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PAPER

Mechanistic comparison of β-H elimination, β-OH elimination, and nucleophilic displacement reactions of β-hydroxy alkyl rhodium porphyrin complexes

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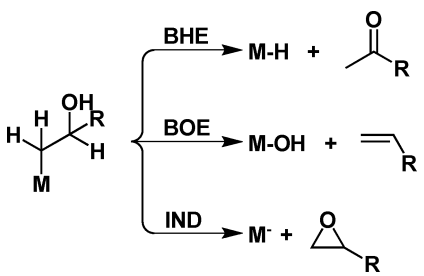
This article reports on kinetic studies for three alternate pathways, including β-hydrogen elimination, β-hydroxy elimination, and intramolecular nucleophilic displacement reactions, for rhodium porphyrin β-hydroxy alkyl reactions in water and DMSO to form ketone, alkene, and epoxide, respectively. Comparisons of activation parameters for these processes indicate that the β-hydroxy elimination process has the lowest activation enthalpy in water, but the intramolecular nucleophilic displacement pathway predominates in DMSO.

Introduction

Metal catalyzed oxidation of alkenes leads to the formation of a variety of value-added organic products including ketones/aldehydes, carboxylic acids, epoxides, and diols where β-hydroxy alkyl metal complexes (M-$CH_2CH(OH)R$) have been reported to be the intermediates in the catalytic oxidation processes.[1–8] Generally, the M-$CH_2CH(OH)R$ may undergo (1) β-hydrogen elimination (BHE) reactions to form enols and metal hydride, (2) β-oxygen elimination (BOE) reactions to form alkenes and metal cation, or (3) intramolecular nucleophilic displacement (IND) reactions to form epoxides and metal anion (Scheme 1).



Scheme 1 Three possible pathways for conversion of β-hydroxy metal alkyl complexes.

Beta hydrogen elimination (BHE) reactions are among the most important fundamental organometallic transformations which are ubiquitously observed in a variety of transition metal alkyl and alkoxide complexes.[9–14] Extensive mechanistic studies of metal alkyl complexes have revealed that BHE is a facile process when the complexes have a vacant *cis* coordination site for binding of the alkene product to reach a four-centered transition state. The BOE processes can be viewed as the microscopic reverse of nucleophilic attack by hydroxide on an alkene coordinated to a transition metal complex.[15,16] There are relatively few reports of direct C–O bond formation through nucleophilic displacement reaction,[7,17,18] and IND processes to form sp^3-carbon–oxygen bonds are also not common.[17] Although each of these processes including BHE, BOE, and IND has been extensively studied, direct observation and comparison of all three processes occurring for a single β-hydroxy metal alkyl complex in water has not been previously reported. Comparison of these three processes provided insights into obtaining selectivity in catalytic oxidation of alkenes and may lead to the development of water soluble catalysts useful for a wide range of "green" oxidation chemistry. This article reports on kinetic studies for these three alternate pathways for rhodium porphyrin β-hydroxy alkyl reactions in water and DMSO. Comparisons of activation parameters for these processes indicate that the BOE process has the lowest activation enthalpy in water, but the IND pathway predominates in DMSO.

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Results

Tetra (*p*-sulfonatophenyl) porphyrin rhodium β-hydroxy alkyl complex (TSPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2OH$ (**1**) was prepared and purified following our previously reported method.[16] The kinetic studies for reactions of **1** were run in J. Young Valve NMR tubes. The organic products were extracted into $CDCl_3$, and the ^{1}H NMR and GC-MS are compared with commercially available samples of alkenes and ketones.

BHE of (TSPP)Rh-$CH_2CH(OD)CH_2CH_2CH_2OD$ in D_2O to form (TSPP)Rh^I/(TSPP)Rh-D and 5-hydroxypentan-2-one

The kinetics of thermal dissociation of **1** resulting in the formation of (TSPP)Rh^I/(TSPP)Rh-D and 5-hydroxypentan-2-one (eqn (1))

at different pH values (pH = 8–12) at 338 K were studied by following the progress of the reaction by ^{1}H NMR.

$$\begin{aligned}&(\text{TSPP})\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{OD} \rightleftharpoons \\ &(\text{TSPP})\text{Rh}^{\text{I}}/(\text{TSPP})\text{Rh-D} + \text{CH}_3\text{C(O)CH}_2\text{CH}_2\text{CH}_2\text{OD}\end{aligned} \quad (1)$$

The rate plots showed that the reaction rates were first order in complex **1** and the rate constant k_{obs} decreased with increasing pH value (Fig. 1).

