Competitive O–H and C–H oxidative addition of CH_3OH to rhodium(II) porphyrins

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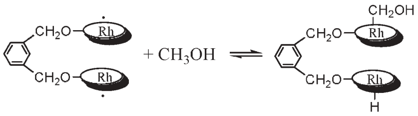
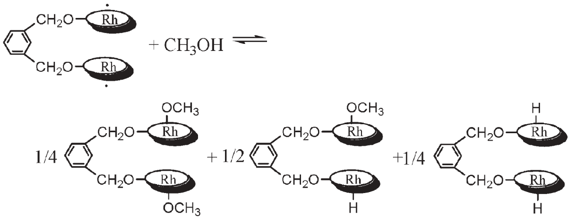
Rhodium(II) porphyrins react with CH_3OH in benzene by alternate mechanisms that give H–CH_2OH and H–OCH_3 bond activation in different methanol concentration regimes which is a rare example of transition metal reactivity with methanol.

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)$\mathrm{Rh}^{\mathrm{II}\bullet}$) 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–OCH_3) complexes as the kinetic products that subsequently react on to hydroxymethyl complexes (Rh–CH_2OH) as the thermodynamically preferred products.[19]

Reactions of *m*-xylyl tethered rhodium bis(phenyltrimesitylporphyrin) bimetallo-radical complex ${}^{\bullet}$Rh(*m*-xylyl)Rh${}^{\bullet}$ (**1**)[19–21] with CH_3OH at relatively low concentrations ($[CH_3OH] = 0.01$–0.1 M) produce the hydroxymethyl–hydride complex (H–Rh(*m*-xylyl)Rh–CH_2OH (**2**)) as the exclusive kinetic and thermodynamic product (eq 1) ($K_1(296\ \mathrm{K}) = 1.5(0.5) \times 10^3$; $\Delta G_1^\circ(296\ \mathrm{K}) = -4.3(0.2)\ \mathrm{kcal\ mol^{-1}}$).[19] At higher concentrations of methanol ($[CH_3OH] > 0.5$ M), ${}^{\bullet}$Rh(*m*-xylyl)Rh${}^{\bullet}$ has now been observed to react with CH_3OH by an alternate reaction pathway that gives H–OCH_3 bond addition to form methoxide and hydride complexes CH_3O–Rh(*m*-xylyl)Rh–OCH_3 (**3**), H–Rh(*m*-xylyl)Rh–OCH_3 (**4**), and H–Rh(*m*-xylyl)Rh–H (**5**) in a mole ratio of 1 : 2 : 1 (eq 2). Oxidative addition of the H–OCH_3 unit to rhodium(II) centers gives a statistical distribution of products which is distinctively different from the selective intramolecular H–CH_2OH oxidative addition at low CH_3OH concentrations. The rapid H–OCH_3 oxidative addition that kinetically dominates at high concentrations of methanol is tentatively ascribed to a route involving donor induced disproportionation of rhodium(II) ($2\mathrm{Rh}^{\mathrm{II}\bullet} + 2{:}\mathrm{B} \rightleftharpoons [\mathrm{Rh}^{\mathrm{III}}(\mathrm{B})_2]^+[\mathrm{Rh}^{\mathrm{I}}]^-$) which has several precedents in rhodium porphyrin chemistry.[22,23] Over a period of days at 296 K, the Rh–OCH_3 centers at 0.1 M CH_3OH are converted quantitatively to Rh–CH_2OH units as the thermodynamic products.



(1)



(2)

Reaction of rhodium(II) tetramesitylporphyrin ((TMP)$\mathrm{Rh}^{\mathrm{II}\bullet}$) (**6**) with methanol qualitatively parallels that of ${}^{\bullet}$Rh(*m*-xylyl)Rh${}^{\bullet}$. At low concentrations of methanol ($[CH_3OH] \sim 0.01$ M) C–H activation occurs slowly to give (TMP)Rh–H and (TMP)Rh–CH_2OH as the exclusive kinetic and thermodynamic product (eq 3). Reaction of (TMP)$\mathrm{Rh}^{\mathrm{II}\bullet}$ (eq 3) is much slower than reaction of ${}^{\bullet}$Rh(*m*-xylyl)Rh${}^{\bullet}$ (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 ($[CH_3OH] \geqslant 0.1$ M), (TMP)$\mathrm{Rh}^{\mathrm{II}\bullet}$ reacts with methanol by a fast H–OCH_3 bond activation that produces the methoxide complex ((TMP)Rh–OCH_3, (**7**)) (eq 4) which then subsequently reacts slowly on to produce the hydroxymethyl complex ((TMP)Rh–CH_2OH, (**8**)) (eq 3) (Fig. 1). Reaction 4 occurs to a ^{1}H NMR observable equilibrium, but reaction 3 proceeds effectively to completion at these conditions. Evaluation of the equilibrium thermodynamics for reaction 4 ($[CH_3OH] = 0.1$ M) gives $K_4(296\ \mathrm{K}) = 4.4(0.6) \times 10^{-2}$, $\Delta G_4^\circ(296\ \mathrm{K}) = 1.84(0.08)\ \mathrm{kcal\ mol^{-1}}$. The methoxide complex occurs as a methanol adduct at 0.10 M CH_3OH. Repeating reaction 4 using toluene permits ^{1}H NMR observation of the coordinated methanol and methoxide at lower temperatures. Exchange of

