

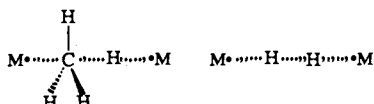
Rhodium(II) Porphyrin Bimetallo-radical Complexes: Preparation and Enhanced Reactivity with CH₄ and H₂

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Metalloradical (M^{*}) reactions with substrates like H₂ and CH₄, where atom abstractions are highly endothermic, can proceed by a concerted interaction of two metalloradicals with the substrate through a four-centered transition state (TS).¹⁻⁴ Reactions that



utilize this type of pathway have relatively low activation enthalpies because of extensive bond-making in the TS, but they generally occur slowly because of the kinetic disadvantages for termolecular processes and the large activation entropies associated with organizing three particles in the TS.¹⁻⁴ (Tetramesitylporphyrinato)rhodium(II) ((TMP)Rh^{II}) is an example of a stable metalloradical that accomplishes activation of CH₄ and H₂ through a four-centered TS^{1,2} and manifests unusual selectivity among metal complexes that activate C-H bonds⁵⁻⁹ by exhibiting a kinetic preference for methane activation compared with the reactivity of other aliphatic and aromatic hydrocarbons. This selective methane reactivity has its origin in the steric demands of the trimolecular transition state which favors the smallest substrate.¹ A potential approach for obtaining improved kinetics is to incorporate two metalloradical centers into a single molecular unit in a manner that provides a bimolecular reaction pathway. The only previously reported dirhodium diporphyrin complex (Rh₂DPB) contains porphyrin units attached to biphenylene at an interporphyrin distance that preorganizes and supports Rh^{II}-Rh^{II} bond formation.¹⁰ This article reports on the formation of a dirhodium diporphyrin complex in which the porphyrin steric requirements prohibit Rh^{II}-Rh^{II} bonding and the resulting bimetallo-radical complex (*Rh(CH₂)₆Rh*) reacts with H₂ and CH₄ at rates that are substantially larger than those for (TMP)-Rh* and (tetraalkylporphyrinato)rhodium(II) dimer, [(TXP)-Rh]₂.

A diporphyrin ligand (3) in which the porphyrin units are tethered by a diether (-O(CH₂)₆O-) spacer was obtained by the reaction sequence described in Scheme 1.^{11,12} Subsequent

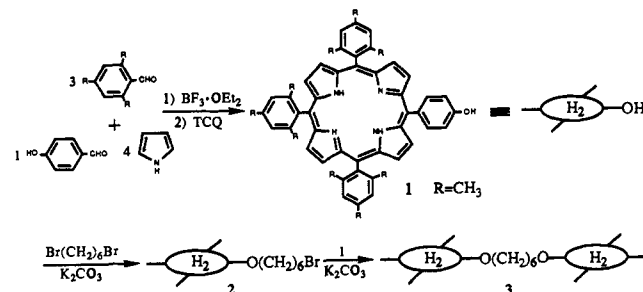
- (1) (a) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1990**, *112*, 1259.
- (2) Wayland, B. B.; Ba, S.; Sherry, A. E. *J. Am. Chem. Soc.* **1991**, *113*, 5305.
- (3) Wayland, B. B.; Ba, S.; Sherry, A. E. *Inorg. Chem.* **1992**, *31*, 148.
- (4) Simandi, L. I.; Budo-Zahonyi, E.; Szeverenyi, Z.; Nemeth, S. *J. Chem. Soc., Dalton Trans.* **1980**, 276.
- (5) (a) Halpern, J.; Pribinic, M. *Inorg. Chem.* **1970**, *9*, 2626. (b) Halpern, J. *Inorg. Chim. Acta* **1982**, *62*, 31. (c) Halpern, J. *Inorg. Chim. Acta* **1983**, *77*, L105.
- (6) (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. (c) Hill, C. L., Ed. *Activation and Functionalization of Alkanes*; Wiley Interscience: New York, 1989.
- (7) Ghosh, C. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4726.
- (8) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (b) Harper, T. G.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7915.
- (9) (a) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2214. (b) Watson, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 6491.
- (10) (a) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (b) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 8109.
- (11) Collman, J. P.; Ha, Y.; Guillard, R.; Lopez, M.-L. *Inorg. Chem.* **1993**, *32*, 1788.

