

Competitive O–H and C–H oxidative addition of CH₃OH to rhodium(II) porphyrins

Shan Li, Weihong Cui and Bradford B. Wayland*

Received (in Berkeley, CA, USA) 5th June 2007, Accepted 17th August 2007

First published as an Advance Article on the web 29th August 2007

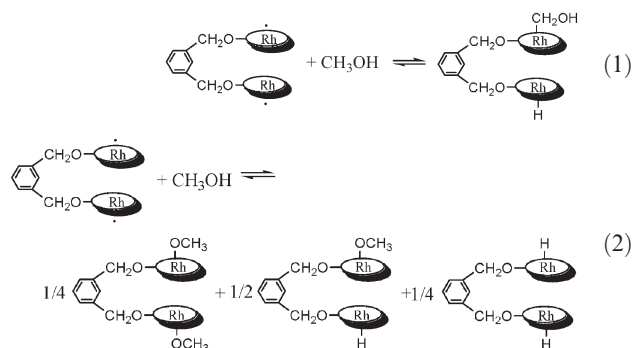
DOI: 10.1039/b708032h

Rhodium(II) porphyrins react with CH₃OH in benzene by alternate mechanisms that give H–CH₂OH and H–OCH₃ bond activation in different methanol concentration regimes which is a rare example of transition metal reactivity with methanol.

Oxidative addition of the O–H units in water and alcohols to late transition metal centers is attracting new interest because of the potential role in catalytic substrate transformations^{1,2} such as olefin hydration^{3,4} and photodissociation of water.^{5–7} Oxidative addition of –O–H fragments is relatively unusual with only a few examples of late 2nd and 3rd transition metal complexes that give this type of reactivity with alcohols^{1,8–12} and water.^{1,13–17} We have recently reported that water oxidatively adds to a rhodium(II) complex of persulfonated tetramesitylporphyrin ((TMPS)Rh^{II}) in water to form equal quantities of hydride ((TMPS)Rh–H) and hydroxide ((TMPS)Rh–OH) complexes.¹⁸ This article reports on reactions of rhodium(II) porphyrins with relatively high concentrations of methanol in benzene that produce rhodium methoxide (Rh–OCH₃) complexes as the kinetic products that subsequently react on to hydroxymethyl complexes (Rh–CH₂OH) as the thermodynamically preferred products.¹⁹

Reactions of *m*-xylyl tethered rhodium bis(phenyltrimesitylporphyrin) bimetallo-radical complex 'Rh(*m*-xylyl)Rh' (1)^{19–21} with CH₃OH at relatively low concentrations ([CH₃OH] = 0.01–0.1 M) produce the hydroxymethyl–hydride complex (H–Rh(*m*-xylyl)Rh–CH₂OH (2)) as the exclusive kinetic and thermodynamic product (eq 1) ($K_1(296\text{ K}) = 1.5(0.5) \times 10^3$; $\Delta G_1^\circ(296\text{ K}) = -4.3(0.2)\text{ kcal mol}^{-1}$).¹⁹ At higher concentrations of methanol ([CH₃OH] > 0.5 M), 'Rh(*m*-xylyl)Rh' has now been observed to react with CH₃OH by an alternate reaction pathway that gives H–OCH₃ bond addition to form methoxide and hydride complexes CH₃O–Rh(*m*-xylyl)Rh–OCH₃ (3), H–Rh(*m*-xylyl)Rh–OCH₃ (4), and H–Rh(*m*-xylyl)Rh–H (5) in a mole ratio of 1 : 2 : 1 (eq 2). Oxidative addition of the H–OCH₃ unit to rhodium(II) centers gives a statistical distribution of products which is distinctively different from the selective intramolecular H–CH₂OH oxidative addition at low CH₃OH concentrations. The rapid H–OCH₃ oxidative addition that kinetically dominates at high concentrations of methanol is tentatively ascribed to a route involving donor induced disproportionation of rhodium(II) ($2\text{Rh}^{\text{II}} + 2:\text{B} \rightleftharpoons [\text{Rh}^{\text{III}}(\text{B})_2]^+[\text{Rh}^{\text{I}}]^-$) which has several precedents in rhodium porphyrin chemistry.^{22,23} Over a period of days at 296 K, the Rh–OCH₃ centers at 0.1 M CH₃OH are converted quantitatively to Rh–CH₂OH units as the thermodynamic products.

