

Metallo-formyl Complexes of Rhodium Tetraphenylporphyrins

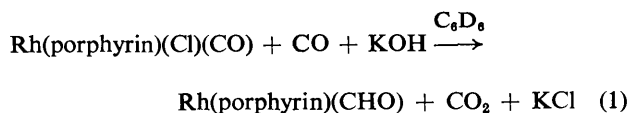
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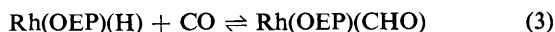
Thermodynamically stable metallo-formyl complexes of rhodium porphyrins are prepared directly by the reaction of benzene solutions of Rh(porphyrin)(Cl)(CO) complexes with CO and solid KOH.

Benzene solutions of Rh(porphyrin)(Cl)(CO) complexes in contact with carbon monoxide (P_{CO} ca. 500 Torr) and solid KOH react to form Rh(porphyrin)(CHO) complexes (reaction 1). This procedure has been successfully applied to both the

octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) macrocycles and should prove general for all Rh(macrocycle)-(Cl)(CO) species where the metallo-formyl is the thermodynamic product.

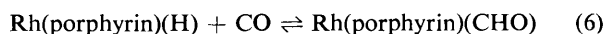
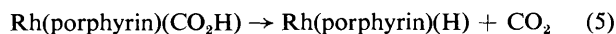
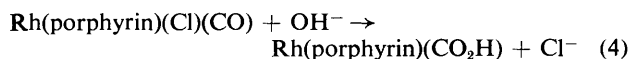


We have previously reported that rhodium octaethylporphyrin dimer $[\text{Rh}(\text{OEP})]_2$ reacts with carbon monoxide and hydrogen in a two-step process to produce the first metallo-formyl complex $[\text{Rh}(\text{OEP})(\text{CHO})]$ available as the thermodynamic product (reactions 2 and 3).^{1,2}



The role of metallo-formyl species as a primary intermediate in the hydrogenation of carbon monoxide³⁻⁶ has stimulated efforts to define the range of rhodium macrocycles capable of producing observable formyl species. Reaction (1) provides a route to rhodium porphyrin formyl complexes from the chloro-(carbonyl)-derivatives. This procedure circumvents the necessity of preparing the metal-metal bonded dimers or metallo-hydride derivatives which at present have been characterized only for Rh(OEP).

Reaction (1) is presumed to occur by nucleophilic attack of hydroxide on the co-ordinated CO, and elimination of CO₂ to produce the hydride complex which then combines with CO to give the metallo-formyl (reactions 4-6).



Reaction (4) is the slowest step in this sequence which precludes direct observation of the proposed carboxylic acid intermediate. This procedure has permitted preparation of the formyl complexes of rhodium(tetraphenylporphyrin) derivatives, Rh(TPP)(CHO) and Rh(pmeTPP)(CHO). Figure 1 illustrates the ¹H and ¹³C n.m.r. spectrum of the formyl group in Rh(TPP)(CHO) and Rh(pmeTPP)(CHO). The coupling constants in Rh(TPP)(¹³CHO) [$J(^{103}\text{Rh}-\text{H})$ 1.8 Hz; $J(^{103}\text{Rh}-^{13}\text{C})$ 29 Hz; $J(^{13}\text{C}-\text{H})$ 200 Hz] are virtually identical to the corresponding values for Rh(OEP)(CHO).¹ These observations are particularly important in establishing the thermodynamic stability of the formyl complexes for diverse porphyrin derivatives which suggests the generality of this unusual chemistry for all rhodium porphyrins.

