Comparison of Rh–OCH_3 and Rh–CH_2OH Bond Dissociation Energetics from Methanol C–H and O–H Bond Reactions with Rhodium(II) porphyrins.

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Supporting Information :

Experimental Procedures:

General Considerations:

All manipulations were performed on a high vacuum line equipped with a Welch Duo–Seal vacuum pump. NMR solvents (C_6D_6, Toluene-d_8 and CD_2Cl_2) were purchased from Cambridge Isotopes Lab, dried over 4Å molecular sieves and degassed by freeze–pump–thaw cycles to remove oxygen. HPLC grade methanol was purchased from Fisher Scientific Company, dried over solid sodium methoxide and degassed by freeze–pump–thaw cycles to remove oxygen as well. All other reagents were purchased from Aldrich Chemicals and used as received. Proton NMR spectra were obtained on a Bruker–DMX 300, Bruker–AMX360 or a Bruker–AMX500 instrument interfaced to an Aspect 300 computer at ambient temperature. All spectra were referenced against the residual solvent proton peaks (benzene–d_6, δ = 7.155 ppm, toluene−d_8, δ = 7.03 ppm, CD_2Cl_2, δ = 5.32 ppm) as the internal standards. Photolysis of rhodium methyl complex [(TMP)Rh–CH_3] to make the metallo radical complex [(TMP)$Rh^{II\bullet}$] was performed using a Rayonet RPR–100 photochemical reactor.

Preparation of Organometallic Complexes

Tetramesitylporphyrin rhodium(II) complex ((TMP)$Rh^{II\bullet}$) (3): The porphyrin rhodium methyl complex (TMP)Rh–CH_3) was synthesized as per published procedures in previous literatures. Degassed solution of ((TMP)Rh–CH_3) in benzene–d_6 (~ 1.0×10^{-3} M) was taken in a vacuum–adapted NMR tube and photolyzed ($\lambda > 350$ nm) for 6 hours in a Rayonet photoreactor. The solvent along with the methane and toluene formed during the photolysis was removed under vacuum to give ((TMP)$Rh^{II\bullet}$) as a solid in yields greater than 90%. ^{1}H NMR (C_6D_6, 296K), δ(ppm): 18.3 (bs, 8h, pyrrole), 8.86 (bs, 8H, *m*–phenyl), 3.51 (s, 12H, *p*–CH_3), 3.55 (bs, 24H, *o*–CH_3).

Tetramesitylporphyrin rhodium methoxide complex ((TMP)Rh–OCH_3)(1) and Tetramesitylporphyrin rhodium hydride complex ((TMP)Rh–H) (4): Tetramesityl rhodium(II) porphyrin ((TMP)$Rh^{II\bullet}$) reacts rapidly with methanol in toluene–d_8 ([CH_3OH] ≥ 0.08 (M)) initially to form equal quantities of rhodium(III) methoxide and hydride complexes. ^{1}H NMR (0.1M CH_3OH in $C_6D_5CD_3$), [(TMP)Rh–OCH_3], δ(ppm): 8.82 (s, 8H, pyrrole), 7.23 (s, 8H, *m*–phenyl), 2.52 (s, 12H, *p*–CH_3), 1.86 (s, 12H, *o*–CH_3), 1.81 (s, 12H, *o*'–CH_3), –2.46 (d, 3H, $^3J_{^{103}Rh-H}$ = 1.5 Hz). [(TMP)Rh–H], δ(ppm): 8.68 (s, 8H, pyrrole), 7.20 (s, 8H, *m*–phenyl), 2.49 (s, 12H, *p*–CH_3), 2.03 (s, 12H, *o*–CH_3), 2.02 (s, 12H, *o*'–CH_3), 39.99 (d, 1H, $^1J_{^{103}Rh-H}$ = 43.2 Hz).

