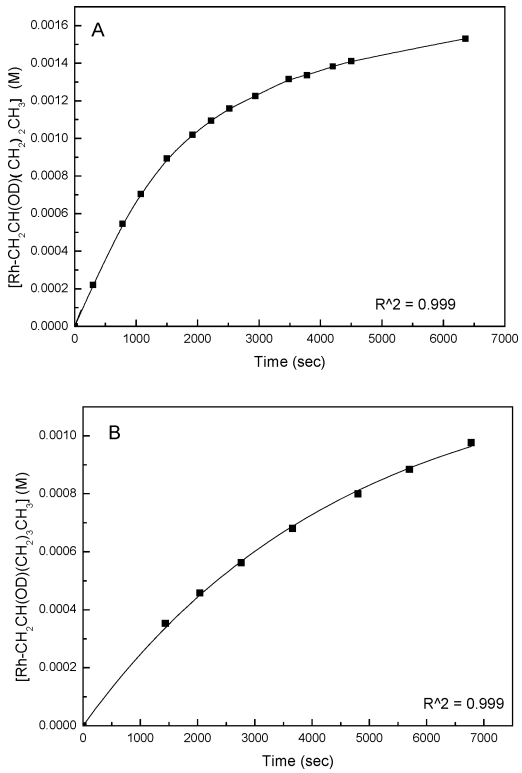
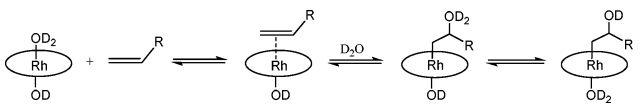



**Fig. 2** Formation of $[(TSPP)Rh–CH_2CH(OD)R(D_2O)]^{4-}$ from $[(TSPP)Rh^{III}(OD)(D_2O)]^{4-}$ with pentene and hexene at 298 K with pH = 9.0 buffer. The solid line is the nonlinear least-square best fit to the equation $d[(TSPP)Rh–CH_2CH(OD)R]/dt = \beta - \alpha[(TSPP)Rh–CH_2CH(OD)R]$, $\beta = k_f c_{(Rh^T)} c_0/(([D^+]/K_1) + (K_2/[D^+]) + 1)$, $\alpha = (\beta/c_{(Rh^T)}) + k_r$ using OriginPro 7.5 software. The initial concentration of $(TSPP)Rh^{III}$, $c_{(Rh^T)}$, equals $1.9 \times 10^{-3}$ M. The saturated solubility of pentene in water, $c_0$, is $2.1 \times 10^{-3}$ M, and hexane is $1.9 \times 10^{-3}$ M.[23] (A) Reaction of pentene gives $\alpha = (5.5 \pm 0.1) \times 10^{-4}$, $\beta = (8.5 \pm 0.1) \times 10^{-7}$, and $k_f = (2.3 \pm 0.1) \times 10^{-1}$ L mol$^{-1}$ s$^{-1}$, $k_r = (10.0 \pm 1.0) \times 10^{-5}$ s$^{-1}$, and $K_{eq} = (2.3 \pm 0.1) \times 10^3$ are derived. (B) Reaction of hexane gives $\alpha = (2.2 \pm 0.1) \times 10^{-4}$, $\beta = (2.7 \pm 0.1) \times 10^{-7}$ and $k_f = (8.0 \pm 0.1) \times 10^{-2}$ L mol$^{-1}$ s$^{-1}$, $k_r = (7.8 \pm 1.0) \times 10^{-5}$ s$^{-1}$, and $K_{eq} = (1.0 \pm 0.1) \times 10^3$ are derived.



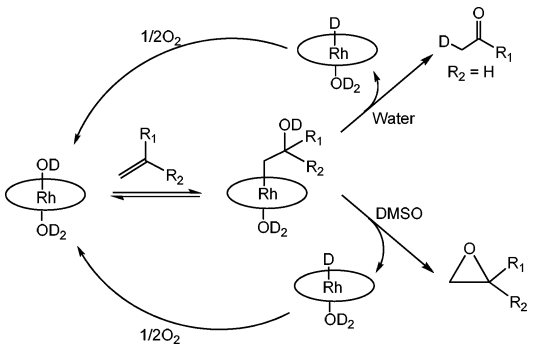

The regioselectivity for the initial nucleophilic attack step is controlled by the sterically bulky porphyrin ligand which favors placing rhodium on the less hindered terminal primary carbon as the kinetic product. In the case of unactivated alkenes the kinetic and thermodynamic products have rhodium on the primary $–CH_2$ ($(TSPP)Rh–CH_2CH(OD)R$), but olefins with electron withdrawing groups (R = phenyl, $CO_2Na$) initially form $(TSPP)Rh–CH_2CH(OD)R$ and then rearrange to $(TSPP)Rh–CH(R)CH_2OD$ as the thermodynamic products.