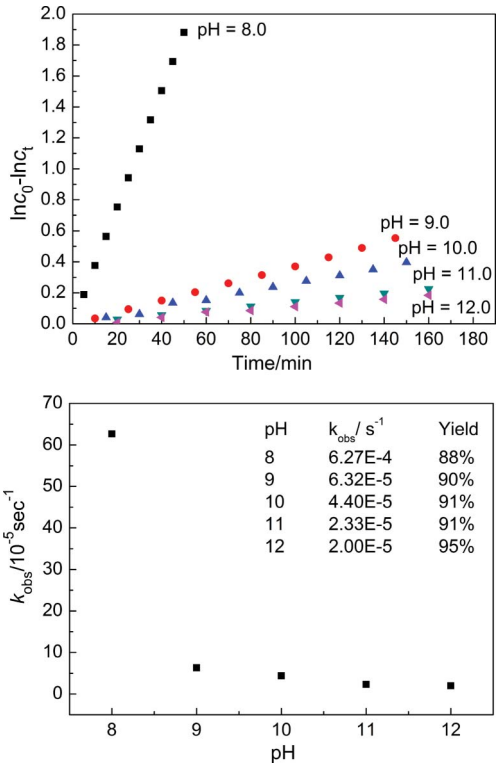
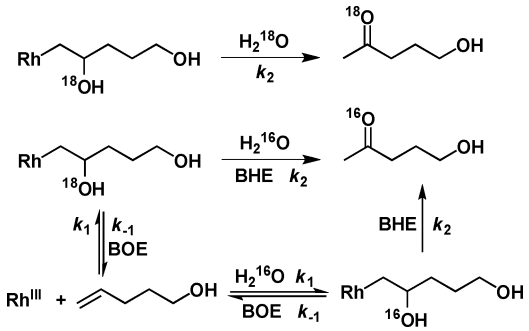


Fig. 1 The thermal dissociation rates of **1** at 338 K in buffers of pH 8–12, respectively. The k_{obs} was measured from first-order decay of the intensity of pyrrole hydrogen resonances of **1** by ^{1}H NMR. $[\mathbf{1}]_0 = 2.9 \times 10^{-3}$ M. The yields were calculated based on the ratio of intensity integration of the resulting products with internal standard.

The thermal dissociation of ^{18}O-labeled complexes **1** (TSPP)Rh-CH$_2$CH(^{18}OH)CH$_2$CH$_2$CH$_2$OH exclusively resulted in the formation of CH$_3$C(^{18}O)CH$_2$CH$_2$CH$_2$OH in H$_2{}^{18}$O while CH$_3$C(^{16}O)CH$_2$CH$_2$CH$_2$OH formed in H$_2{}^{16}$O from GC-MS analysis (Scheme 2). The loss of ^{18}O in the product when the reaction was performed in H$_2{}^{16}$O suggested that both the forward (k_1) and reverse (k_{-1}) reaction occurred before BHE (k_2) occurred, *i.e.* $k_1 > k_{-1} > k_2$. So the k_{obs} is dominated by the BHE rate, k_2 (Scheme 2).

The activation parameters of BHE of **1** were obtained by measuring the rate constant in pH = 8.0 buffers through the temperature range of 318–338 K. The first order rate kinetics at different temperatures from ^{1}H NMR spectroscopy (Fig. 2) gave the activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for BHE of **1** which are estimated as 24.2 ± 0.9 kcal mol^{-1} and −1.8 ± 3.0 cal mol^{-1}K^{-1}, respectively, according to the Eyring plot (Fig. 2).



Scheme 2 Thermal reaction of ^{18}O-labeled complexes **1** in water.