Tetramesitylporphyrin rhodium methoxide complex ((TMP)Rh–OCH_3) from ((TMP)Rh-I): Rhodium methoxide complex (TMP)Rh-OCH_3 was prepared from the precursor iodide complex (TMP)Rh-I by slightly modifying the published synthetic method developed by Collman and Boulatov.[15] Under dry nitrogen atmosphere, (TMP)Rh-I (5 mg, 4.9×10^{-6} mol) was dissolved in 10 ml of dry CD_2Cl_2. To this solution solid $AgPF_6$ (1.5 mg, 5.9×10^{-6} mol) was added and the reaction mixture was stirred at room temperature under nitrogen for 2 hours. The precipitated AgI was filtered out under inert atmosphere and to the filtrate was added excess solid Sodium methoxide ($NaOCH_3$) (0.5 mg, 9.2×10^{-6} mol, approximately 2 equivalents) and reaction mixture was stirred under nitrogen for an additional 30 minutes. Reaction mixture was filtered to remove any solid precipitate and solvent was removed under vacuum to yield

(TMP)Rh-OCH_3. ^{1}H NMR (CD_2Cl_2) δ(ppm): 8.87 (s, 8H, pyrrole), 7.26 (s, 8H, *m*−phenyl), 2.67 (s, 12H, *p*−CH_3), 2.06 (s, 12H, *o*−CH_3), 1.96 (s, 12H, *o*−CH_3), −2.35 (s, 3H, −OCH_3).

Equilibrium constant measurement for the formation of 1:1 methanol adduct (TMP)Rh−OCH_3(CH_3OH) in CD_2Cl_2:

In a NMR tube, CD_2Cl_2 solution of (TMP)Rh−OCH_3 (0.5 ml 2.35×10^{-3} M = $[(TMP)Rh-OCH_3]_i$) was titrated by stepwise addition of methanol (CH_3OH) in increments of 5µl and ^{1}H NMR spectrum of the sample was recorded after each addition. Total concentration of methanol $[CH_3OH]_i$ was calculated for each increment by taking into consideration the total volume of solution in NMR tube after each addition of methanol. The change in the chemical shift of the mole fraction averaged pyrrole resonance ($\delta_{pyrrole}$) with respect to the two extreme values of pyrrole resonances for uncoordinated species (TMP)Rh−OCH_3 ($\delta_{initial}$) and 1:1 methanol adduct (TMP)Rh−OCH_3(CH_3OH) after attaining equilibrium (δ_{final}) was used for each spectrum to calculate the relative concentrations of the uncoordinated and coordinated species (TMP)Rh−OCH_3, [(TMP)Rh−OCH_3] and (TMP)Rh−OCH_3(CH_3OH), [(TMP)Rh−OCH_3(CH_3OH)] present in the sample solution at progressively increasing methanol concentrations. The calculations for estimation of equilibrium constant for 1:1 methanol adduct formation at each representative concentration of methanol in solution (Figure SI 1) is carried out in the method shown below:

At a total methanol concentration of $[CH_3OH]_i$,

$$(TMP)Rh\text{-}OCH_3 + CH_3OH \rightleftharpoons (TMP)Rh\text{-}OCH_3(CH_3OH) \qquad (A)$$

Chemical shift: $\delta_{initial} = 8.874$ ppm $\qquad$ $\delta_{final} = 8.820$ ppm

Mole fraction: χ_A $\qquad$ χ_B

$$\delta_{pyrrole} = \delta_{initial} \times \chi_A + \delta_{final} \times \chi_B$$

$$= (8.874) \times \chi_A + (8.820) \times (1 - \chi_A)$$

$$= 8.820 + 0.054 \times \chi_A$$

$$\chi_A = \frac{\delta_{(pyrrole)} - 8.820}{0.054}$$

$$\chi_B = (1 - \chi_A)$$

$$[(TMP)Rh-OCH_3] = [(TMP)Rh-OCH_3]_i \times \chi_A$$

$$[(TMP)Rh-OCH_3(CH_3OH)] = \chi_B \times [(TMP)Rh-OCH_3]_i$$

Assuming that methanol forms a 1:1 adduct with (TMP)Rh−OCH_3) to form (TMP)Rh−OCH_3(CH_3OH), concentration of uncoordinated methanol present in the solution can be expressed as