Table 1. Initial Rates (M s⁻¹) for Reactions of (Por)Rh^{II} Complexes with H₂ and CH₄ (296 K)^{a,b}

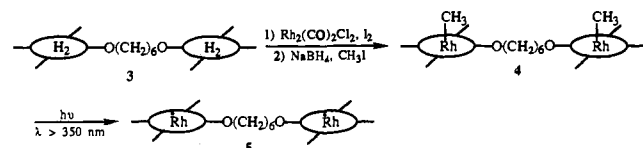
| | *Rh(CH ₂) ₆ Rh* | ((TXP)Rh) ₂ | (TMP)Rh* |
|-----------------|--|---------------------------------|---------------------------------|
| H ₂ | (2.7 ± 0.1) × 10 ⁻⁶ | (4.4 ± 0.3) × 10 ⁻¹⁰ | (4.0 ± 0.3) × 10 ⁻⁹ |
| CH ₄ | (2.5 ± 0.3) × 10 ⁻⁸ | (1.7 ± 0.2) × 10 ⁻¹¹ | (1.9 ± 0.2) × 10 ⁻¹⁰ |

^a The initial rates were calculated from the observed rate constants using the same molar concentration of substrates and Rh(II) sites. [Rh(II)]_i = 2.55 × 10⁻⁴ M, [H₂]_i = [CH₄]_i = 2.30 × 10⁻² M. ^b Initial rate = (d[Rh(II)]/dt)_{t=0} = 2(d[*Rh(CH₂)₆Rh*]/dt)_{t=0} = 2(d[(TXP)Rh]₂/dt)_{t=0} = (d[(TMP)Rh*]/dt)_{t=0}.

Scheme 1



Scheme 2



conversion to the dirhodium(II) derivative is accomplished by procedures^{1,13,14} outlined in Scheme 2. The dimethyl derivative 4 photolyzes in benzene to form a dirhodium(II) complex (*Rh(CH₂)₆Rh*) (5) which is shown to be a persistent bimetallo-radical through observation of Curie behavior for the porphyrin pyrrole contact shifts (350–200 K) and EPR spectra in toluene glass (90 K) that are characteristic of low-spin rhodium(II)¹⁵ (*g*_{||} = 1.93, *g*_⊥ = 2.66; *A*¹⁰³Rh(*g*_{||}) = 159 MHz). Mesityl groups in the diporphyrin ligand prohibit Rh^{II}-Rh^{II} bonding, and 5 thus provides a stable bimetallo-radical for comparative studies with (TMP)Rh^{II}. The bimetallo-radical, *Rh(CH₂)₆Rh* (5), readily reacts with CH₄ and H₂ in C₆D₆ (*T* = 296 K; *P*_{H₂} = 0.70 atm, *P*_{CH₄} = 1.0 atm) to form HRh(CH₂)₆RhCH₃ (6) and HRh(CH₂)₆-

(11) (a) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828. (b) Little, R. G. *J. Heterocycl. Chem.* **1978**, *15*, 203.