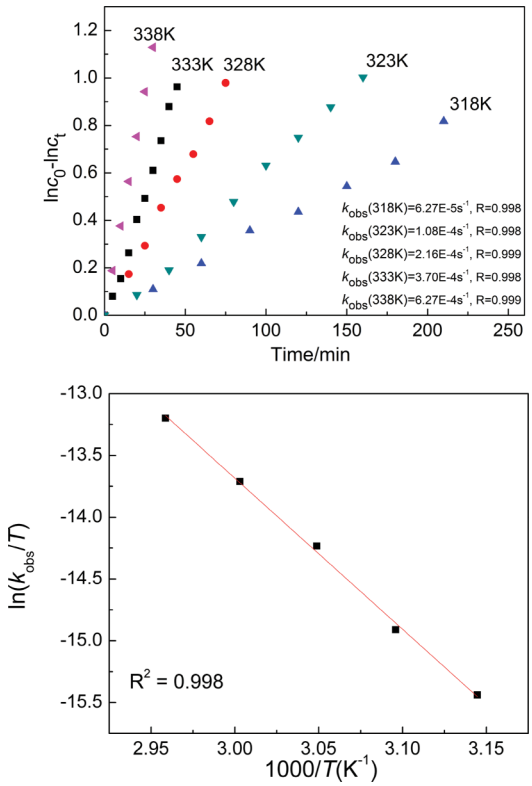


Fig. 2 BHE kinetics of **1** in pH = 8.0 buffers at 318 ~ 338 K. $[\mathbf{1}]_0 = 4.4 \times 10^{-3}$ M. Activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for BHE of **1** are estimated as 24.2 ± 0.9 kcal mol^{-1} and −1.8 ± 3.0 cal mol^{-1}K^{-1}.

BOE of (TSPP)Rh-CH$_2$CH(OD)CH$_2$CH$_2$CH$_2$OD in D$_2$O to form (TSPP)Rh$^{\text{III}}$ and 4-penten-1-ol

Addition of strong donor ligands such as pyridine, pyrrolidine, and butylamine to an aqueous solution of **1** resulted in an immediate color change from red to pink and the high field ^{1}H NMR resonances for the Rh-alkyl group of **1** shifted significantly indicative of adduct formation. The ^{1}H NMR changes upon pyridine complex formation with **1** (**1(py)**) are shown in Fig. 3 (eqn (2)).

$$\begin{aligned}&[(\text{TSPP})\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{OD(D}_2\text{O)}]^{-4} + \text{py} \rightleftharpoons \\ &[(\text{TSPP})\text{Rh-CH}_2\text{CH(OD)CH}_2\text{CH}_2\text{CH}_2\text{OD(py)}]^{-4} + \text{D}_2\text{O}\end{aligned} \quad (2)$$

Heating the solution of **1** with 10 equiv. of pyridine at 353 K for 35 min, both Rh$^{\text{III}}$(py)$_2$ and 4-penten-1-ol were formed with 95% yields as observed by ^{1}H NMR spectroscopy and GC-MS (eqn (3), Table 1).

Table 1 Thermal dissociation of **1** at 353 K with different ligands

Entry	Ligand	Time	Product	
			BHE	BOE
1	D_2O/OD^-(pH = 9)	3 h	90%	10%
2	Triethylamine	2 h	90%	10%
3	CD_3OD	2 h	82%	NA
4	Pyrrolidine	45 min	9%	91%
5	Pyridine	35 min	<5%	>95%
6	n-butylamine	25 min	0%	100%

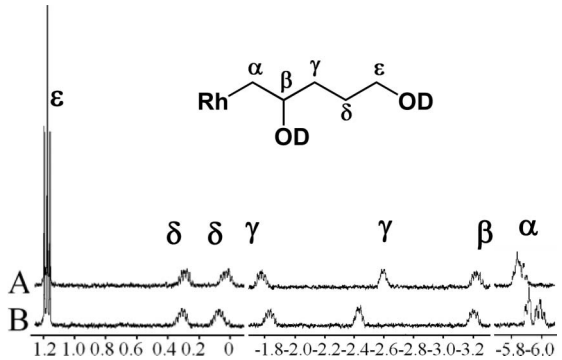


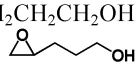
Fig. 3 High field ^{1}H NMR (400 MHz) for **1** in D_2O. (A) before addition of pyridine, (B) after addition of pyridine.

$$[(TSPP)Rh\text{-}CH_2CH(OD)CH_2CH_2CH_2OD(py)]^{-4} + py \rightleftharpoons [(TSPP)Rh^{III}(py)_2]^{-3} + CH_2{=}CHCH_2CH_2CH_2OD + OD^- \quad (3)$$

The rate constants for BOE of **1** (eqn (3)) at 288–308 K in pH = 9.0 buffers with addition of 30 equiv. of pyrrolidine gave the activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) 16.4 ± 0.6 kcal mol^{-1} and −19.9 ± 2.0 cal mol^{-1} K^{-1}, respectively (Fig. 4).

