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LETTER

# A model study of the mechanism of the homogeneous catalytic hydroformylation of formaldehyde

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## Abstract

The anionic mechanism for the Rh-catalyzed hydroformylation of formaldehyde was supported by the synthesis of a key model rhodium acyl intermediate which, upon hydrogenolysis, gave the model product and regenerated the catalyst.

The homogeneous catalytic hydroformylation of formaldehyde is an important reaction in the field of syngas chemistry [1–7].

$$H_2CO + H_2 + CO \xrightarrow{\text{cat.}} HOCH_2CHO \qquad (1)$$

The glycoaldehyde product can be used to make large volume chemicals such as ethylene glycol or high-valued products such as serine. In our previous study of the rhodium phosphine catalyst system we found that small amounts of an organic base such as triethylamine significantly increased the rate of the hydroformylation of formaldehyde [1]. To explain this and other relevant observations we proposed a mechanism involving an anionic catalyst which reacts with formaldehyde via nucleophilic attack [8] (Fig. 1).

The existence of anionic Rh complexes under the reaction conditions was confirmed by an *in situ* high pressured IR study [1] and an X-ray crystallographic study [9]. Since the rate limiting step in the catalytic reaction is the binding of formaldehyde to the catalyst, the subsequent intermediates in the catalytic cycle cannot be detected and studied. For the purpose of a better understanding of the reaction mechanism of this reaction, it is of interest to synthesize model complexes to mimic the key intermediates and study their reactions. In this paper we wish to report the results of this attempt.

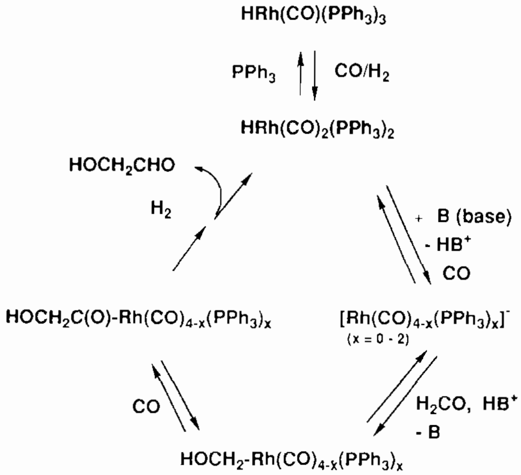


Fig. 1. A proposed mechanism for the base-promoted, Rh-catalyzed hydroformylation of formaldehyde.

The first complex in the catalytic cycle immediately after the rate-limiting step is $HOCH_2$–$Rh(CO)_2(PPh_3)_2$. However, this complex is expected to be unstable owing to a facile $\beta$-hydride abstraction.

$$HOCH_2\text{–}Rh(CO)_2(PPh_3)_2 \longrightarrow HRh(CO)_2(PPh_3)_2 + H_2CO \qquad (2)$$

To overcome this problem and to synthesize a model complex that is stable enough to be characterized, we decided to replace the $HOCH_2$ group with a $CH_3OCH_2$ group which mimics the former functionality and yet does not have the problem of $\beta$-hydride abstraction. Our strategy was to prepare the anionic complex from $RhCl(CO)(PPh_3)_2$ and then allow the anionic species to react with $CH_3OCH_2Cl$.

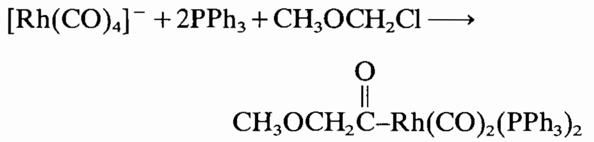
When $RhCl(CO)(PPh_3)_2$ was reduced with sodium amalgam in tetrahydrofuran under atmospheric pressure of CO, $[Rh(CO)_4]^-$ was produced as the dominant species along with a small amount of $[Rh(CO)_3(PPh_3)]^-$ [8].

$$RhCl(CO)(PPh_3)_2 \xrightarrow[\text{THF}]{\text{Na–Hg, CO atm}} [Rh(CO)_4]^- + 2PPh_3 \qquad (3)$$

$$(+\text{trace } [Rh(CO)_3(PPh_3)]^-)$$

When one equivalent of $CH_3OCH_2Cl$ was added to the product mixture from eqn. (3), we found that instead of $CH_3OCH_2Rh(CO)_2(PPh_3)_2$, $CH_3OCH_2C(O)$–

$Rh(CO)_2(PPh_3)_2$ was produced immediately as the exclusive product.

