

Bimetallo-Radical Carbon–Hydrogen Bond Activation of Methanol and Methane

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Development of effective strategies for selective hydrocarbon activation and functionalization continues as a set of premier issues in chemical reactivity and transformation.^{1–5} The limited information available on metallo-radical activation of hydrocarbons indicates a reaction specificity for saturated hydrocarbons over that of aromatics, and among hydrocarbons there is a selectivity preference for methane.^{6,7} Metallo-radical ($M\cdot$) reactions with substrates such as hydrocarbons^{6,7} and hydrogen,^{8–10} where atom abstractions are highly endothermic, often proceed by a concerted interaction of two metallo-radicals with the substrate through a four-centered transition state.^{6–10} The structure for this type of transition state



provides an opportunity to obtain kinetic selectivity based on the substrate size and shape and is responsible for metallo-radicals manifesting unusual selectivities for C–H bond activation.^{6,7} Reactions that utilize this type of pathway have relatively low activation enthalpies because of extensive bond making in the transition state, but they generally occur slowly because of the kinetic disadvantage for termolecular processes and the large activation entropies associated with organizing three particles in the transition state.^{6–11} One example is (tetramesitylporphyrinato)-rhodium(II) ((TMP)Rh \cdot), which manifests relatively small activation enthalpy ($\Delta H^\ddagger = 7.1 \text{ kcal mol}^{-1}$) and large unfavorable activation entropy ($\Delta S^\ddagger = -40 \text{ cal K}^{-1} \text{ mol}^{-1}$) in the reaction with CH₄ to form (TMP)Rh–CH₃ and (TMP)Rh–H.^{6,7} A potential approach for obtaining improved kinetics while retaining the unusual selectivity is to incorporate two metallo-radical centers into a single molecular unit capable of attaining a bimolecular reaction pathway.^{12–14} This article reports on carbon–hydrogen bond homolysis reactions of CH₃OH and CH₄ with a dirhodium(II) diporphyrin bimetallo-radical complex that illustrate the efficacy of this strategy. These C–H bond reactions occur by a pathway that is first order in bimetallo-radical with reduced activation entropy and kinetic preference for CH₄ over CH₃OH.

The diporphyrin ligand and the dirhodium(II) bimetallo-radical complex selected for C–H bond reaction studies are illustrated in Figure 1. Steric demands of the porphyrin units that prohibit intermolecular and intramolecular Rh(II)–Rh(II) bonding and a tether unit that has an appropriate size and flexibility to permit the two metal centers to reach the transition state for an intramolecular substrate reaction are essential design features that have been successfully incorporated into the diporphyrin ligand.¹⁴ An additional important feature of this biporphyrin is that the ¹H NMR of the methylene groups of the *m*-xylene tether is sensitive to the chemical environment and is well separated from all other resonances, which provides a useful observable for identifying solution species and facilitating kinetic-mechanistic studies.

Methanol (0.01–0.12 M) is observed to react with **1** ($\sim 2.0 \times 10^{-3}$ M) exclusively by C–H bond cleavage to form Rh–CH₂OH and Rh–H units. Time evolution of the ¹H NMR for the Rh–CH₂–

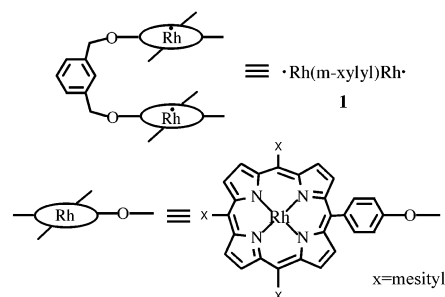


Figure 1. Illustration of the dirhodium(II) diporphyrin bimetallo-radical complex.