Thermal dissociation of (TSPP)Rh-$CH_2CH(OH)(CH_2)_3OH$ in DMSO

Groves previously reported a facile C–O reductive elimination from β-hydroxy alkyl complexes of rhodium tetraphenyl porphyrin in KO^{t}Bu/C_6D_6 by a proposed S_N2 pathway.[17] The KOH/DMSO solution of complex **1** underwent immediate (<5 min) IND at room temperature to form (TSPP)Rh^I and 1,2-epoxyalkanes in quantitative yield which was observed by both ^{1}H NMR and GC-MS (eqn (4)). The six-membered-ring product 3-hydroxytetrahydropyran that would result from IND of the distal hydroxyl group was not observed. The IND process is sufficiently more favorable kinetically over the BHE and BOE processes that neither the ketone product from BHE nor the alkene product from BOE was observed in KOH/DMSO medium.

$$(TSPP)Rh\text{-}CH_2CH(OH)CH_2CH_2CH_2OH + OH^- \rightleftharpoons (TSPP)Rh^I + H_2O + \text{  } \quad (4)$$

Reactions of (TPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2CH_3$ in hydrocarbon media

When the analogous complex tetraphenyl porphyrin rhodium β-hydroxy hexyl (TPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2CH_3$ (**2**), was heated in benzene at 353 K for 24 h, no products from BHE, BOE, or IND were observed by ^{1}H NMR or GC-MS. Addition of pyrrolidine or other amines to a C_6D_6 solution of **2** resulted in an immediate color change from orange–yellow to orange–red and the high field resonances of Rh-alkyl group in ^{1}H NMR changed significantly indicating pyrrolidine coordinated *trans* to the (TPP)Rh-alkyl group. However, complex **2** was stable and no further reaction occurred after heating at 353 K for 24 h.

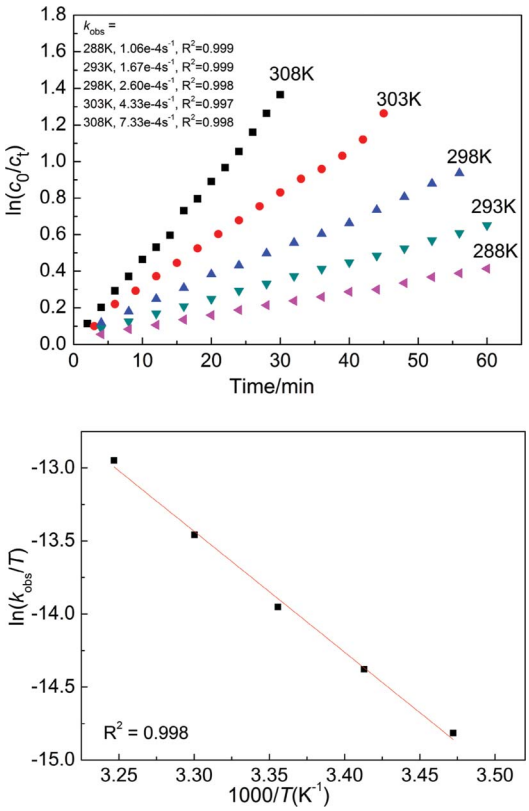


Fig. 4 BOE kinetics of **1** in pH = 9.0 buffers at 288–308 K. $[\mathbf{1}]_0 = 2.9 \times 10^{-3}$ M. Activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) for BOE of **1** are estimated as 16.4 ± 0.6 kcal mol^{-1} and −19.9 ± 2.0 cal mol^{-1}K^{-1}.

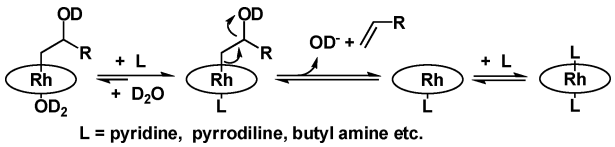
Discussion

The mechanistic details of BHE of porphyrin rhodium alkyl complexes where porphyrin ligand blocks the *cis* coordination site are not yet known. Metal complexes that lack a *cis* coordination site such as coenzyme B_{12}, generally undergo BHE by a radical pathway through homolysis of the Co–C bond. Many tetraazamacrocyclic transition metal complexes were used as model molecules of coenzyme B_{12} to elucidate mechanistic features of this rare BHE process by trapping the intermediates.[19–22] The reported BHE of porphyrin rhodium alkyl complexes in hydrocarbon media most probably occurs by bond homolysis to form metal-centered and alkyl radicals.[22,23] Observation of BHE for (TSPP)Rh-$CH_2CH(OH)R$ in water compared with the absence of BHE for (TPP)Rh-$CH_2CH(OH)R$ in benzene along with TEMPO not affecting the BHE rate supports a non-radical pathway in water.

