

Comparison of Rh–OCH₃ and Rh–CH₂OH Bond Dissociation Energetics from Methanol C–H and O–H Bond Reactions with Rhodium(II) Porphyrins

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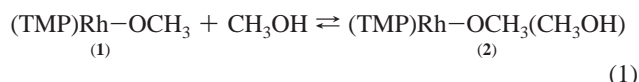
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Abstract: Reaction of methanol in toluene with tetramesityl rhodium(II) porphyrin ((TMP)Rh^{II}) produces a ¹H NMR-observable equilibrium with rhodium methoxide ((TMP)Rh–OCH₃(CH₃OH)) and rhodium hydride ((TMP)Rh–H) complexes. Equilibrium concentrations for each of these species, obtained from integration of ¹H NMR spectra, were used in determining the equilibrium constant, $K(298\text{ K}) = [\text{Rh–OCH}_3(\text{CH}_3\text{OH})][\text{Rh–H}]/[\text{Rh}^{\text{II}}][\text{CH}_3\text{OH}]^2 = 3.0(0.3)$, and free energy change, $\Delta G^0(298\text{ K}) = -0.65(0.5)\text{ kcal mol}^{-1}$, for the reaction. Equilibrium thermodynamic measurements in CD₂Cl₂ give $\Delta G^0(298\text{ K}) = -5.5(0.2)\text{ kcal mol}^{-1}$ for association of methanol with (TMP)Rh–OCH₃ to form the six-coordinate 18-electron complex (TMP)Rh–OCH₃(CH₃OH). Equilibrium measurements in conjunction with (TMP)Rh–H and CH₃O–H bond energetics are used to evaluate the (TMP)Rh–OCH₃ bond dissociation free energy (Rh–OCH₃ BDFE(298 K) = 38 (1.3) kcal mol⁻¹), which is 15 kcal mol⁻¹ smaller than the Rh–H BDFE and approximately equal to the Rh–CH₂OH BDFE.

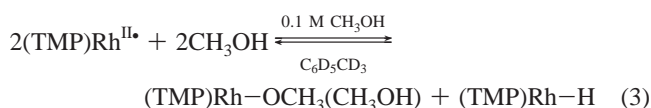
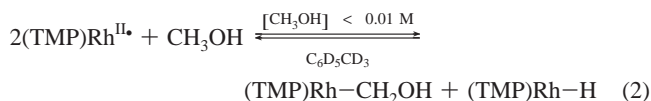
Late transition metal alkoxides (M–OR)^{1–4} and α -hydroxyalkyl (M–CH(R)OH)^{5–7} complexes are important precursors and intermediates for a diverse range of organic transformations such as alcohol⁸ and olefin oxidation,⁹ C–O coupling,¹⁰ and carbonyl hydrogenation.¹¹ Substantial effort has been directed toward evaluating the differences in thermodynamic and kinetic mechanistic factors that govern the formation and utilization of an isoelectronic series of transition metal complexes that include methoxide (M–OCH₃), hydroxymethyl (M–CH₂OH), and ethyl (M–CH₂CH₃) derivatives.⁶ Computational and experimental studies that compare β -H migration,¹² CO insertion,¹³ and solution equilibria¹⁴ have advanced this area, but direct comparisons of metal methoxide (M–OCH₃) bond dissociation energetics with those of hydroxymethyl (M–CH₂OH) and ethyl (M–CH₂CH₃) derivatives has eluded experimental evaluation. This Communication reports on using equilibrium thermodynamic measurements for the reactions of methanol both with rhodium tetramesityl porphyrin methoxide¹⁵ ((TMP)Rh–OCH₃, **1**) to form (TMP)Rh–OCH₃(CH₃OH) (**2**) and with (TMP)Rh^{II} (**3**) to produce **2** and (TMP)Rh–H (**4**) in order to evaluate the Rh^{III}–OCH₃ bond dissociation energetics for **1**.

The five-coordinate methanol-free methoxide complex **1** was prepared by Collman's method¹⁵ of sequential additions of AgPF₆ and NaOCH₃ to a dichloromethane solution of (TMP)Rh–I. The equilibrium constant for methanol coordination with **1** to form the six-coordinate 18-electron complex **2** (eq 1) in

methylene chloride was evaluated from the methanol concentration dependence of the porphyrin pyrrole resonance position ($K_1(298\text{ K}) = 11(2) \times 10^3$; $\Delta G^0_1(298\text{ K}) = -5.5(0.2)\text{ kcal mol}^{-1}$) (Figure SI 1, Supporting Information).

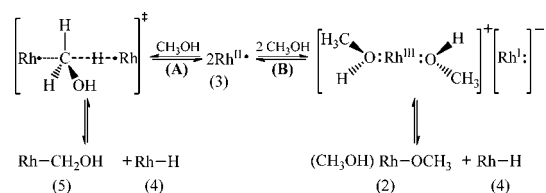


Toluene solutions of **3** ($1.0 \times 10^{-3}\text{ M}$) react slowly (Figure S2, Supporting Information) with methanol at low concentrations ($[\text{CH}_3\text{OH}] < 0.01\text{ M}$) by H–CH₂OH bond cleavage to form the hydroxymethyl complex **5** and hydride **4** (eq 2), but at higher methanol concentrations ($[\text{CH}_3\text{OH}] > 0.08\text{ M}$) the net H–OCH₃ bond cleavage occurs to form the methoxide complex **2** and hydride **4** (eq 3).