(12) 1: ¹H NMR (C₆D₆) δ 8.92 (d, 2H, ³J_{H-H} = 4.8 Hz, pyrrole), 8.85 (d, 2H, ³J_{H-H} = 4.8 Hz, pyrrole), 8.84 (d, 2H, ³J_{H-H} = 4.8 Hz, pyrrole), 8.82 (d, 2H, ³J_{H-H} = 4.8 Hz, pyrrole), 7.78 (d, 2H, ³J_{H-H} = 8.2 Hz, *o*-phenyl), 7.11 (s, 6H, *m*-phenyl), 6.42 (d, 2H, ³J_{H-H} = 8.2 Hz, *m*-phenyl), 4.25 (br s, 1H, -OH), 2.45 (s, 6H, *p*-CH₃), 2.41 (s, 3H, *p*'-CH₃), 1.96 (s, 12H, *o*-CH₃), 1.84 (s, 6H, *o*'-CH₃), -1.73 (br s, 2H, -NH); HRMS-FAB (M⁺) calcd for C₅₃H₄₈N₄O 756.3829, found 756.3894; isolated yield, 16%. 2: HRMS-FAB (M⁺) calcd for C₅₉H₅₉N₄OBr 918.3837, found 918.3840; isolated yield, 72%. 3: ¹H NMR (C₆D₆) δ 9.04 (d, 4H, ³J_{H-H} = 4.8 Hz, pyrrole), 8.89 (d, 4H, ³J_{H-H} = 4.8 Hz, pyrrole), 8.86 (d, 4H, ³J_{H-H} = 4.8 Hz, pyrrole), 8.83 (d, 4H, ³J_{H-H} = 4.8 Hz, pyrrole), 7.98 (d, 4H, ³J_{H-H} = 8.5 Hz, *o*-phenyl), 7.18 (s, 12H, *m*-phenyl), 7.14 (d, 4H, ³J_{H-H} = 8.5 Hz, *m*-phenyl), 3.88 (t, 4H, ³J_{H-H} = 6.1 Hz, -OCH₂-), 2.45 (s, 12H, *p*-CH₃), 2.41 (s, 6H, *p*'-CH₃), 1.97 (s, 24H, *o*-CH₃), 1.85 (s, 12H, *o*'-CH₃), 1.54–1.36 (m, 8H, -CH₂CH₂CH₂CH₂-), -1.68 (br s, 4H, -NH); HRMS-FAB (M⁺) calcd for C₁₁₂H₁₀₆N₈O₂ 1594.8441, found 1594.8412; isolated yield, 58%.

(13) Ogoshi, H.; Setsune, J.; Omura, T.; Yoshida, Z. *J. Am. Chem. Soc.* **1975**, *97*, 6461.

(14) 4: ¹H NMR (C₆D₆) δ -5.29 (dd, 6H, Rh-¹³CH₃, ²J_{Rh-H} = 2.9 Hz, ¹J_{13C-H} = 141.5 Hz); ¹³C NMR (CD₃C₆D₅) δ -13.58 (qd, ¹J_{Rh-13C} = 29 Hz, ¹J_{H-13C} = 141.5 Hz); HRMS-FAB (M⁺) calcd for C₁₁₂H₁₀₆N₈O₂Rh₂ 1828.6773, found 1828.6842; yield, 85%. 5: ¹H NMR (C₆D₆, 296 K) δ 18.57 (br s, 16H, pyrrole), 11.36 (br s, 8H, *o*-H + *m*-H), 8.90 (s, 12H, *m*'-H), 5.10 (s, 4H, -OCH₂-), 3.58 (br s, 36H, *o*-CH₃), 3.52 (s, 18H, *p*-CH₃), 2.77 (s, 8H, -CH₂CH₂CH₂CH₂-); EPR (90 K, toluene glass) *g*_{xy} = 2.66, *g*_z = 1.93, *A*¹⁰³Rh(*g*_z) = 158 MHz; yield, >96%.

(15) Sherry, A. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1989**, *111*, 5010.

Table 2. Rate Constants for CH Bond Reactions of $^*\text{Rh}(\text{CH}_2)_6\text{Rh}^*$ with Substrates at 296 K^a

| substrate | H ₂ | CH ₄ | CH ₃ CH ₃ | CH ₃ OH |
|--|--------------------------------|--------------------------------|---------------------------------|--------------------------------|
| k (M ⁻¹ s ⁻¹) | $(9.3 \pm 0.5) \times 10^{-1}$ | $(8.6 \pm 0.3) \times 10^{-3}$ | $(1.5 \pm 0.1) \times 10^{-5}$ | $(5.3 \pm 0.3) \times 10^{-5}$ |

^a Rate = $k[^*\text{Rh}(\text{CH}_2)_6\text{Rh}^*][\text{HX}]$; X = H, CH₃, CH₂CH₃, CH₂OH.