Effect of adduct formation on the reactivity of 1

Dramatic decrease of the reaction rate of BHE with increasing pH values of the solution (Fig. 1) may result from hydroxide occupying the sixth coordination site as a more strongly bound ligand than

D_2O. Strong bonding of ligands to the metal β-hydroxy alkyl complex is expected to slow down or entirely shut off the BHE reaction. The loss of O^{18} in the product when BHE of (TSPP)Rh-$CH_2CH(^{18}OH)CH_2CH_2CH_2OH$ occurs in H_2O^{16} indicates that k_{-1} is much larger than k_2 (Scheme 2) and BOE is highly favored over BHE in water. The BOE is an unproductive process due to the relatively fast reversible β-hydroxyalkyl complex formation in basic aqueous solution. Nitrogen donor ligands like pyridine tenaciously bind to (TSPP)Rh^{III} to form (TSPP)$Rh^{III}(py)_2$ (eqn (3)) (Scheme 3) which blocks the coordination site for alkene binding and direct the reaction exclusively toward product formation by BOE.



Scheme 3 The proposed mechanism for BOE of β-hydroxyalkyl rhodium porphyrin complexes.

Solvent effects on reaction pathways

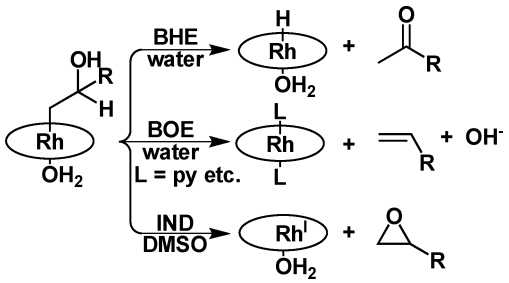
Both BHE and BOE were observed when the reactions were run in water. However, the analogous complex of **1**, (TPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2CH_3$ (**2**) showed no reactivity with and without nitrogen ligand in benzene.[24] The facile BOE and BHE in water which were not observed in benzene most probably resulted from the efficacy of ionic pathways for these processes in water.[16,25] The origin of rapid and selective formation of epoxide in KOH/DMSO solution may be due to the enhanced nucleophilicity of the alkoxy group which is dramatically reduced in water due to the solvation. And the favored formation of three-membered oxygen heterocycles through IND is driven by the strong nucleophilicity of the alkoxy group formed from deprotonation in strong basic conditions of the KOH/DMSO medium.

Comparisons of activation parameters

The activation enthalpy of BHE was 8.3 kcal mol^{-1} higher than that of the BOE process which accounted for the favorable formation of $Rh^{III}(py)_2$ and 4-penten-1-ol through the lower energy pathway of the BOE reaction. The small $\Delta S^{\ddagger}$ value for the β-H process is consistent with an intramolecular elimination although further details for this reaction mechanism are not yet known. The large negative value of $\Delta S^{\ddagger}$ of BOE may result from a second amine binding with the pyridine adduct of **1**.

Conclusions

Rhodium porphyrin β-hydroxyalkyl complexes ((TSPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2OH$) in water undergo BHE to form (TSPP)Rh–H and ketones, nitrogen donor ligands direct the reaction toward irreversible BOE to form alkenes by producing coordinately saturated complexes of (TSPP)Rh^{III}, but in KOH/DMSO exclusive formation of epoxides occurs by an IND process (Scheme 4). Reactivity studies and activation parameters indicate that the BOE reaction is highly favored over BHE and IND in water.



Scheme 4 BHE, BOE and IND of β-hydroxy alkyl rhodium porphyrin complexes.

Experimental

General considerations

D_2O, DMSO-d_6 and $CDCl_3$ were purchased from Cambridge Isotope Laboratory Inc., tetra (*p*-sulfonatophenyl) porphyrin from Tokyo Chemical Industry (TCI), $(Rh(CO)_2Cl)_2$ from Stream, and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. Room temperature ^1H NMR spectra were recorded on a Bruker AV-400 spectrometer and variant temperature ^1H NMR spectra on a Bruker AV-600 spectroscopy. The chemical shifts were referenced to 3-trimethylsilyl-1-propanesulfonic acid sodium salt. The products of dissociation of complex **1** were extracted by $CDCl_3$ for ^1H NMR and GC-MS analysis.