Electron withdrawing groups better stabilize the negative charge and provide an electronic energy term that favors placing the metal on the same carbon as the electron withdrawing group which for the phenyl and $CO_2Na$ derivatives more than compensates for the unfavorable steric effect.[21,24]

An octaethylporphyrin rhodium ethene π complex $((OEP)Rh(CH_2{=}CH_2))^+$ has been directly observed in toluene by $^1$H NMR at 243 K. The β-hydroxyalkyl complex of rhodium octaethylporphyrin ($(OEP)Rh–CH_2CH_2OH$) was formed in hydrocarbon media through hydroxide nucleophilic addition to $((OEP)Rh(CH_2{=}CH_2))^+$.[25] Olefin π complexes of $(TSPP)Rh^{III}$ in water at 298 K have not yet been observed by $^1$H NMR even when the conditions for π complex formation are optimized by using high concentrations of water-soluble olefins and slightly acidic aqueous media where the diaquo complex **1** dominates.

## Thermal dissociation of β-hydroxyalkyl rhodium porphyrin complexes

β-Hydroxyalkyl rhodium porphyrin complexes are intermediate organometallic complexes for both β-C–H elimination reactions that produce ketones in pH 9.0 aqueous solution and intramolecular C–O elimination to form epoxides quantitatively in KOH/DMSO (Scheme 1).



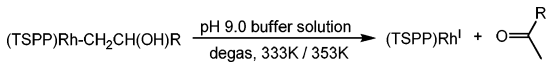

**Scheme 1** Thermal dissociation pathways of β-hydroxyalkyl rhodium porphyrin complexes.

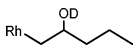
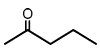
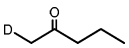
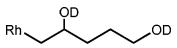
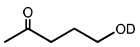
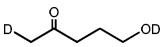
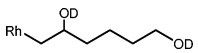
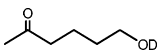
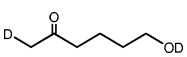
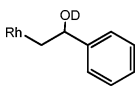
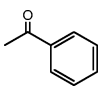
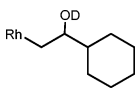
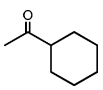
**β-Hydrogen elimination of β-hydroxyalkyl rhodium porphyrin complexes in water.** β-Hydrogen elimination reactions are among the most important fundamental organometallic transformations in a variety of transition metal alkyl and alkoxide complexes. The hydrogen migration or elimination usually occurs in coordinately unsaturated complexes through use of a vacant *cis* coordination site. However, β-hydrogen elimination processes for alkyl rhodium porphyrin complexes must utilize a different mechanism because all of the *cis* coordination sites are occupied by the porphyrin pyrrole nitrogen donors.[26] The β-hydroxyalkyl complexes formed by reaction (3) in water spontaneously transform to (TSPP)Rh–H and ketones in the absence of air by an effective β-hydrogen elimination (eqn (5), Table 2).[22]

$$[(TSPP)Rh–CH_2CH(OD)R(D_2O)]^{4-} \rightleftharpoons [(TSPP)Rh(H)(D_2O)]^{4-} + CH_2DC(O)R \quad (5)$$

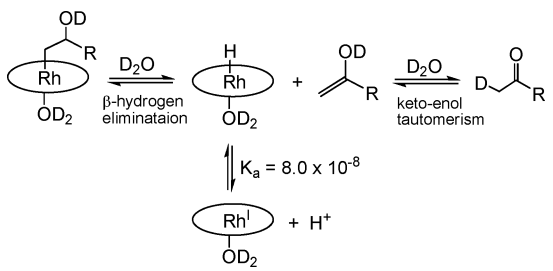
Thermal reaction of $(TSPP)Rh–CH_2CH(OD)(CH_2)_2CH_3$ in $D_2O$ results in the formation of (TSPP)Rh–H and a monodeuterated 2-pentanone ($CH_2(D)C(O)CH_2CH_2CH_3$) where deuterium is selectively incorporated into the methyl group. The selective deuteration indicates that β-hydrogen elimination produces an enol containing an OD unit (Scheme 2). This mechanistic feature is different from the Pd(II) Wacker oxidation where deuterium from $D_2O$ does not occur in the oxidation product. Isomerization of β-hydroxyalkyl to the α-hydroxy isomer that occurs prior to the product forming step in the Wacker reaction cannot occur for the rhodium porphyrin because the *cis* coordination sites are blocked.