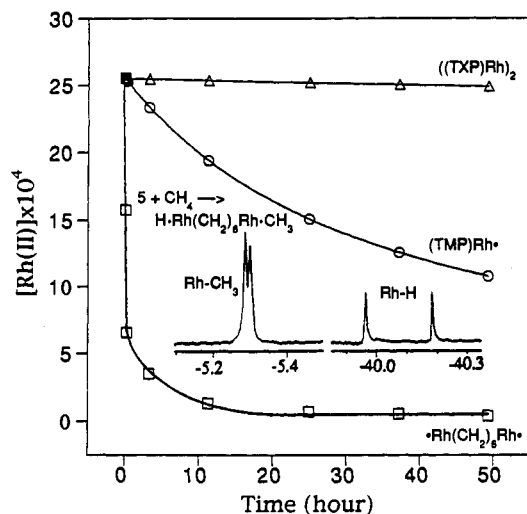


Figure 1. Comparison of the change in molar concentrations of rhodium-(II) centers with time for the reactions of CH₄ with $^*\text{Rh}(\text{CH}_2)_6\text{Rh}^*$ (5), (TMP)Rh^{*}, and ((TXP)Rh)₂ ($T = 296$ K, $P_{\text{CH}_4} = 1.0$ atm, $[\text{Rh}(\text{II})]_0 = 2.552 \times 10^{-3}$ M). Inset: ¹H NMR for the Rh-CH₃ and Rh-H sites in HRh(CH₂)₆RhCH₃ in C₆D₆ ($\delta_{\text{Rh-H}} = -40.07$ ppm, $J_{\text{105Rh-H}} = 43.4$ Hz; $\delta_{\text{Rh-CH}_3} = -5.29$ ppm, $J_{\text{105Rh-CH}_3} = 3.0$ Hz).

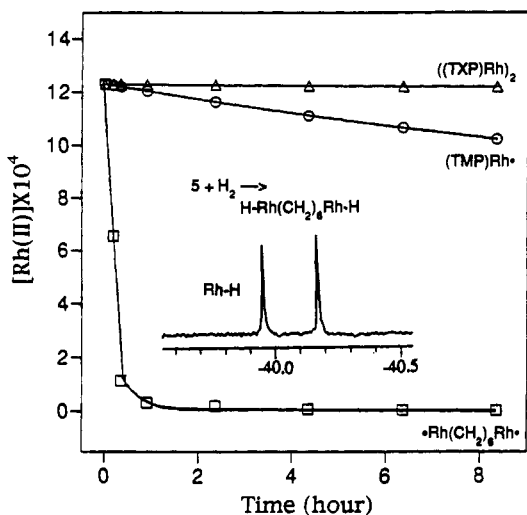
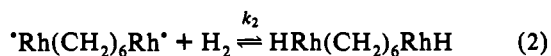
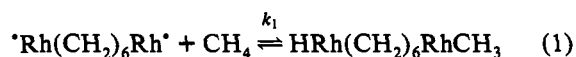


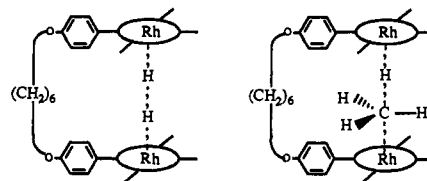
Figure 2. Comparison of the change in molar concentrations of rhodium-(II) centers with time for the reactions of H₂ with $^*\text{Rh}(\text{CH}_2)_6\text{Rh}^*$ (5), (TMP)Rh^{*}, and ((TXP)Rh)₂ ($T = 296$ K, $P_{\text{H}_2} = 0.7$ atm, $[\text{Rh}(\text{II})]_0 = 1.23 \times 10^{-3}$ M). Inset: ¹H NMR for the Rh-H group in HRh(CH₂)₆RhH in C₆D₆ ($\delta_{\text{Rh-H}} = -40.07$ ppm, $J_{\text{105Rh-H}} = 43.4$ Hz).

