Ruthenium PNP complex 1a ($\text{RuH(CO)Cl(HN(C_2H_4Pi-Pr_2)_2)}$) represents a state-of-the-art catalyst for low-temperature (<100 °C) aqueous methanol dehydrogenation to $\text{H}_2$ and $\text{CO}_2$. Herein, we describe an investigation that combines experiment, spectroscopy, and theory to provide a mechanistic rationale for this process. During catalysis, the presence of two anionic resting states was revealed, Ru–dihydride (3⁻) and Ru–monohydride (4⁻) that are deprotonated at nitrogen in the pincer ligand backbone. DFT calculations showed that $\text{O-}$- and $\text{CH-}$- coordination modes of methoxide to ruthenium compete, and form complexes 4⁻ and 3⁻, respectively. Not only does the reaction rate increase with increasing KOH, but the ratio of 3⁻/4⁻ increases, demonstrating that the “inner-sphere” $\text{C—H}$ cleavage, via $\text{C—H}$ coordination of methoxide to Ru, is promoted by base. Protonation of 3⁻ liberates $\text{H}_2$ gas and formaldehyde, the latter of which is rapidly consumed by KOH to give the corresponding gem-diolate and provides the overall driving force for the reaction. Full MeOH reforming is achieved through the corresponding steps that start from the gem-diolate and formate. Theoretical studies into the mechanism of the catalyst Me-1a (N-methylated 1a) revealed that $\text{C—H}$ coordination to Ru sets-up $\text{C—H}$ cleavage and hydride delivery; a process that is also promoted by base, as observed experimentally. However, in this case, Ru–dihydride Me-3 is much more stable to protonation and can even be observed under neutral conditions. The greater stability of Me-3 rationalizes the lower rates of Me-1a compared to 1a, and also explains why the reaction rate then drops with increasing KOH concentration.

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