$$[CH_3OH] = [CH_3OH]_i - [(TMP)Rh-OCH_3(CH_3OH)]$$

Thus by knowing the equilibrium values of [(TMP)Rh−OCH_3], [(TMP)Rh−OCH_3(CH_3OH)] and equilibrium concentration of uncoordinated methanol in solution [CH_3OH], the equilibrium constant at room temperature for each total concentration of methanol in solution for reaction A can be calculated as

$$K_{(298K)} = \frac{[(TMP)Rh-OCH_3(CH_3OH)]}{[(TMP)Rh-OCH_3][CH_3OH]}$$

The free energy of formation of 1:1 methanol adduct (TMP)Rh−OCH_3(CH_3OH) at 298K can then be calculated using equation

$$\Delta G^o_{(289K)} = -RT\ln K_{(298K)}$$

R = Universal Gas constant (R = 1.985 cal $K^{-1}mol^{-1}$)
T = solution temperature in Kelvin (T = 298K)

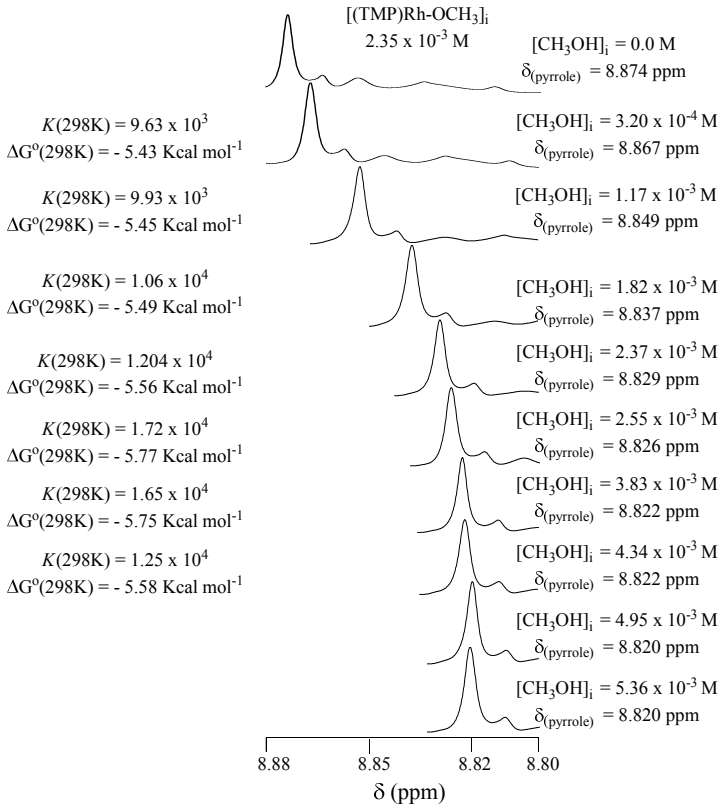

Figure SI 1. ^{1}H NMR Equilibrium thermodynamic study for estimation of Free Energy ($\Delta G^0(298K)$) of formation of methanol adduct [(TMP)Rh-$OCH_3(CH_3OH)$] from [(TMP)Rh-OCH_3] in CD_2Cl_2. $[(TMP)Rh\text{-}OCH_3]_i$ = starting concentration of [(TMP)Rh-OCH_3] in experimental CD_2Cl_2 solution, $[CH_3OH]_i$ = initial concentration of methanol in CD_2Cl_2 solution of sample, $\delta_{(pyrrole)}$ = mole fraction averaged pyrrole resonance for samples containing both ((TMP)Rh-OCH_3) and ((TMP)Rh-$OCH_3(CH_3OH)$).