Reactivity¹⁶ and EPR¹⁷ studies have shown that one of the general reactions of rhodium(II) porphyrin complexes is donor-induced disproportionation to Rh(I) and Rh(III) species. The rhodium–methoxide unit (Rh–OCH₃) in **1** and **2** subsequently reacts to give the thermodynamically preferred hydroxymethyl species, Rh–CH₂OH (Figure S2). The hydroxymethyl complex is formed by a relatively slow termolecular pathway⁶ but is thermodynamically favored at all concentrations of CH₃OH. The methoxide complex forms by a donor-induced metalloradical disproportionation route that is kinetically preferred at high methanol concentrations (Scheme 1).

Scheme 1. Proposed Pathways for (A) C–H Bond Activation by (TMP)Rh^{II} Metallo-radicals and (B) O–H Bond Activation through Donor-Induced Disproportionation of (TMP)Rh^{II}



Reaction of a 0.10 M solution of methanol in toluene-*d*₈ with **3** ($1.0 \times 10^{-3}\text{ M}$) gives a ¹H NMR-observable equilibrium distribution of **3** with rhodium methoxide **2** and rhodium hydride **4** (eq 3). Complexes **2**, **3**, and **4** are readily identified by ¹H NMR (Figure

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1). The high-field doublet from $^{103}\text{Rh}-\text{OCH}$ coupling ($J^{103}\text{Rh}-\text{OCH} = 1.5$ Hz) centered at -2.46 ppm is associated with **2**, and the resonance centered at -40.0 ppm with a $^{103}\text{Rh}-\text{H}$ coupling of 43.2 Hz identifies the five-coordinate hydride complex **4**.

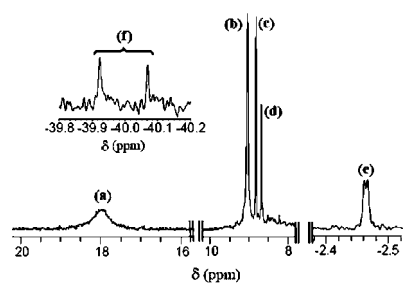
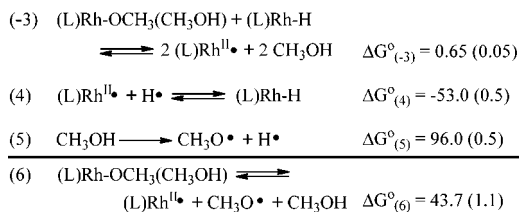


Figure 1. Characteristic ^1H NMR (500 MHz) for an equilibrium distribution of $(\text{TMP})\text{Rh}-\text{OCH}_3(\text{CH}_3\text{OH})$ (**2**) and $(\text{TMP})\text{Rh}-\text{H}$ (**4**) from reaction of $(\text{TMP})\text{Rh}^{\text{II}}$ (**3**, 1×10^{-3} M) with CH_3OH (0.10 M) in toluene at 298 K: (a) pyrrole of **3**, (b) *m*-phenyl of **3**, (c) pyrrole of **2**, (d) pyrrole of **4**, (e) $-\text{OCH}_3$ of **2**, and (f) hydride of **4**.

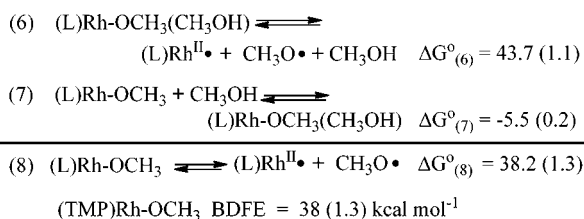
The concentrations of **2**, **3**, and **4** obtained from integration of the ^1H NMR spectrum were utilized in determining the equilibrium constant at 298 K for reaction 3 ($K_3(298\text{ K}) = 3.0(0.3)$; $\Delta G^\circ(298\text{ K}) = -0.65(0.05)$ kcal mol $^{-1}$). The free energy change for the reverse of reaction 3 in combination with the bond dissociation free energies (BDFEs) of $\text{Rh}-\text{H}^6$ (eq 4) and $\text{CH}_3\text{O}-\text{H}^{20}$ (eq 5) gives a free energy change of 43.7(1.1) kcal mol $^{-1}$ for reaction 6 (Scheme 2). The sum of the $\text{Rh}-\text{OCH}_3$ BDFE and the free energy change to form the methanol complex **2** is $\sim 43.7(1.1)$ kcal mol $^{-1}$.