Preparation of (TSPP)Rh-$CH_2CH(OD)CH_2CH_2CH_2OD$ (1) in water

Tetra (*p*-sulfonatophenyl) porphyrin rhodium complexes (TSPP)Rh^{III} (1.1 mg, 0.001 mmol) and 4-penten-1-ol (0.01 mmol) were dissolved in 0.4 mL borate buffer D_2O solution (pH = 9.0) in J. Young Valve NMR tubes at room temperature, respectively. The reaction reached completion within 5 min.

Typical procedure for β-hydrogen elimination of (1) in water

The (**1**) was dissolved in fresh D_2O in the J. Young Valve NMR tube and subjected to three freeze–pump–thaw cycles. The sample was heated in a water bath and the progress of the reaction was monitored by ^1H NMR spectroscopy. When the reactions reached completion where all the (TSPP)Rh-$CH_2CH(OD)CH_2CH_2CH_2OD$ complex was converted to ketones and (TSPP)Rh^{I}.

Thermal reactions of ^{18}O-labeled (TSPP)Rh-$CH_2CH(^{18}OH)CH_2CH_2CH_2OH$

The ^{18}O-labeled complex **1** was obtained by adding 4-penten-1-ol (0.01 mmol) to the 0.4 mL borate buffer $H_2{}^{18}O$ solution of (TSPP)Rh^{III} (1.1 mg, 0.001 mmol) in a J. Young Valve NMR tube and the extra alkene was extracted by Et_2O. After solvent $H_2{}^{18}O$ was pumped out, fresh $H_2{}^{18}O$ was added to ^{18}O-labeled complexes **1**. The solution was heated at 353 K for 4 h after degassing. The product, mono ^{18}O-substituted-5-hydroxypentan-2-one ($CH_3C(^{18}O)CH_2CH_2CH_2OH$), was extracted into Et_2O and examined by GC-MS. A parallel sample of (TSPP)Rh-$CH_2CH(^{18}OH)CH_2CH_2CH_2OH$ in $H_2{}^{16}O$ was also heated under

the same reaction conditions resulting in 5-hydroxypentan-2-one ($CH_3C(^{16}O)CH_2CH_2CH_2OH$) which was extracted by Et_2O for GC-MS analysis.

Kinetics of BHE of (1) in pH = 8.0 buffers at 318–338 K

The degassed samples containing complex **1** and 10 equiv. of 4-penten-1-ol in pH = 8.0 buffers were heated in a water bath at 318–338 K, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. The BHE kinetics data were obtained from the integration ratio of pyrrole hydrogen resonances in ^{1}H NMR of **1** and (TSPP)Rh^{I}. First order rate kinetics were observed at different temperatures from ^{1}H NMR spectroscopy and the activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of the BHE of **1** are derived according to the Eyring plot.

BHE of (1) in pH = 9.0 buffers at 353 K with TEMPO

The degassed sample containing complex **1** and TEMPO in pH = 9.0 buffer D_2O solution in a J. Young Valve NMR tube was heated in a water bath at 353 K for 4 h. After the reactions reached completion, ketones and (TSPP)Rh^{I} were confirmed by ^{1}H NMR spectroscopy.

Kinetics of BOE of (1) in pH = 9.0 buffers at 288–308 K

The complex **1** and 30 equiv. of pyrrolidine in pH = 9.0 buffers were transferred to J. Young Valve NMR tubes and degassed. The progress of the reaction was monitored by ^{1}H NMR spectroscopy in the range of 288–308 K. First order rate kinetics were observed at different temperatures from ^{1}H NMR spectroscopy. The first order rate kinetics of BOE at different temperatures gave activation enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of the BOE of **1** according to the Eyring plot.

The IND of (TSPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2OH$ in DMSO

The (TSPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2OH$ was dissolved in KOH/DMSO-d_6 (c_{KOH} = 3.3 mg mL^{-1}) under an argon atmosphere in vacuum adapted NMR tubes and the solution underwent a color change to a brownish solution within minutes at room temperature. ^{1}H NMR spectra confirmed the formation of (TSPP)Rh^{I}. The resulting 4,5-epoxypentan-1-ol was extracted into Et_2O and examined by GC-MS.

