

Chemistry of Octaethylporphyrinatorhodium Hydride
and Octaethylporphyrinatorhodium(II) Dimer

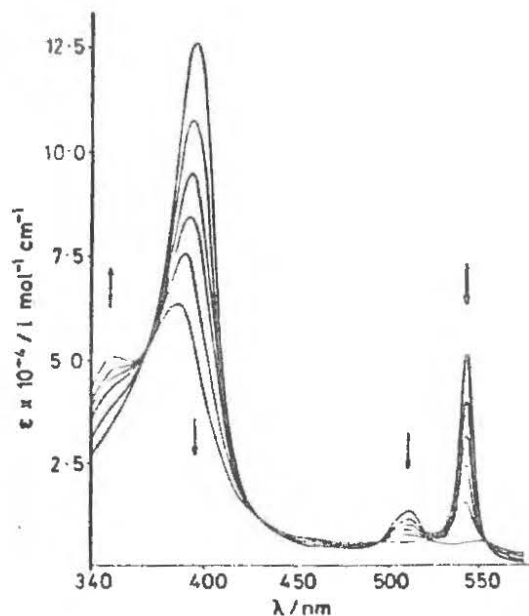
Thomas G. Gardner

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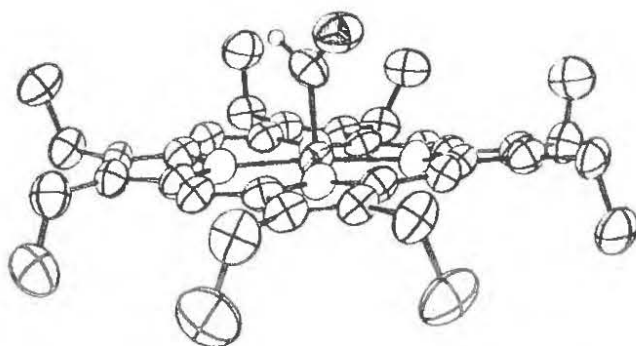
Interest in rhodium porphyrins originated in the biomimetic chemistry of cobalt complexes, such as vitamin B-12 [1,2,3]. However, many unique aspects of rhodium porphyrin chemistry have been observed. Rhodium(III)-carbon bonds have higher bond dissociation energies (i.e., are thermally more stable) than their cobalt(III) analogues [3]. Some rhodium porphyrin complexes provide models for intermediates in the water gas shift reaction (WGSR) [4] and in the Fischer-Tropsch reaction [5]. In addition, rhodium(II) porphyrins tend to exist as diamagnetic dimers with the rhodium centers singly bonded [6,7,8]. This metal-metal bond is easily homolyzed [9,10] to produce a highly reactive "metallo-radical" intermediate, which reacts with aromatic hydrocarbons [9,10], carbon monoxide, and olefins [11].

Octaethylporphyrinatorhodium(III) hydride (OepRhH) is in equilibrium with octaethylporphyrinatorhodium(II) dimer ((OepRh)₂) and molecular hydrogen in benzene solution [6,7,8]. Therefore, any reaction involving OepRhH will also occur with (OepRh)₂ in the presence of dihydrogen. The conversion of OepRhH to (OepRh)₂ may be followed with visible spectroscopy, as shown below [13]:



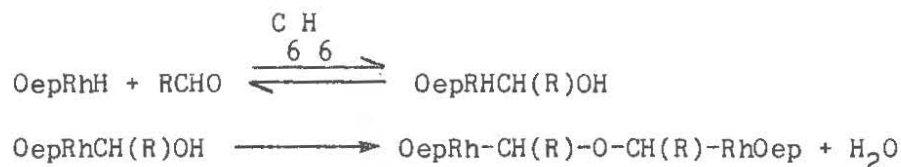
Visible spectrum change:
(OEP)Rh^{III}-H \rightarrow [(OEP)Rh^{II}]₂

OepRhH reacts reversibly with carbon monoxide to give a formyl complex, OepRh(CHO) [4,11,13]. This formyl complex is represented by the ORTEP diagram given below:

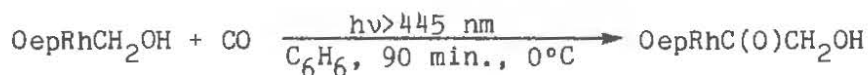


ORTEP representation for RhOEP(CHO). Bond lengths and angles for the RhCHO unit are as follows: Rh-C, 1.896 (6) Å; C-O, 1.175 (5) Å; C-H, 1.09 (1) Å; Rh-C-O, 129.6 (5)°; Rh-C-H, 129.9 (4)°.

This represents the first example of a formyl formed directly from a metal hydride and carbon monoxide (or from a metal complex, $(\text{OepRh})_2$, with dihydrogen and carbon monoxide). The infrared spectroscopic study of this species indicates that metal-carbonyl back-bonding is not significant in the formyl; therefore, this functional group is likely to exhibit reactivity similar to organic aldehydes. OepRhH nucleophilically adds to aldehydes, yielding hydroxyalkyl rhodium octaethylporphyrin [5,15], which can eliminate water to form a symmetrical metallo-ether [5]:



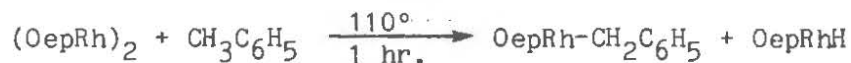
The hydroxymethyl complex also reacts with excess OepRhH to reductively eliminate methanol, the first such example from a hydroxymethyl intermediate. Carbon monoxide can be inserted into the rhodium-carbon bond of the hydroxymethyl complex, providing a pathway to a two-carbon organic molecule.



The addition is believed to occur through free radical intermediates, and the stereochemistry is guided primarily by steric effects.

The key feature of the chemistry of $(\text{OepRh})_2$ is its ability to undergo homolysis of the rhodium-rhodium bond, leaving a paramagnetic intermediate, which can react with Lewis bases by a general mechanism characteristic of free radical reactions. An example of the mechanism is the Arbusov rearrangement of trimethyl phosphite to the phosphonate catalyzed by $(\text{OepRh})_2$ [16]. In the presence of water, carbon monoxide reacts with $(\text{OepRh})_2$ to yield the formyl, OepRhCHO , the carbon dioxide [4]. Since the formyl can equilibrate back to OepRhH and carbon monoxide, and photolysis of OepRhH yields $(\text{OepRh})_2$ and molecular hydrogen, the $(\text{OepRh})_2$ dimer shows potential for use as a WCSR catalyst.

Aromatic hydrocarbons (e.g., toluene, ethylbenzene, etc.) are observed to react with $(\text{OepRh})_2$, resulting in the activation of the carbon-hydrogen bond alpha to the aromatic ring, and yielding a benzyl derivative [9,10].



With longer chain alkyl groups, rearrangement occurs slowly to yield products with rhodium-carbon bonds in alkyl positions other than alpha. The $(\text{OepRh})_2$ dimer also reacts with styrene [11], acetylenes [6,13,17], and ethyl vinyl ether [12,13,17] to give products in which the unsaturated carbon-carbon bond has inserted into the rhodium-rhodium bond of the dimer.



Current investigations into the chemistry of OepRhH and $(\text{OepRh})_2$ involve the heterolytic cleavage of the rhodium-rhodium bond of the dimer by a strong Lewis base donor ligand such as pyridine. There is also ongoing interest in completing a Fischer-Tropsch catalytic cycle using OepRhH as the active catalyst.

References

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