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323, USA. E-mail: wayland@sas.upenn.edu; Fax: 215573 6743; Tel: 215898 8633



Reaction of rhodium(II) tetramesitylporphyrin ((TMP)Rh^{II}) (6) with methanol qualitatively parallels that of 'Rh(*m*-xylyl)Rh'. At low concentrations of methanol ([CH₃OH] ~ 0.01 M) C–H activation occurs slowly to give (TMP)Rh–H and (TMP)Rh–CH₂OH as the exclusive kinetic and thermodynamic product (eq 3). Reaction of (TMP)Rh^{II} (eq 3) is much slower than reaction of 'Rh(*m*-xylyl)Rh' (eq 1) because of the loss of preorganization of the transition state and the change from a bimolecular process to a termolecular process.¹⁹ At higher concentrations of methanol ([CH₃OH] ≥ 0.1 M), (TMP)Rh^{II} reacts with methanol by a fast H–OCH₃ bond activation that produces the methoxide complex ((TMP)Rh–OCH₃, (7)) (eq 4) which then subsequently reacts slowly on to produce the hydroxymethyl complex ((TMP)Rh–CH₂OH, (8)) (eq 3) (Fig. 1). Reaction 4 occurs to a ¹H NMR observable equilibrium, but reaction 3 proceeds effectively to completion at these conditions. Evaluation of the equilibrium thermodynamics for reaction 4 ([CH₃OH] = 0.1 M) gives $K_4(296\text{ K}) = 4.4(0.6) \times 10^{-2}$, $\Delta G_4^\circ(296\text{ K}) = 1.84(0.08)\text{ kcal mol}^{-1}$. The methoxide complex occurs as a methanol adduct at 0.10 M CH₃OH. Repeating reaction 4 using toluene permits ¹H NMR observation of the coordinated methanol and methoxide at lower temperatures. Exchange of

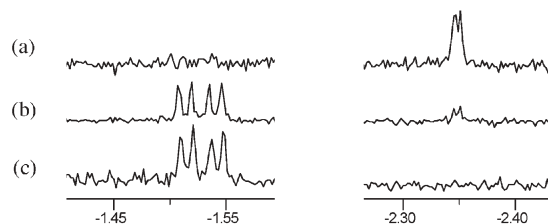
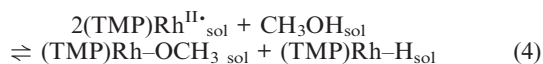
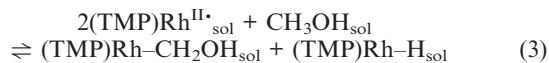


Fig. 1 High-field ¹H NMR (C₆D₆) resonances for the reaction of (TMP)Rh^{II} with CH₃OH ([CH₃OH] = 0.1 M). Reaction time: (a) 10 minutes; (b) 5 days; (c) 11 days. (Rh–OCH₃: δ = –2.35 ppm, d, 3H, ³J_{103Rh–H} = 1.5 Hz; Rh–CH₂OH: δ = –1.53 ppm, dd, 2H, ³J_{H–H} = 8.0 Hz, ²J_{103Rh–H} = 3.3 Hz).

methanol from (TMP)Rh–OCH₃(CH₃OH) with the bulk broadens the NMR resonance of the coordinated CH₃OH beyond observation at 296 K. Temperature dependence of the coordinated methanol provides activation parameters for the exchange. The oxygen donor and hydrogen bonding capability for CH₃OH results in self association and adduct formation with the rhodium complexes. Differential solvation of reactants and products complicates the precise descriptions for reactions 3 and 4 and the interpretation of the solution equilibrium studies for reaction 4.



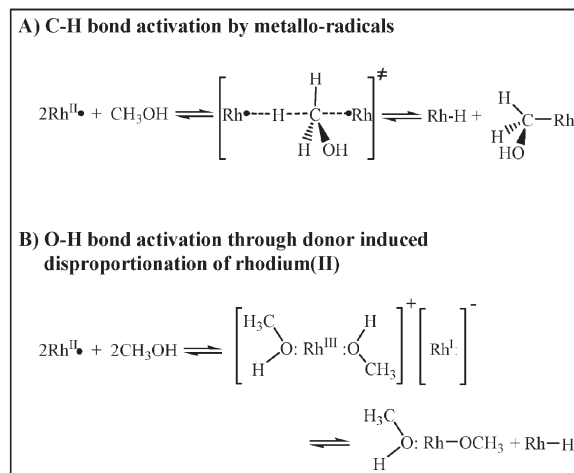
The combination of equilibrium studies (eq 1, 4) indicates that isomerisation (eq 5) of a rhodium porphyrin methoxide complex ((por)Rh–OCH₃) to a hydroxymethyl species ((por)Rh–CH₂OH) at 0.1 M methanol is free energy favorable ($\Delta G_5^\circ \sim -6 \text{ kcal mol}^{-1}$).