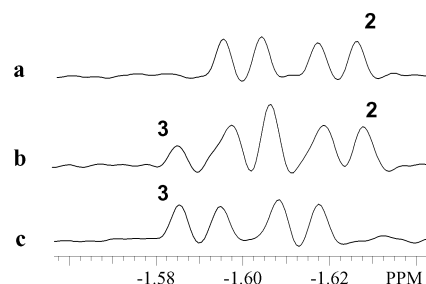


Figure 2. Time evolution of the ¹H NMR for the Rh–CH₂OH unit of the diamagnetic products of reaction **1** with CH₃OH (0.11 M): (a) $t = 3 \text{ h}$ ($\delta = -1.611 \text{ ppm}$, $^3J_{\text{H-H}} = 8.2 \text{ Hz}$, $^2J_{\text{103Rh-H}} = 3.4 \text{ Hz}$); (b) $t = 4 \text{ days}$; (c) $t = 20 \text{ days}$ ($\delta = -1.602 \text{ ppm}$, $^3J_{\text{H-H}} = 8.2 \text{ Hz}$, $^2J_{\text{103Rh-H}} = 3.4 \text{ Hz}$) (spectra were enhanced with Gaussian multiplication; **2** = HOCH₂–Rh(*m*-xylyl)–Rh–H; **3** = HOCH₂–Rh(*m*-xylyl)–Rh–CH₂OH).

OH diamagnetic species produced by reaction of CH₃OH with **1** is illustrated in Figure 2. A C–H bond reaction with a substrate like CH₃OH that involves the intermolecular use of Rh^{II} sites from different molecules of **1** would produce two diamagnetic complexes containing a Rh–CH₂OH unit (HOCH₂–Rh(*m*-xylyl)–Rh–H (**2**) and HOCH₂–Rh(*m*-xylyl)–Rh–CH₂OH (**3**)), but an intramolecular use of two Rh^{II} centers produces a single diamagnetic species containing the Rh–CH₂OH unit (HOCH₂–Rh(*m*-xylyl)–Rh–H). Time evolution for the ¹H NMR of the Rh–CH₂OH fragment in the reaction of **1** with CH₃OH illustrates the relatively fast formation of a single diamagnetic species containing a Rh–CH₂OH unit and then a very slow evolution of a second type of diamagnetic Rh–CH₂OH species. The second species formed (Figure 2, species **3**) is shown to be identical to an authentic sample of HOCH₂–Rh(*m*-xylyl)–Rh–CH₂OH (**3**) produced by directed synthesis from sequential reaction of **1** with H₂ and CH₂O in benzene. H–Rh(*m*-xylyl)–Rh–CH₂OH (**2**) thus forms as the exclusive initial diamagnetic species (Figure 2, species **2**), and a much slower subsequent process results in the appearance and growth of **3**. This sequence of events is explained by a fast initial intramolecular reaction that exclusively forms **2**, followed by much slower intermolecular processes that result in reductive elimination of H₂ and formation of **3**. The most important conclusion is that an intramolecular

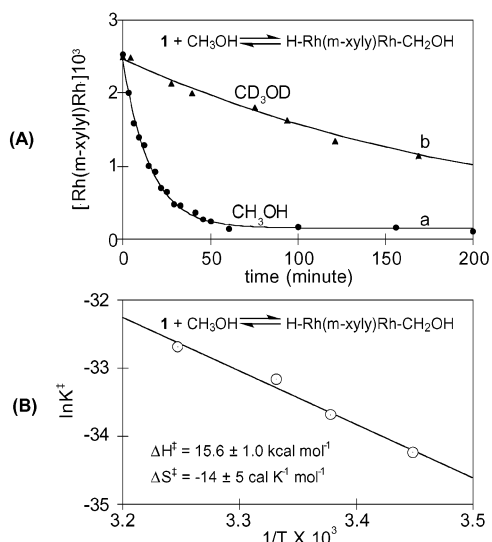


Figure 3. (A) Changes in the $[\cdot\text{Rh}(m\text{-xylyl})\text{Rh}\cdot]$ ($[\text{I}]_0 = 2.5 \times 10^{-3} \text{ M}$) in C_6D_6 at 296 K with time in the reaction of (a) CH_3OH (0.067 M); $k(\text{CH}_3\text{OH}) = 1.45 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ and (b) CD_3OD (0.050 M); $k(\text{CD}_3\text{OD}) = 1.50 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. (B) Determination of the activation parameters for reaction of $\cdot\text{Rh}(m\text{-xylyl})\text{Rh}\cdot$ with CH_3OH .

