

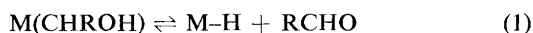
Formation of α -Hydroxyalkyl Complexes from the Reaction of Rhodium Octaethylporphyrin Hydride with Aldehydes

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Rhodium octaethylporphyrin hydride reacts reversibly with aldehydes to form metallo α -hydroxyalkyl complexes.

Recent interest in metallo α -hydroxyalkyl species has been stimulated by their proposed intermediacy in the formation of organic molecules from reactions of CO with H₂.¹ Metallo α -hydroxyalkyl complexes are unusual because they are generally thermodynamically unstable with respect to dissociation into metal hydride and aldehyde units [reaction (1)].²



We report that rhodium octaethylporphyrin hydride, Rh(OEP)(H), reacts reversibly with aldehydes (RCHO; R = H, Me, Et, or Ph) to form a series of α -hydroxyalkyl species



[reaction (2)]. To our knowledge, Rh(OEP)(H) is the first metal hydride reported for which the reverse of reaction (1) is in general thermodynamically favourable ($\Delta G^\circ < 0$) regardless of the choice of organic aldehyde.

In a typical experiment, Rh(OEP)(H) (1.0 mg) was treated with a ten-fold molar excess of acetaldehyde in the presence of H₂ (200 torr) in a sealed n.m.r. tube using [D₈]toluene as solvent. Formation of the α -hydroxyalkyl complex Rh(OEP)-(CHMeOH) (1) was followed by appearance in the ¹H n.m.r. spectrum of the metal-bound α -hydroxyalkyl resonances

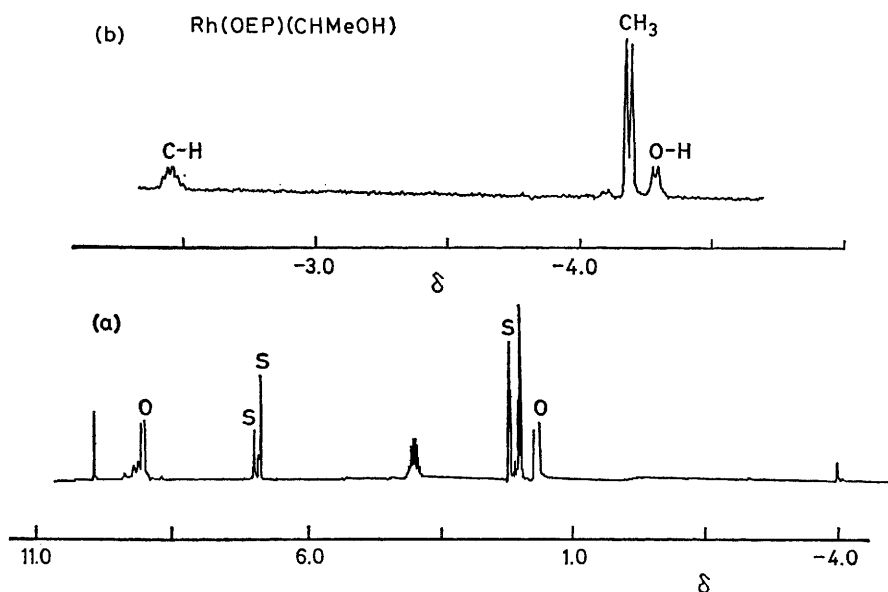
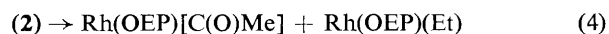
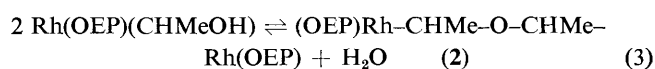


Figure 1. (a) ¹H N.m.r. spectrum of (1) in [D₈]toluene in the presence of excess of MeCHO. Porphyrin resonances: δ 10.26 (CH), 4.08 (CH₂), and 2.01 (CH₃); -CHMeOH ligand: δ -2.45 (CH), -4.19 (Me), and -4.29 (OH); $J(\text{CH}-\text{CH}_3)$ 4.75 Hz, $J(^{103}\text{Rh}-\text{CH})$ 3.5 Hz, $J(\text{CH}-\text{OH})$ 4.75 Hz; S = toluene solvent peaks, O = MeCHO peak. (b) Expansion of the spectrum of the CHMeOH ligand.