The difference in the substrate bond dissociation enthalpy values (kcal mol^{-1}) (CH₃O–H (104.6) and HOCH₂–H (96.1))²⁴ is the dominant energy contribution that makes conversion of the methoxy to the hydroxymethyl complex thermodynamically favorable.

The reaction of the C–H bond of methanol with rhodium(II) (eq 1) has previously been shown to occur by a metallo-radical pathway that involves two rhodium(II) centers and the substrate in the transition state (Scheme 1A). The C–H bond reactions of rhodium(II) with CH₃OH (eq 1, 3) are thermodynamically more favorable than the H–OCH₃ oxidative addition even at high concentrations of methanol ([CH₃OH] ~ 3 M). The observed O–H bond activation must result from a pathway that becomes more kinetically preferred as the concentration of methanol increases. Strong donor molecules like pyridine (>2 equiv.) are known to produce disproportionation of rhodium(II) porphyrins into rhodium(I) and rhodium(III) bis-donor adducts. Substantially stronger bonding of rhodium(III) with donor molecules compared to rhodium(II) is the thermodynamic driving force for the disproportionation. Methanol adduct formation with (por)Rh^{II} at high concentrations of CH₃OH is proposed to induce disproportionation to rhodium(III) and rhodium(I) and provide a facile route for the observed H–OCH₃ bond cleavage and addition to the rhodium centers (Scheme 1B).

The observed isomerization of the methoxide complexes ((por)Rh–OCH₃) to hydroxymethyl species ((por)Rh–CH₂OH) is proposed to go through the metallo-radicals ((por)Rh^{II•}) that occur in equilibrium. At very high concentrations of methanol in benzene ([CH₃OH] > 5 M) or in pure methanol, fully selective H–OCH₃ bond activation occurs (eq 4) and the methoxide product (Rh–OCH₃) is indefinitely kinetically trapped relative to conversion to the thermodynamically preferred hydroxymethyl complex (Rh–CH₂OH) by the vanishingly small equilibrium concentration of rhodium(II).



Scheme 1 Proposed reaction pathways for C–H and O–H bond reactions of rhodium(II) porphyrins.

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

Notes and references

- O. Blum and D. Milstein, *J. Am. Chem. Soc.*, 2002, **124**, 11456.
- G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, Wiley, New York, 2nd edn, 1992, pp. 100–104.
- B. Cornils and W. A. Herrmann, *Aqueous-Phase Organometallic Catalysis*, Wiley, Weinheim, Germany, 2nd edn, 2004, p. 51.
- N. D. Jones, P. Meessen, U. Losehand, B. O. Patrick and B. R. James, *Inorg. Chem.*, 2005, **44**, 3290.
- N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15729.
- R. S. Paonessa, A. L. Prignano and W. C. Troglor, *Organometallics*, 1985, **4**, 647.
- V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta and M. Gleria, *Science*, 1975, **189**, 852.
- R. Dorta, H. Rozenberg, L. J. W. Shimon and D. Milstein, *Chem.–Eur. J.*, 2003, **9**, 5237.
- O. Blum and D. Milstein, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 229.
- M. B. Sponsler, B. H. Weiller, P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.*, 1989, **111**, 6841.
- P. K. Monaghan and R. J. Puddephatt, *Inorg. Chim. Acta*, 1982, **65**, L59.
- D. Milstein, *J. Am. Chem. Soc.*, 1986, **108**, 3525.
- R. Dorta, H. Rozenberg, L. J. W. Shimon and D. Milstein, *J. Am. Chem. Soc.*, 2002, **124**, 188.
- D. Morales-Morales, D. W. Lee, Z. Wang and C. M. Jensen, *Organometallics*, 2001, **20**, 1144.
- M. J. Burn, M. G. Fickes, J. F. Hartwig, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1993, **115**, 5875.
- T. Yoshida, T. Okano, K. Saito and S. Otsuka, *Inorg. Chim. Acta*, 1980, **44**, L135.
- M. Yoon and D. R. Tyler, *Chem. Commun.*, 1997, 639.
- X. Fu, S. Li and B. B. Wayland, *Inorg. Chem.*, 2006, **45**, 9884.
- W. Cui and B. B. Wayland, *J. Am. Chem. Soc.*, 2004, **126**, 8266.
- W. Cui, X. P. Zhang and B. B. Wayland, *J. Am. Chem. Soc.*, 2003, **125**, 4994.
- X.-X. Zhang and B. B. Wayland, *J. Am. Chem. Soc.*, 1994, **116**, 7897.
- L. Zhang, C. W. Fung and K. S. Chan, *Organometallics*, 2006, **25**, 5381.
- B. B. Wayland, K. J. Balkus, Jr. and M. D. Farnos, *Organometallics*, 1989, **8**, 950.
- S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.*, 2003, **36**, 255.