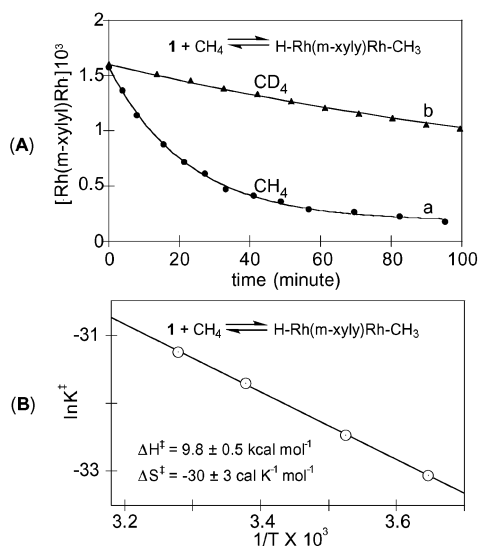
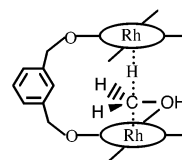


Figure 4. (A) Changes in the $[\cdot\text{Rh}(m\text{-xylyl})\text{Rh}\cdot]$ ($[\text{I}]_0 = 1.6 \times 10^{-3} \text{ M}$) in C_6D_6 at 296 K with time in the reaction of (a) CH_4 ($6.3 \times 10^{-3} \text{ M}$); $k(\text{CH}_4) = 0.105 \text{ M}^{-1} \text{ s}^{-1}$ and (b) CD_4 ($8.7 \times 10^{-3} \text{ M}$); $k(\text{CD}_4) = 9.7 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. (B) Determination of the activation parameters for reaction of $\cdot\text{Rh}(m\text{-xylyl})\text{Rh}\cdot$ with CH_4 .

utilization of the two Rh(II) sites in $\cdot\text{Rh}(m\text{-xylyl})\text{Rh}\cdot$ is operating as the pathway for the relatively fast reaction of CH_3OH with **1**.

Representative kinetic data ($T = 296 \text{ K}$) for reactions of $\text{CH}_3\text{OH}/\text{CD}_3\text{OD}$ and CH_4/CD_4 with **1** are given in Figures 3 and 4. Rate constants are obtained by fitting the kinetic data to a process that is first order in both substrate and **1** approaching equilibrium. The second-order rate constant for the reaction of methane with **1**

is found to be substantially larger than the value for methanol ($k(\text{CH}_4)/k(\text{CH}_3\text{OH}) = 7.2$, $T = 296 \text{ K}$). Large kinetic isotope effects are observed at 296 K for the reactions of **1** with methanol ($k(\text{CH}_3\text{OH})/k(\text{CD}_3\text{OD}) = 9.7 \pm 0.8$) (Figure 3A) and methane ($k(\text{CH}_4)/k(\text{CD}_4) = 10.8 \pm 1.0$) (Figure 4A), which are consistent with a rate-determining step involving C–H bond homolysis through a near linear transition state.



Temperature dependence of the rate constants for the C–H activation reactions are used in deriving activation parameters for reaction of **1** with methanol ($\Delta H^\ddagger = 15.6 \pm 1.0 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -14 \pm 5 \text{ cal K}^{-1} \text{ mol}^{-1}$) (Figure 3B) and methane ($\Delta H^\ddagger = 9.8 \pm 0.5 \text{ kcal mol}^{-1}$; $\Delta S^\ddagger = -30 \pm 3 \text{ cal K}^{-1} \text{ mol}^{-1}$) (Figure 4B).

The primary initial objectives for designing bimetallo-radical species were to test the strategy to obtain rate enhancements for metallo-radical reactions by converting from a termolecular process to a bimolecular reaction with reduced activation entropy while retaining selectivity. These objectives have been realized in the reaction of $\cdot\text{Rh}(m\text{-xylyl})\text{Rh}\cdot$ with methane, which occurs as a bimolecular process with reduced activation entropy as compared to the methane reaction of $(\text{TMP})\text{Rh}\cdot$.^{6,7a} Realization of additional rate enhancements and substrate selectivity in this system requires reducing the activation enthalpy through designing bimetallo-radical structures that more closely emulate the transition state.

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Supporting Information Available: Experimental procedures, data analysis, and ^1H NMR for compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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