Notes and references

1 B. de Bruin, P. H. M. Budzelaar and A. W. Gal, *Angew. Chem., Int. Ed.*, 2004, **43**, 4142.
2 C. Hahn, *Chem.–Eur. J.*, 2004, **10**, 5888–5899.
3 A. R. Chianese, S. J. Lee and M. R. Gagné, *Angew. Chem., Int. Ed.*, 2007, **46**, 4042.
4 K. M. Gligorich and M. S. Sigman, *Chem. Commun.*, 2009, 3854.
5 S. S. Stahl, *Angew. Chem., Int. Ed.*, 2004, **43**, 3400–3420.
6 T. Punniyamurthy, S. Velusamy and J. Iqbal, *Chem. Rev.*, 2005, **105**, 2329–2363.
7 C. Liu, C. F. Bender, X. Han and R. A. Widenhoefer, *Chem. Commun.*, 2007, 3607.
8 (*a*) D. Dolphin, A. Matsumoto and C. Shortman, *J. Am. Chem. Soc.*, 1989, **111**, 411; (*b*) Y. S. Lin, S. Takeda and K. Matsumoto, *Organometallics*, 1999, **18**, 4897; (*c*) N. Saeki, N. Nakamura, T. Ishibashi, M. Arime, H. Sekiva, K. Ishihara and K. Matsumoto, *J. Am. Chem. Soc.*, 2003, **125**, 3605; (*d*) D. J. Nelson, R. Li and C. Brammer, *J. Am. Chem. Soc.*, 2001, **123**, 1564.
9 (*a*) O. Blum and D. Milstein, *J. Am. Chem. Soc.*, 1995, **117**, 4582; (*b*) A. Vigalok, H. B. Kraatz, L. Konstantinovsky and D. Milstein, *Chem.–Eur. J.*, 1997, **3**, 253; (*c*) M. E. Van Der Boom, C. L. Higgitt and D. Milstein, *Organometallics*, 1999, **18**, 2413; (*d*) O. Blum and D. Milstein, *J. Organomet. Chem.*, 2000, **593–594**, 479.
10 (*a*) E. J. Alexanian and J. F. Hartwig, *J. Am. Chem. Soc.*, 2008, **130**, 15627; (*b*) J. Zhao, H. Hesslink and J. F. Hartwig, *J. Am. Chem. Soc.*, 2001, **123**, 7220; (*c*) C. Krug and J. F. Hartwig, *J. Am. Chem. Soc.*, 2002, **124**, 1674.
11 (*a*) J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.*, 1976, **98**, 6521; (*b*) J. A. Keith, J. Oxgaard and W. A. Goddard III, *J. Am. Chem. Soc.*, 2006, **128**, 3132; (*c*) K. A. Bernard, W. M. Rees and J. D. Atwood, *Organometallics*, 1986, **5**, 390; (*d*) J. C. M. Ritter and R. G. Bergman, *J. Am. Chem. Soc.*, 1998, **120**, 6826; (*e*) J. Vela, S. Vaddadi, T. R. Cundari, J. M. Smith, E. A. Gregory, R. J. Lachicotte, J. Flaschenriem and P. L. Holland, *Organometallics*, 2004, **23**, 5226; (*f*) D. M. Hoffman, D. Lappas and D. A. Wierda, *J. Am. Chem. Soc.*, 1989, **111**, 1531.
12 (*a*) H. E. Bryndza, J. C. Calabrese, M. Marsi, D. C. Roe, W. Tam and J. E. Bercaw, *J. Am. Chem. Soc.*, 1986, **108**, 4805; (*b*) P. J. Chirik and J. E. Bercaw, *Organometallics*, 2005, **24**, 5407; (*c*) P. J. Chirik, M. W. Day, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc.*, 1999, **121**, 10308.
13 (*a*) J. P. Collman, A. S. Chien, T. A. Eberspacher and J. I. Brauman, *J. Am. Chem. Soc.*, 1998, **120**, 425; (*b*) J. P. Collman and R. Boulatov, *Inorg. Chem.*, 2001, **40**, 560.
14 (*a*) N. A. Smythe, K. A. Grice, B. S. Williams and K. I. Goldberg, *Organometallics*, 2009, **28**, 277; (*b*) T. R. Cundari and C. D. Taylor, *Organometallics*, 2003, **22**, 4047; (*c*) I. Matas, J. Cámpora, P. Palma and E. Álvarez, *Organometallics*, 2009, **28**, 6515; (*d*) J. Muzart, *Tetrahedron*, 2007, **63**, 7505.