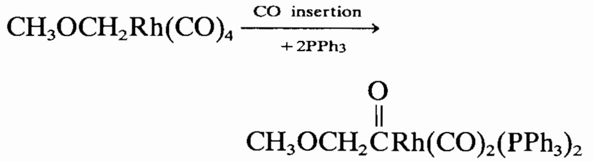


$$[Rh(CO)_4]^- + 2PPh_3 + CH_3OCH_2Cl \longrightarrow CH_3OCH_2\overset{\overset{O}{\|}}{C}\text{–}Rh(CO)_2(PPh_3)_2 \quad (4)$$

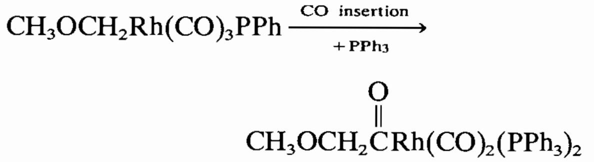
$(CO = 1986, 1941, 1663\ cm^{-1})$

(The assignment of this rhodium acyl dicarbonyl bisphosphine species is consistent with the corresponding iridium complex which has similar carbonyl stretching frequencies and has been unambiguously characterized by X-ray crystallography [10].)

The mechanism for the formation of $CH_3OCH_2C(O)\text{–}Rh(CO)_2(PPh_3)_2$ can be proposed as follows. When $CH_3OCH_2Cl$ was added to a solution of the anionic Rh species, both $[Rh(CO)_4]^-$ and $[Rh(CO)_3(PPh_3)]^-$ reacted with the activated alkyl halide via nucleophilic displacement to generate $CH_3OCH_2\text{–}Rh(CO)_4$ and $CH_3OCH_2\text{–}Rh(CO)_3(PPh_3)$, respectively. In contrast to the anionic Rh species which were more stable with the electron-withdrawing ligands such as CO [8], the neutral species thus formed preferred stabilizing donor ligands such as triphenylphosphine. Therefore, a rapid CO insertion and triphenylphosphine association generated the rhodium acyl dicarbonyl bis(phosphine) complex.



$$CH_3OCH_2Rh(CO)_4 \xrightarrow[+2PPh_3]{\text{CO insertion}} CH_3OCH_2\overset{\overset{O}{\|}}{C}Rh(CO)_2(PPh_3)_2 \quad (5)$$



$$CH_3OCH_2Rh(CO)_3PPh \xrightarrow[+PPh_3]{\text{CO insertion}} CH_3OCH_2\overset{\overset{O}{\|}}{C}Rh(CO)_2(PPh_3)_2 \quad (6)$$

The complex $CH_3OCH_2C(O)\text{–}Rh(CO)_2(PPh_3)_2$ was also prepared by reacting $CH_3OCH_2C(O)Cl$ with the solution of the anionic rhodium species.

$$\begin{tikzcd} CH_3OCH_2C(O)Cl + [Rh(CO)_4]^- \arrow[r] & {} \\ & CH_3OCH_2C(O)\text{–}Rh(CO)_4 \arrow[d, shift left, "2PPh_3"] \\ & CH_3OCH_2(O)\text{–}Rh(CO)_2(PPh_3)_2 \arrow[u, shift left] \end{tikzcd} \quad (7)$$

$$\begin{tikzcd} CH_3OCH_2C(O)Cl + [Rh(CO)_3(PPh_3)]^- \arrow[r] & {} \\ & CH_3OCH_2C(O)\text{–}Rh(CO)_3(PPh_3) \arrow[d, shift left, "PPh_3"] \\ & CH_3OCH_2C(O)\text{–}Rh(CO)_2(PPh_3)_2 \arrow[u, shift left] \end{tikzcd} \quad (8)$$

The IR spectrum of the product thus obtained was identical to that recorded for the product in reactions (5) and (6).

When a THF solution of $CH_3OCH_2C(O)\text{–}Rh(CO)_2(PPh_3)_2$ was stirred under $H_2/CO$, $CH_3OCH_2CHO$ and $HRh(CO)_2(PPh_3)_2$ were generated. This reaction completed the modeling for the catalytic hydroformylation of formaldehyde. This study clearly supports the proposed anionic mechanism for the Rh-catalyzed hydroformylation of formaldehyde.

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