When excess of CO is removed from the presence of Rh(porphyrin)(CHO), the reverse of reaction (6) occurs, which in the case of Rh(OEP)(CHO) results in the formation of the well characterized metallo-hydride Rh(OEP)(H): $\nu_{\text{Rh}-\text{H}}$ 2220 cm⁻¹ (ref. 7); ¹H n.m.r. $\delta_{\text{Rh}-\text{H}} = -41.2$. The corresponding process for Rh(TPP)(CHO) fails to produce a benzene solution species with either a high-field Rh-H ¹H n.m.r. peak or a $\nu_{\text{Rh}-\text{H}}$ vibrational band. Reintroduction of carbon monoxide (P_{CO} ca. 500 Torr) results in the immediate reappearance of Rh(TPP)(CHO). These observations demonstrate the facile reversibility for reaction (6) and support the strong acid

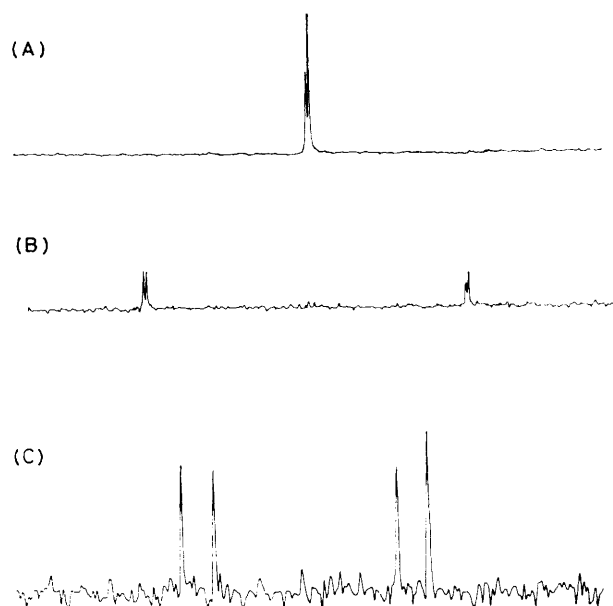


Figure 1. (A) ¹H N.m.r. spectrum for the formyl hydrogen atom of Rh(TPP)(¹²CHO) in C₆D₆ [$\delta(\text{CHO})$ 3.278; $J(^{103}\text{Rh}-\text{CHO})$ 1.8 Hz]. (B) ¹H N.m.r. spectrum for the formyl hydrogen atom of Rh(TPP)(¹³CHO) in C₆D₆ [$J(^{13}\text{C}-\text{H})$ 200 Hz]. (C) Gated ¹³C n.m.r. spectrum of Rh(TPP)(¹³CHO) in C₆D₆ [$\delta(^{13}\text{C})$ 194.1 p.p.m.; $J(^{103}\text{Rh}-^{13}\text{C})$ 29 Hz; $J(^{13}\text{C}-\text{H})$ 200 Hz].

formulation for Rh(TPP)(H) previously made by James and Stynes.⁸

Rh(OEP)(H) is a very weak acid compared to the Rh(TPP) derivatives and the relative rate for reaction (6) is much slower. Reaction (6) probably involves heterolytic cleavage of the Rh-H bond and subsequent addition of CO by a mechanism analogous to the reported *trans*-addition of Rh(OEP)(H) to phenylacetylene.⁹ The union of H₂ and CO to produce the metallo-formyl (reactions 2 and 3) requires activation of dihydrogen (reaction 2). Metal site co-ordination and activation of carbon monoxide could play an important kinetic role in other metallo-species, but it is not an essential feature for the hydrogenation of carbon monoxide.

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References

- 1 B. B. Wayland and B. A. Woods, *J. Chem. Soc., Chem. Commun.*, 1981, 700.
- 2 B. B. Wayland, B. A. Woods, and R. Pierce, *J. Am. Chem. Soc.*, 1982, **104**, 302.
- 3 D. R. Fahey, *J. Am. Chem. Soc.*, 1981, **103**, 136.
- 4 J. A. Gladysz, *Adv. Organomet. Chem.*, 1982, **20**, 1.
- 5 C. Masters, *Adv. Organomet. Chem.*, 1979, **17**, 61.
- 6 E. L. Muetterties and J. Stein, *Chem. Rev.*, 1979, **79**, 479.
- 7 H. Ogoshi, J. Setsune, and Z. Yoshida, *J. Am. Chem. Soc.*, 1977, **99**, 3869.
- 8 B. R. James and D. V. Stynes, *J. Am. Chem. Soc.*, 1972, **94**, 6225.
- 9 H. Ogoshi, J. Setsune, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, 1975, **97**, 6461.