**Table 2** Formation of ketones through β-hydrogen elimination of β-hydroxyalkyl rhodium porphyrin complexes in pH = 9.0 buffer[a]




| Entry | Substrate | *t*/h | Solvent | Product |
|---|---|---|---|---|
| 1 |  | 9[b] | $H_2O$ |  |
| | | | $D_2O$ |  |
| 2 |  | 16.5[b] | $H_2O$ |  |
| | | 3[c] | $D_2O$ |  |
| 3 |  | 9[c] | $H_2O$ |  |
| | | | $D_2O$ |  |
| 4 |  | 3[c] | $H_2O$ |  |
| 5 |  | 3[c] | $H_2O$ |  |

[a] The reactions were performed in borate buffers with pH = 9.0 in the absence of air, and the ketone products were nearly quantitatively formed as measured by $^1$H NMR spectroscopy although small amounts of (TSPP)Rh$^{III}$ were also observed. [b] 333 K. [c] 353K.

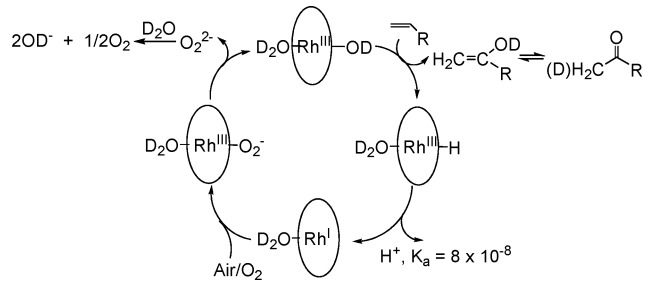



**Scheme 2** Formation of ketones through (i) thermal β-hydrogen elimination of **4** and (ii) keto–enol tautomerism in water.

The observed fast reactions of rhodium porphyrin hydrides with olefins in water compared to benzene is ascribed to water supporting ionic reaction pathways.[27] In aqueous solution the hydride complex [(TSPP)Rh$^{III}$(D)(D$_2$O)]$^{4-}$ functions as a weak acid and partially dissociates into D$^+$ and [(TSPP)Rh$^I$(D$_2$O)]$^{5-}$. The rhodium(I) porphyrin complex in water is proposed to activate olefins which subsequently protonate to form rhodium alkyl complexes. The β-C–H elimination or migration process is the microscopic reverse of the addition of the rhodium hydride to olefins in water which is proposed to occur by dissociation of Rh–H into H$^+$ and Rh(I)$^-$ and subsequent stepwise addition.[27] The complex (TSPP)Rh–CH$_2$C(OD)(CH$_3$)(CH$_2$CH$_3$) **5** lacks a β-hydrogen atom and thus is not capable of producing carbonyl compounds.

**Aerobic oxidation of (TSPP)Rh–H to (TSPP)Rh$^{III}$ in water.**

The [(TSPP)Rh(H)(D$_2$O)]$^{4-}$ species formed in reaction (5) in a rapid dissociation equilibrium with [(TSPP)Rh$^I$(D$_2$O)]$^{5-}$ and H$^+$ undergo an immediate color change to a clear dark red solution when exposed to air. The distinctive pyrrole hydrogen resonance associated with (TSPP)Rh$^{III}$ species is observed by $^1$H NMR. The sequence of reactions with dioxygen to convert (TSPP)Rh–H/(TSPP)Rh$^I$ to (TSPP)Rh$^{III}$ is depicted by Scheme 3.

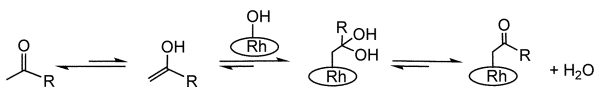



**Scheme 3** Aerobic oxidations of (TSPP)Rh–H/(TSPP)Rh$^I$ to (TSPP)Rh$^{III}$ in water.

Rapid air oxidation of Rh(I) to Rh(III) completes the cycle which provides the potential for catalytic oxidation of olefins.