A time evolved ^{1}H NMR spectrum of a solution of $(TMP)Rh^{II\bullet}$ (1.0×10^{-3} M) with CH_3OH in toluene–d_8 ($[CH_3OH] = 0.1$M) shows the immediate formation of the kinetic product ((TMP)Rh–OCH_3) and the hydride complex ((TMP)Rh–H) (Fig.SI 2, spectrum (a)). The methoxide complex thus obtained slowly gets converted to the thermodynamically more stable hydroxymethyl complex ((TMP)Rh–CH_2OH) over a period of 11 days (Fig. SI 2, spectra (b) and (c)). This slow rate of conversion of the methoxide complex to the thermodynamically more stable hydroxymethyl complex for the reaction of ($(TMP)Rh^{II\bullet}$) with methanol in effect provides a convenient lifetime of the methoxide complex to evaluate the equilibrium constant for the formation of 1:1 adduct of ((TMP)Rh–OCH_3) with methanol (eq. A) to form the six coordinate species ((TMP)Rh–$OCH_3(CH_3OH)$).

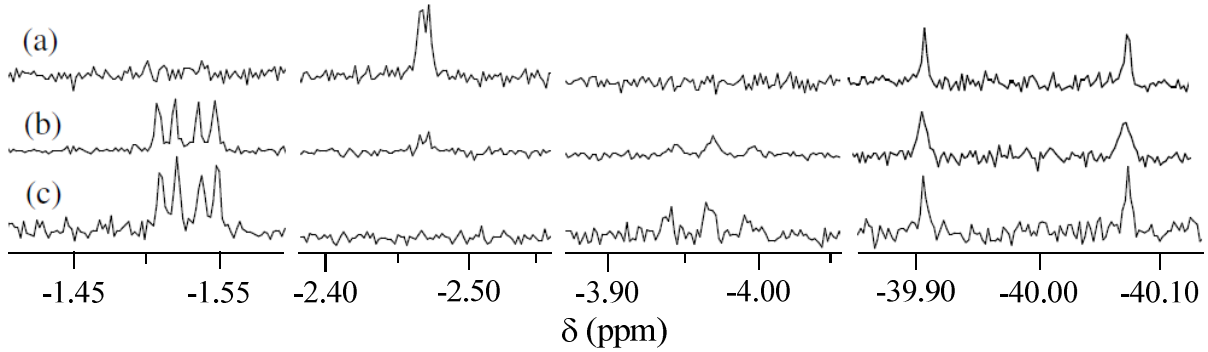

Figure SI 2. High field ^{1}H NMR resonances for the reaction of $(TMP)Rh^{II\bullet}$ (1.0×10^{-3} M) with CH_3OH in toluene–d_8 ($[CH_3OH] = 0.1$M). Reaction time: (a) 10 minutes; (b) 5 days; (c) 11 days. Rh–OCH_3: (δ = -2.46 ppm, d, 3H, $^3J_{^{103}Rh–OCH}$ = 1.5 Hz); Rh–CH_2OH: (–CH_2: δ = –1.53 ppm, dd, 2H, $^3J_{H\text{-}H}$ = 8.0 Hz, $^2J_{^{103}Rh–H}$ = 3.3 Hz; –OH: δ = –3.97ppm, t, 1H, $^3J_{H–H}$ = 8.0Hz); Rh–H: (δ = –40.0 ppm, d, 1H, $^1J_{^{103}Rh–H}$ = 43.2 Hz).