RhH (7) respectively (eqs 1 and 2). Substantial rate increases



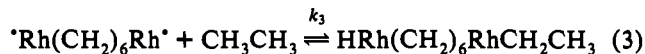
are observed for reactions 1 and 2 compared with the corresponding reactions of (TMP)Rh^{*} and ((TXP)Rh)₂^{1,2} (Figures 1 and 2; Table 1). Reactions 1 and 2 could occur through bimolecular or trimolecular transition states that utilize metalloradicals in one and two molecular units, respectively. Observation that the methane reaction (eq 1) is first order in 5, exclusively produces

HRh(CH₂)₆RhCH₃, and occurs with large rate enhancements over the trimolecular process for (TMP)Rh^{II*} are indicative of a dominant bimolecular pathway. Preliminary equilibrium

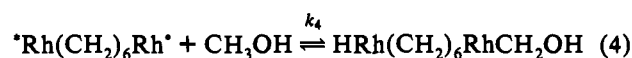


constant measurements by ¹H NMR for reactions 1 and 2 at 296 K ($K_1 = (2.0 \pm 0.2) \times 10^3$; $K_2 = (2.3 \pm 0.8) \times 10^6$) combined with the estimate that ΔS_1^\ddagger and ΔS_2^\ddagger will be in the range of -20 to -25 cal K⁻¹ mol⁻¹ provides estimates of $\sim 60 \pm 2$ and $\sim 56 \pm 3$ kcal mol⁻¹ for the Rh-H and Rh-CH₃ bond dissociation enthalpies, respectively, in compounds 6 and 7, which are indistinguishable from values estimated for (TMP)Rh-H (60 kcal mol⁻¹) and (TMP)Rh-CH₃ (57 kcal mol⁻¹).¹

Ethane reacts with 5 exclusively at the C-H unit to form HRh(CH₂)₆RhCH₂CH₃ (8) (eq 3) rather than cleaving the C-C bond to produce the dimethyl complex 4, even though 4 is the thermodynamically favored product by more than 10 kcal mol⁻¹ (D (kcal mol⁻¹): H₃C-CH₃, 90,¹⁶ H₃CCH₂-H, 100,¹⁶ Rh-H, ~ 60 , Rh-CH₃, ~ 56 , Rh-CH₂CH₃, ~ 49 ¹⁷). The absence of



observed C-C bond cleavage is kinetic in origin and suggests that the interaction of the Rh^{II*} center with the C-H unit is directing the overall near-concerted cleavage of the CH₃CH₂-H bond. Methanol and 5 also react with complete regioselectivity for the C-H unit to form HRh(CH₂)₆RhCH₂OH (9) (eq 4) rather than C-O or O-H bond cleavage to form HORh(CH₂)₆RhCH₃ or HRh(CH₂)₆RhOCH₃, respectively. Ratios of the rate constants



for the reaction of 5 with methane at 296 K to those for ethane ($k_1/k_3 = 5.7 \times 10^2$) and methanol ($k_1/k_4 = 1.6 \times 10^2$) illustrate the kinetic preference for the methane C-H bond reaction over those for substrates where the C-H bonds are activated relative to CH₄ (Table 2) (D (C-H) (kcal mol⁻¹): H₃C-H, 105;¹⁶ CH₃-CH₂-H, 100,¹⁶ HOCH₂-H, 94).¹⁸

The observed rate enhancement for substrate reactions of 5 compared with (TMP)Rh^{*} and ((TXP)Rh)₂ illustrate the kinetic advantage that occurs by preorganization of two metalloradical units in a molecular species where reactions can proceed via a bimolecular pathway. Our current studies are directed toward obtaining additional rate enhancements through structural preorganization of the transition states for small molecule reactions with both homo- and heterobimetallic diporphyrin complexes.

Acknowledgment. Support for this research from the National Science Foundation and the Gas Research Institute through Contract No. 5091-260-2183 is acknowledged.

(16) Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347.

(17) *Energetics of Organometallic Species*; Simões, J. A. M., Ed.; Kluwer Publishers: The Netherlands, 1992; p 73.

(18) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.