**Formation of β-carbonyl alkyl rhodium porphyrin complexes in water**

Aqueous buffer solutions of (TSPP)Rh$^{III}$ species react with ketones and aldehydes to produce β-carbonyl derivatives [(TSPP)Rh–CH$_2$C(O)R(D$_2$O)]$^{4-}$ (**6**), which has a precedent in reaction of [(OEP)Rh$^{III}$]$^+$ with ketones.[28] This electrophilic C–H activation by the cationic metal center is thought to proceed through a stepwise mechanism similar to that of reaction (3), in which the enol intermediate reacts with (TSPP)Rh$^{III}$ to give (TSPP)Rh–CH$_2$C(OD)$_2$R, followed by the dehydration step of the unstable *gem*-diol complex.




Reaction of the acetaldehyde methyl C–H unit occurs with high regioselectivity to form (TSPP)Rh–CH$_2$CHO (eqn (6)). No evidence is found for reaction of the weaker aldehydic C–H bond, which is analogous to reactions of (por)Rh$^{II}$ complexes with CH$_3$CHO in benzene.[29]

$$[(TSPP)Rh–OD(D_2O)]^{4-} + CH_3CHO \rightleftharpoons [(TSPP)Rh–CH_2CHO(D_2O)]^{4-} + HOD \quad (6)$$

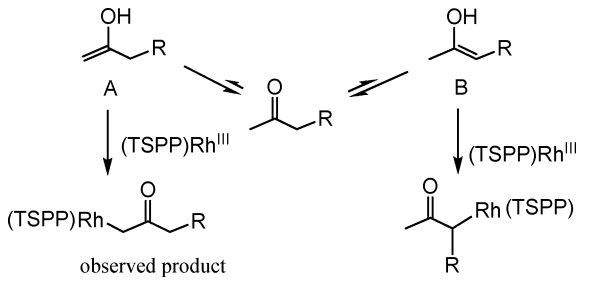
The compound formed from reaction of (TSPP)Rh$^{III}$ with acetone (eqn (7)) has an identical $^1$H NMR spectrum with the complex formed from reaction of (TSPP)Rh$^I$ in water with ClCH$_2$C(O)CH$_3$ that produces (TSPP)Rh–CH$_2$C(O)CH$_3$.

$$[(TSPP)Rh–OD(D_2O)]^{4-} + CH_3C(O)CH_3 \rightleftharpoons [(TSPP)Rh–CH_2C(O)CH_3(D_2O)]^{4-} + HOD \quad (7)$$

Addition of 300 equiv. of 2-pentanone to an aqueous solution of (TSPP)Rh$^{III}$ in pH 9.0 D$_2$O buffer resulted in an equilibrium distribution of (TSPP)Rh–CH$_2$C(O)CH$_2$CH$_2$CH$_3$ and

(TSPP)Rh$^{III}$ which permitted evaluation of the equilibrium constant ($K_{eq}$(298 K) = 33). The relatively slow reaction rates of ketones compared to alkenes may result from the very low enol concentration. The enolization equilibrium constant $K_E$ for acetone[30] is $(4.69 \pm 0.19) \times 10^{-9}$ and the resulting low concentration of enol place limits on the rate of β-carbonyl formation. 2-Pentanone can enolize in two ways resulting in regio-isomeric enols, $CH_2$=C(OD)$CH_2CH_2CH_3$ (**A**) and $CH_3$C(OD)=$CHCH_2CH_3$ (**B**), but the reaction of (TSPP)Rh$^{III}$ with 2-pentanone exclusively produces (TSPP)Rh–$CH_2$C(O)$CH_2CH_2CH_3$. The origin of this result may be the thermodynamic preference for primary alkyl rhodium complexes.



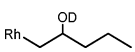
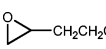
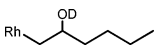
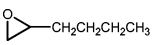
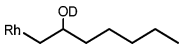
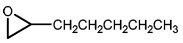
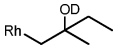
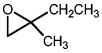

The ketone products react with the (TSPP)Rh(III) oxidation catalyst resulting in a product inhibited catalytic oxidation of olefins which limits the numbers of turnovers.