Scheme 2. Free Energy Change ($\Delta G^\circ(298\text{ K})$, kcal mol $^{-1}$) for the Homolytic Dissociation of $(\text{TMP})\text{Rh}-\text{OCH}_3(\text{CH}_3\text{OH})$ (**2**) in Toluene ($T = 298\text{ K}$; L = TMP)



Evaluation of $\Delta G^\circ_{(7)}(298\text{ K})$ for methanol complex formation with **1** permits closing the thermodynamic cycle to obtain the $\text{Rh}-\text{OCH}_3$ BDFE for **1** (38.2(1.7) kcal mol $^{-1}$, Scheme 3). Dissociative processes like **8** typically have ΔS° values $\sim 27(4)$ cal K $^{-1}$ mol $^{-1}$,⁶ which provides an estimate of 46(2) kcal mol $^{-1}$ for the $\text{Rh}-\text{OCH}_3$ bond dissociation enthalpy (BDE) for **1**.

Scheme 3. Evaluation of the $(\text{TMP})\text{Rh}-\text{OCH}_3$ (**1**) Bond Dissociation Free Energy (ΔG° , kcal mol $^{-1}$; $T = 298\text{ K}$; L = TMP)



A series of (porphyrin)Rh-X BDFE values including $\text{Rh}-\text{H}$ (53 kcal mol $^{-1}$), $\text{Rh}-\text{CH}_3$ (49 kcal mol $^{-1}$), $\text{Rh}-\text{CH}_2\text{CH}_3$ (42 kcal mol $^{-1}$), and $\text{Rh}-\text{CH}_2\text{OH}$ (39 kcal mol $^{-1}$)^{6,18} are available for comparison with the $\text{Rh}-\text{OCH}_3$ BDFE value of 38 kcal mol $^{-1}$. The BDFE for **1** is 15 kcal mol $^{-1}$ smaller than that of **3**, which is distinctly different from

prior estimates of the near equivalence of late transition metal M-H and M-OCH₃ bond energetics.²¹ The $\text{Rh}-\text{OCH}_3$ BDFE is ~ 4 kcal mol $^{-1}$ smaller than the $\text{Rh}-\text{CH}_2\text{CH}_3$ BDFE and is virtually equal to the BDFE for the isomeric $\text{Rh}-\text{CH}_2\text{OH}$ unit.

Coordinated alkoxide groups in late transition metal complexes have been shown by Bergman's group to function as remarkably strong donors in hydrogen bonding with alcohols.³ Exceptionally strong MOR-alcohol bonds may result from synergism of hydrogen bonding with decreasing the $d\pi-\pi\pi$ repulsions. Binding of methanol with the methoxide in $\text{H}(\text{Ir}(\text{OCH}_3)(\text{PEt}_3)_3\text{Cl})$ was suggested as a possible explanation for the large entropy change ($\Delta S^\circ = -67(4)$ cal K $^{-1}$ mol $^{-1}$) in the oxidative addition of $\text{CH}_3\text{O}-\text{H}$ with $\text{Ir}(\text{PEt}_3)_3\text{Cl}$.¹⁴ The effective $\text{Ir}-\text{OCH}_3$ BDE of 61–68 kcal mol $^{-1}$ may thus be a composite of the $\text{Ir}-\text{OCH}_3$ BDE and the dissociation of a hydrogen-bonded methanol, similar to reaction 6, where $(\text{TMP})\text{Rh}-\text{OCH}_3(\text{CH}_3\text{OH})$ (**2**) involves dissociation of a Rh-methanol complex and $\text{Rh}-\text{OCH}_3$ bond homolysis. Spectroscopic and equilibrium studies of the interaction of methanol with solutions of $(\text{TMP})\text{Rh}-\text{OCH}_3$ (**1**) are consistent with formation of only the 18-electron complex $(\text{TMP})\text{Rh}-\text{OCH}_3(\text{CH}_3\text{OH})$ (**5**) in the range of methanol concentrations studied ($[\text{CH}_3\text{OH}] = 0.001-1.0$ M). Hydrogen bonding of methanol with the coordinated methoxide in **1** and **2** is inhibited by the steric demands of the porphyrin mesityl groups.

Isomerization of **1** to **5** (eq 9) in toluene is observed by ^1H NMR to proceed effectively to completion.



Rearrangement of the $-\text{OCH}_3$ organic fragment to CH_2OH is thermodynamically favored by ~ 8.5 kcal mol $^{-1}$,²⁰ and trading an O-H for a C-H unit thus drives the isomerization.

Late transition metal alkoxides ($\text{M}-\text{OCHR}_2$) with filled $d\pi$ orbitals should be thermodynamically unstable with respect to isomerization to α -hydroxyalkyl ($\text{M}-\text{C}(\text{OH})\text{R}_2$) complexes in the absence of additional energy terms from interactions such as M-OR alkoxide hydrogen bonding with alcohols. Addition of late transition metal hydrides with aldehydes and ketones should invariably have a thermodynamic preference to produce metal α -hydroxyalkyl derivatives over metal alkoxides.

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Supporting Information Available: Details on the solution structures and equilibrium measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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