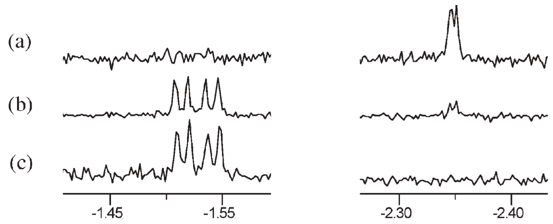


Fig. 1 High-field ^{1}H NMR (C_6D_6) resonances for the reaction of (TMP)$\mathrm{Rh}^{\mathrm{II}\bullet}$ with CH_3OH ($[CH_3OH] = 0.1$ M). Reaction time: (a) 10 minutes; (b) 5 days; (c) 11 days. (Rh–OCH_3: $\delta = -2.35$ ppm, d, 3H, $^3J_{103\mathrm{Rh-H}} = 1.5$ Hz; Rh–CH_2OH: $\delta = -1.53$ ppm, dd, 2H, $^3J_{\mathrm{H-H}} = 8.0$ Hz, $^2J_{103\mathrm{Rh-H}} = 3.3$ Hz).

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methanol from (TMP)Rh–OCH$_3$(CH$_3$OH) with the bulk broadens the NMR resonance of the coordinated CH$_3$OH 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 CH$_3$OH 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.

$$2(\mathrm{TMP})\mathrm{Rh}^{\mathrm{II}\bullet}{}_{\mathrm{sol}} + \mathrm{CH_3OH_{sol}} \rightleftharpoons (\mathrm{TMP})\mathrm{Rh–CH_2OH_{sol}} + (\mathrm{TMP})\mathrm{Rh–H_{sol}} \qquad (3)$$

$$2(\mathrm{TMP})\mathrm{Rh}^{\mathrm{II}\bullet}{}_{\mathrm{sol}} + \mathrm{CH_3OH_{sol}} \rightleftharpoons (\mathrm{TMP})\mathrm{Rh–OCH_3}{}_{\mathrm{sol}} + (\mathrm{TMP})\mathrm{Rh–H_{sol}} \qquad (4)$$

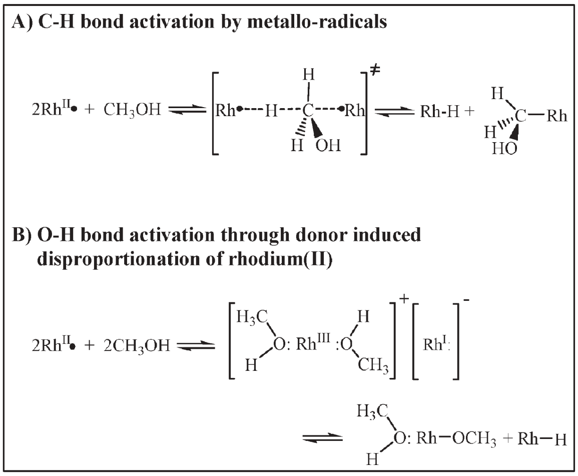
The combination of equilibrium studies (eq 1, 4) indicates that isomerisation (eq 5) of a rhodium porphyrin methoxide complex ((por)Rh–OCH$_3$) to a hydroxymethyl species ((por)Rh–CH$_2$OH) at 0.1 M methanol is free energy favorable ($\Delta G_5^\circ \sim -6$ kcal mol^{-1}).

$$(\mathrm{TMP})\mathrm{Rh–OCH_3}{}_{\mathrm{sol}} \rightleftharpoons (\mathrm{TMP})\mathrm{Rh–CH_2OH_{sol}} \qquad (5)$$

The difference in the substrate bond dissociation enthalpy values (kcal mol^{-1}) (CH$_3$O–H (104.6) and HOCH$_2$–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 CH$_3$OH (eq 1, 3) are thermodynamically more favorable than the H–OCH$_3$ oxidative addition even at high concentrations of methanol ([CH$_3$OH] ~ 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$^{\mathrm{II}\bullet}$ at high concentrations of CH$_3$OH is proposed to induce disproportionation to rhodium(III) and rhodium(I) and provide a facile route for the observed H–OCH$_3$ bond cleavage and addition to the rhodium centers (Scheme 1B).

The observed isomerization of the methoxide complexes ((por)Rh–OCH$_3$) to hydroxymethyl species ((por)Rh–CH$_2$OH) is proposed to go through the metallo-radicals ((por)Rh$^{\mathrm{II}\bullet}$) that occur in equilibrium. At very high concentrations of methanol in benzene ([CH$_3$OH] > 5 M) or in pure methanol, fully selective H–OCH$_3$ bond activation occurs (eq 4) and the methoxide product (Rh–OCH$_3$) is indefinitely kinetically trapped relative to conversion to the thermodynamically preferred hydroxymethyl complex (Rh–CH$_2$OH) 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.

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