### Formation of epoxides from β-hydroxyalkyl rhodium porphyrin complexes

The β-hydroxyalkyl rhodium porphyrin complexes, (TSPP)Rh–$CH_2CH(OD)(CH_2)_nCH_3$ ($n$ = 2–4) (eqn (8)) undergo immediate (<5 min) epoxide forming elimination reactions in KOH/DMSO-$d_6$ ($c_{KOH}$ = 3.3 mg mL$^{-1}$) at room temperature to give quantitative formation of (TSPP)Rh–D which is rapidly deprotonated to form (TSPP)Rh$^{I}$ and 1,2-epoxyalkanes as observed by both $^1$H NMR and GC-MS (Table 3).

$$[(TSPP)Rh\text{-}CH_2CH(OD)R(D_2O)]^{4-} \rightleftharpoons [(TSPP)Rh(D)(D_2O)]^{4-} + \text{epoxide} \quad (8)$$

**Table 3** Formation of 1,2-epoxyalkanes through epoxide-forming elimination of β-hydroxyalkyl rhodium porphyrin complexes in KOH/DMSO

| Entry | Substrate | $t$ | Product |
|---|---|---|---|
| 1 |  | <5 min |  |
| 2 |  | <5 min |  |
| 3 |  | <5 min |  |
| 4 |  | <5 min |  |

The reactions were performed in KOH/DMSO ($c_{KOH}$ = 3.3 mg mL$^{-1}$) and the product epoxides were formed quantitatively as measured by $^1$H NMR spectroscopy. The resulting 1,2-epoxyalkanes were extracted into $Et_2O$ and examined by GC-MS.

A brownish solution characteristic of (TSPP)Rh$^{I}$ is observed to form immediately after (TSPP)Rh–$CH_2CH(OD)(CH_2)_nCH_3$ is dissolved in KOH/DMSO-$d_6$. C–O reductive elimination from the d$^6$ metal center usually occurs through an $S_N2$ route and a direct C–O elimination pathway.[31] Groves reported a facile C–O reductive elimination from β-hydroxyalkyl complexes of rhodium tetraphenyl porphyrin in KO$t$Bu/$C_6D_6$ by a proposed $S_N2$ pathway.[19]

The origin of the selective formation of ketone in water and epoxide in KOH/DMSO may be that the nucleophilicity of the alkoxy group is dramatically reduced in water due to the solvation. β-Hydroxyalkyl rhodium porphyrin complexes thus proceed through the alternate usually higher energy β-H elimination pathway which produces ketones. The favored formation of three-membered oxygen heterocycles through intramolecular C–O bond formation is driven by the strong nucleophilicity of the alkoxy group formed in strongly basic conditions of the (KOH/DMSO) medium.

## Conclusions

(TSPP)Rh$^{III}$ reacts with terminal alkenes to form β-hydroxy alkyl rhodium porphyrin complexes with high conversion in pH 9.0 aqueous buffer solution at room temperature. Regioselectivity of the reaction is controlled by the sterically bulky porphyrin ligand and the less-substituted alkyl rhodium complexes are formed as the kinetic products. The equilibrium constant of reaction of (TSPP)Rh$^{III}$ with pentene was evaluated as $K = (2.3 \pm 0.1) \times 10^3$ from kinetic simulation. The β-hydroxyalkyl rhodium porphyrin complexes underwent the β-hydrogen elimination reaction to produce ketones in pH 9.0 aqueous solution and near quantitative intramolecular formation of epoxides in KOH/DMSO. Product inhibited catalytic oxidation of olefins to ketones by (TSPP)Rh$^{III}$ is accomplished by using dioxygen as the oxidant.

## Experimental

### Typical procedure for preparation of (TSPP)Rh–$CH_2CH(OD)R$ in water

Alkenes (0.01 mmol) and **1** (1.1 mg, 0.001 mmol) were dissolved in 0.4 mL borate buffer $D_2O$ solution (pH = 9.0) in J. Young valve adapted NMR tubes at room temperature. The progress of the reaction was monitored by $^1$H NMR spectroscopy.