15 (*a*) R. Pryadun, D. Sukumaran, R. Bogadi and J. D. Atwood, *J. Am. Chem. Soc.*, 2004, **126**, 12414; (*b*) R. S. Pryadun and J. D. Atwood, *Organometallics*, 2007, **26**, 4830.
16 X. Fu, S. Li and B. B. Wayland, *J. Am. Chem. Soc.*, 2006, **128**, 8947.
17 (*a*) Y. Han, M. S. Sanford, M. D. England and J. T. Groves, *Chem. Commun.*, 2006, 549; (*b*) M. S. Sanford and J. T. Groves, *Angew. Chem., Int. Ed.*, 2004, **43**, 588.
18 (*a*) B. S. Williams and K. I. Goldberg, *J. Am. Chem. Soc.*, 2001, **123**, 2576; (*b*) B. S. Williams, A. W. Holland and K. I. Goldberg, *J. Am. Chem. Soc.*, 1999, **121**, 252; (*c*) A. J. Canty, M. C. Denney, G. Koten, B. W. Skelton and A. H. White, *Organometallics*, 2004, **23**, 5432; (*d*) U. Fekl and K. I. Goldberg, *Adv. Inorg. Chem.*, 2003, **54**, 259; (*e*) A. N. Vedernikov, S. A. Binfield, P. Y. Zavalij and J. R. Khusnutdinova, *J. Am. Chem. Soc.*, 2006, **128**, 82; (*f*) J. R. Khusnutdinova, P. Y. Zavalij and A. N. Vedernikov, *Organometallics*, 2007, **26**, 3466; (*g*) J. R. Khusnutdinova, L. L. Newman, P. Y. Zavalij, Y.-F. Lam and A. N. Vedernikov, *J. Am. Chem. Soc.*, 2008, **130**, 2174.
19 (*a*) G. N. Schrauzer and J. H. Grate, *J. Am. Chem. Soc.*, 1981, **103**, 541; (*b*) J. H. Grate and G. N. Schrauzer, *J. Am. Chem. Soc.*, 1979, **101**, 4601.
20 (*a*) B. P. Hay and R. G. Finke, *J. Am. Chem. Soc.*, 1987, **109**, 8012; (*b*) G. N. Schrauzer, J. H. Weber and T. M. Beckham, *J. Am. Chem. Soc.*, 1970, **92**, 7079.
21 (*a*) T. Tsou, M. Loots and J. Halpern, *J. Am. Chem. Soc.*, 1982, **104**, 623–624; (*b*) J. Halpern, *Acc. Chem. Res.*, 1982, **15**, 238–244; (*c*) M. P. Jensen and J. Halpern, *J. Am. Chem. Soc.*, 1999, **121**, 2181; (*d*) M. Okazaki, H. Tobita and H. Ogino, *Dalton Trans.*, 2003, 493.
22 (*a*) K. J. Del Rossi and B. B. Wayland, *J. Am. Chem. Soc.*, 1985, **107**, 7941; (*b*) B. B. Wayland, S. L. V. Voorhees and K. J. Del Rossi, *J. Am. Chem. Soc.*, 1987, **109**, 6513.
23 (*a*) K. W. Mak and K. S. Chan, *J. Am. Chem. Soc.*, 1998, **120**, 9686; (*b*) S. K. Yeung and K. S. Chan, *Organometallics*, 2005, **24**, 2561; (*c*) K. W. Mak, F. Xue, T. C. W. Mak and K. S. Chan, *Dalton. Trans.*, 1999, 3333.
24 (TPP)Rh-$CH_2CH(OH)CH_2CH_2CH_2CH_3$ was synthesized following reference 17a. To a solution of 10 mg (TPP)Rh–I in 10 mL of degassed ethanol, 0.5 mL of 0.5 N aqueous NaOH solution containing 5 mg $NaBH_4$was added. The mixture was degassed and stirred at 60 °C for 2 h and then cooled down to room temperature. 1,2-expoxyhexane (2 mL) was added and the product was isolated by chromatographic column.
25 (*a*) J. Zhang, B. B. Wayland, L. Yun, S. Li and X. Fu, *Dalton Trans.*, 2010, **39**, 477; (*b*) J. Zhang, B. B. Wayland, L. Yun, S. Li and X. Fu, *Dalton Trans.*, 2010, **39**, 477; (*c*) L. Liu, M. Yu, B. B. Wayland and X. Fu, *Chem. Commun.*, 2010, **46**, 6353.