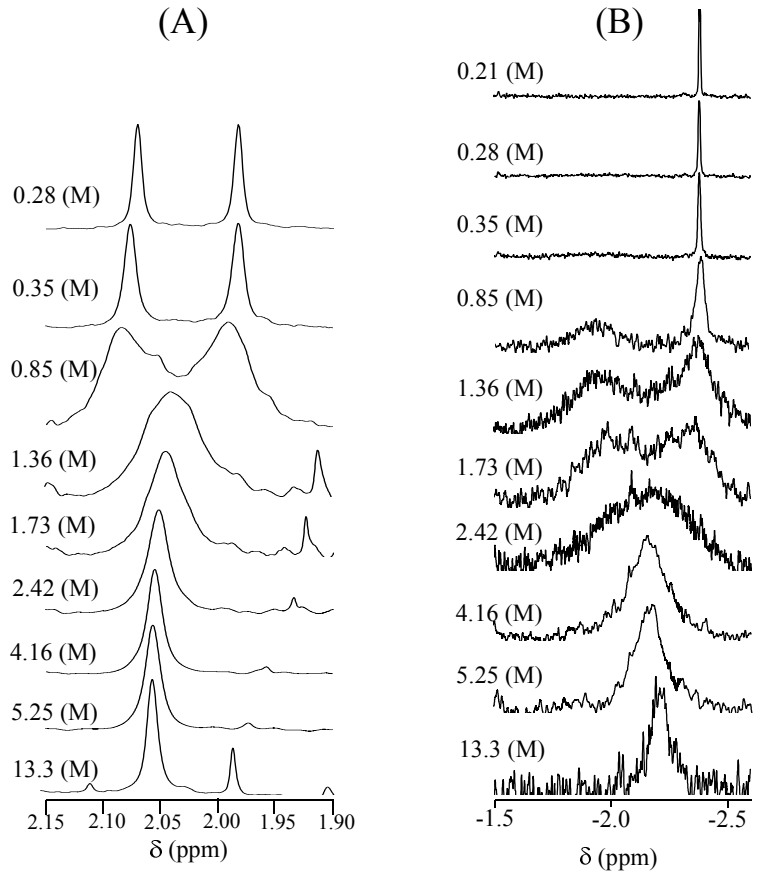

Figure SI 3. Concentration dependent ^{1}H NMR spectra of ((TMP)Rh–OCH_3) (1.0×10^{-3} M) with progressively increasing concentration of methanol (CH_3OH) in benzene–d_6. (A) changes in the ^{1}H NMR resonances for the mesityl *o*-CH_3 alpha-phenyl methyl protons of the tetramesityl porphyrin ligand, (B) changes in the ^{1}H NMR resonance for the coordinated methoxide protons of ((TMP)Rh–OCH_3) with increasing concentration of methanol.

The splitting of the mesityl *o*-CH_3 alpha-phenyl methyl proton resonances of ((TMP)Rh–OCH_3) (Fig. SI 3 (A)) bears evidence of the fact that the mesityl *o*-CH_3 alpha-phenyl methyl protons above and below the plane of the metalloporphyrin experience distinct magnetic anisotropy because of the different groups (methoxide and methanol) occupying opposite faces of the species ((TMP)Rh–OCH_3(CH_3OH)) formed by 1:1 adduct formation reaction of ((TMP)Rh–OCH_3) with methanol (eq. A). Reaction A achieves a ^{1}H NMR observable equilibrium at a methanol concentration of approximately 5×10^{-3} M (Fig. SI 1). The relative constancy in the chemical shift of the methyl protons of the coordinated methoxide with an increase in concentration of methanol in solution up to 0.35 M suggests that under the given reaction conditions the methanol molecules in bulk solvent do not form hydrogen bond with the coordinated –OCH_3 of ((TMP)Rh–OCH_3), which is supported by the fact that the mesityl *o*-CH_3 alpha-phenyl methyl protons of the (TMP) ligand placed nearly perpendicular to the plane of the metallorporphyrin create a pocket around the methoxide ligand coordinated to the central metal, thus sterically prohibiting the possibility of a methanol molecule in bulk solvent from interacting with the coordinated methoxide group. This in conjunction with Fig. SI 1 suggests that the methanol molecule from solvent, coordinating with the metalloporphyrin species ((TMP)Rh–OCH_3), is binding to the vacant sixth coordination site on the central rhodium metal, opposite to the site occupied by the methoxide group coordinated –OCH_3 group. The fact that the mesityl *o*-CH_3 alpha-phenyl methyl proton resonances merge to a single peak with an increase in concentration of methanol in solution from 0.85 M to 1.36 M and beyond (Fig. SI 3 (A)) and the emergence of a new high field peak at –1.9 ppm and subsequent merging of this peak with that of the coordinated methoxide methyl protons (Fig. SI 3(B)) with an increase in molar concentration of methanol in solution further supports the contention that methoxide and methanol are binding to opposite sites on the central metal. Both of these dynamic phenomena can be explained as a result of a degenerate hydrogen transfer between the coordinated methoxide and methanol groups resulting in making the two opposite faces of the metallo porphyrin equivalent.