### Typical procedure for β-hydrogen elimination of (TSPP)Rh–$CH_2CH(OD)R$ in water

The (TSPP)Rh–$CH_2CH(OD)R$ complexes were prepared according to the procedure given above, which exclusively converted (TSPP)Rh$^{III}$ into (TSPP)Rh–$CH_2CH(OD)R$. The excesses of alkenes and solvent $D_2O$ were pumped out. Fresh $D_2O$ was added into the NMR tube and subjected to three freeze–pump–thaw cycles. The initial $^1$H NMR spectrum was recorded to show the formation of Rh–$CH_2CH(OD)R$ and a clean range from 0 to 4 ppm. The sample (TSPP)Rh–$CH_2CH(OD)R$ was heated in a water-bath at 60 °C (or 80 °C) for a period of hours, and the progress of the reaction was monitored by $^1$H NMR spectroscopy. When the reactions reached completion after all (TSPP)Rh–$CH_2CH(OD)R$ complexes were converted to ketones

and (TSPP)Rh–D (which was rapidly deprotonated to form (TSPP)Rh$^{I}$), the product ketones were extracted by $CDCl_3$. A parallel sample of (TSPP)Rh–$CH_2CH(OH)R$ dissolved in $H_2O$ was also heated under the same reaction conditions, and extracted by $CDCl_3$. Both $^1H$ NMR and GC-MS were used to characterize the product ketones.

**Kinetic simulation for reaction of (TSPP)Rh$^{III}$ with pentene**

$$[(TSPP)Rh^{III}(D_2O)_2]^{3-}\ (\mathbf{1}) \overset{K_1}{\rightleftharpoons} [(TSPP)Rh^{III}(OD)(D_2O)]^{4-}\ (\mathbf{2}) + D^+ \quad (9)$$

$$[(TSPP)Rh^{III}(OD)(D_2O)]^{4-}\ (\mathbf{2}) \overset{K_2}{\rightleftharpoons} [(TSPP)Rh^{III}(OD)_2]^{5-}\ (\mathbf{3}) + D^+ \quad (10)$$

$$[(TSPP)Rh-OD(D_2O)]^{4-} + CH_2=CHCH_2CH_2CH_3 \overset{K_3}{\rightleftharpoons} [(TSPP)Rh-CH_2CH(OD)(CH_2)_2CH_3(D_2O)]^{4-}\ (\mathbf{4}) \quad (11)$$

We then have:

$$d[\mathbf{4}]/dt = k_3[\mathbf{2}]c_0 - k_{-3}[\mathbf{4}]$$

$$[\mathbf{1}] = [\mathbf{2}][D^+]/K_1,$$

$$[\mathbf{3}] = [\mathbf{2}]K_2/[D^+],$$

$$[\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}] + [\mathbf{4}] = c_{(Rh^T)}$$

$$c_0 = [CH_2=CHCH_2CH_2CH_3]$$

The concentration of **2** is related to **4**,

$$[\mathbf{2}] = \frac{c_{(Rh^T)} - [\mathbf{4}]}{\frac{[D^+]}{K_1} + 1 + \frac{K_2}{[D^+]}}$$

As stated above:

$$d[\mathbf{4}]/dt = k_3[\mathbf{2}]c_0 - k_{-3}[\mathbf{4}]$$

$$= \beta - \alpha[\mathbf{4}]$$

where

$$\beta = \frac{k_3 c_{(Rh^T)} c_0}{\frac{[D^+]}{K_1} + 1 + \frac{K_2}{[D^+]}},\ \alpha = \frac{\beta}{c_{(Rh^T)}} + k_{-3}$$

so

$$[\mathbf{4}]_t = (\beta/\alpha)[1 - \exp(-\alpha t)]$$

$\beta = (8.5 \pm 0.1) \times 10^{-7}$, $\alpha = (5.5 \pm 0.1) \times 10^{-4}$ are obtained from simulation, and $k_3 = (2.3 \pm 0.1) \times 10^{-1}$ L mol$^{-1}$ s$^{-1}$, $k_{-3} = (10.0 \pm 1.0) \times 10^{-5}$ s$^{-1}$, and $K_3 = (2.3 \pm 0.1) \times 10^3$ are derived when $c_{(Rh^T)} = 1.9 \times 10^{-3}$ M and $c_0 = [CH_2=CHCH_2CH_2CH_3] = 2.1 \times 10^{-3}$ M are used.

## Acknowledgements

This work was supported by a starter grant from Peking University, NSFC (grants 20841002 and 20801002), and the U.S. Department of Energy, Division of Chemical Sciences, Office of Science DE-FG02–09ER16000.