which are shifted upfield from Me_3Si by the large ring-current effects of the metallo-porphyrin (Figure 1). The spectrum indicated a quantitative yield of (1) after 6 h. Double-resonance experiments were used in assigning the spectrum. Addition of D_2O to the sample resulted in disappearance of the resonance at $\delta -4.29$, consistent with assignment to the O-H proton. Yields of (1) were reduced in the absence of excess of H_2 gas because of the alternative reaction of $\text{Rh}(\text{OEP})(\text{H})$ to produce $[\text{Rh}(\text{OEP})]_2$ and H_2 . $\text{Rh}(\text{OEP})(\text{CHMeOH})$ was isolated by slow evaporation of toluene or benzene solutions containing excess of MeCHO , $\nu_{\text{OH}} 3550 \text{ cm}^{-1}$. Analogous reactions of $\text{Rh}(\text{OEP})(\text{H})$ with HCHO , EtCHO , and PhCHO also produced the corresponding α -hydroxyalkyl species in benzene solution.

Compound (1) reacted slowly in benzene in the manner reported for other metallo α -hydroxyalkyls by forming a symmetrical ether^{3,4} which subsequently underwent hydride-transfer disproportionation to produce metallo acyl and alkyl complexes⁴ [reactions (3) and (4)]. $\text{Rh}(\text{OEP})[\text{C}(\text{O})\text{Me}]$ and



$\text{Rh}(\text{OEP})(\text{Et})$ were identified by comparison with authentic samples prepared by published procedures.^{5,6} The symmetrical ether (2) was identified by ^1H n.m.r. spectroscopy and found to occur as equal amounts of two diastereoisomers (*erythro* and *threo*). This reactivity of metallo α -hydroxyalkyls removes oxygen in the form of H_2O from the organometallic species and provides a possible route for obtaining non-oxygen-containing organic molecules from reactions of CO and H_2 .

Metallo-complexes containing the α -hydroxyalkyl ligand are usually prepared by indirect approaches such as reactions of hydroxyalkyl radicals ($-\text{CHROH}$),⁷ hydrolysis of metalloethers ($\text{M}-\text{CH}_2\text{OR}$),³ and reactions of metal-co-ordinated formyl groups.⁸ In these cases, it is uncertain whether the resulting α -hydroxyalkyl complex is the thermodynamic or kinetic product in reaction (1). The direct reaction of aldehydes with a metal hydride ensures that the resulting α -hydroxyalkyl complex is the thermodynamic product. Vaughn and Gladysz have recently demonstrated this direct approach for the first time by the reaction of $\text{Mn}(\text{CO})_5\text{H}$ with an aldehyde elegantly designed to contain a phosphorus donor group that would provide extra stabilization of the α -hydroxyalkyl complex through ring formation with the metal.⁴ The first example of a stable α -hydroxyalkyl complex, $(\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2[\text{C}(\text{CF}_3)_2\text{OH}]$,⁹ was isolated from the reaction of $[(\eta^5-\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2]^-$ with $(\text{CF}_3)_2\text{CO}$ and subsequent acidification, and this is probably similar to the direct metal hydride route. The unusual stability of this complex is ascribed to the presence of highly electron-withdrawing (CF_3) groups on the

α -hydroxyalkyl ligand. $\text{Rh}(\text{OEP})(\text{H})$ is at present the only metal hydride reported to react generally with aldehydes to produce α -hydroxyalkyl complexes. An approximate bond dissociation energy (B.D.E.) analysis of reaction (1) indicates that formation of a $\text{M}(\text{CHROH})$ complex will be exothermic when the $\text{M}-\text{H}$ B.D.E. is no more than *ca.* 86 kJ mol^{-1} larger than the $\text{M}-\text{C}$ B.D.E. and that ΔG° for the reverse of reaction (1) will be negative when the $\text{M}-\text{H}$ B.D.E. is no more than *ca.* 56 kJ mol^{-1} larger than the $\text{M}-\text{C}$ B.D.E. The general thermodynamic stability for $\text{Rh}(\text{OEP})(\text{CHROH})$ complexes must result from unusually strong $\text{Rh}-\text{C}$ bonding, which is supported by the short $\text{Rh}-\text{C}$ bond distances in related complexes, $\text{Rh}(\text{OEP})(\text{Me})$ ($\text{Rh}-\text{C}$, 2.03 \AA)¹⁰ and $\text{Rh}(\text{OEP})(\text{CHO})$ ($\text{Rh}-\text{C}$, 1.89 \AA).¹¹ Available data for approximate $\text{M}-\text{H}$ and $\text{M}-\text{C}$ B.D.E.s¹² suggest that α -hydroxyalkyl complexes could be common for 2nd and 3rd transition series metals but should remain rare for metals of the 1st transition series.

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