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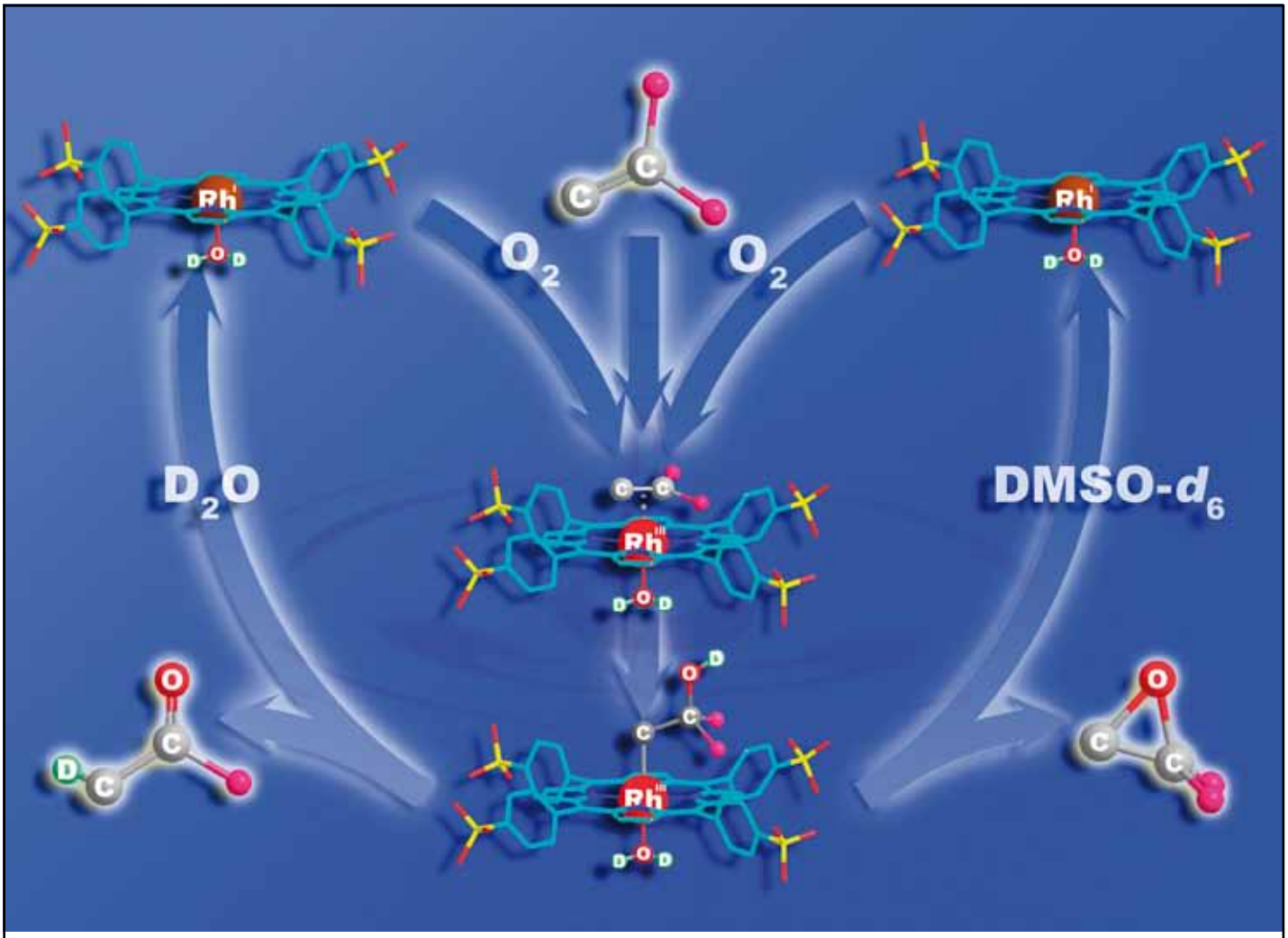


**Porphyrin rhodium(I) reacts with terminal alkenes to form β-hydroxy alkyl rhodium porphyrin complexes which undergo βC-H elimination to produce ketones in water and intramolecular C-O elimination to form epoxides in KOH/DMSO. Rapid aerobic oxidation of Rh(I) to Rh(III) provides the possibility for catalytic oxidation of olefins in water.**

**Title: Reactivity and kinetic-mechanistic studies of regioselective reactions of rhodium porphyrins with unactivated olefins in water that form beta-hydroxyalkyl complexes and conversion to ketones and expoxides**

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