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# A mechanistic study of rhodium tri(*o*-t-butylphenyl)phosphite complexes as hydroformylation catalysts

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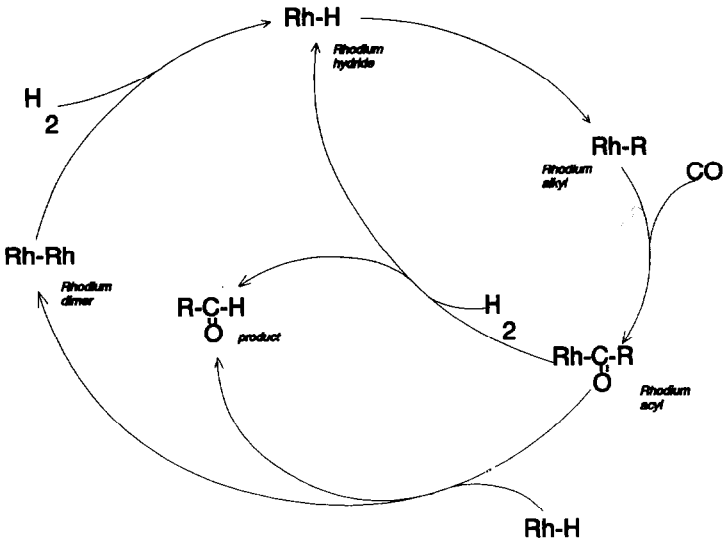
**Abstract**

A mechanistic study of the hydroformylation cycle with a rhodium tri(*o*-t-butylphenyl)phosphite complex as catalyst is presented. Spectroscopic experiments prove that under hydroformylation conditions this complex is coordinated by only one phosphite. The complex has a high activity in the hydroformylation of otherwise unreactive alkenes. The catalyst also gives a very high rate of isomerization. Isotope studies indicate that the aldehyde-forming step proceeds via a direct reaction of the rhodium acyl complex with dihydrogen and not via a bimolecular reaction of a rhodium hydride and a rhodium acyl complex.

## Introduction

Previously we have reported [1] on the activity and selectivity of various rhodium tris(hydrocarbyl) phosphite complexes as hydroformylation catalysts. Certain phosphites were shown to give highly active catalysts for otherwise unreactive alkenes. The most active catalysts were formed when either phosphites with high $\pi$ acidity (high $\chi$-value [2]) or very bulky groups (high $\theta$-value) were used. It was suggested that both types of ligands give rise to complexes with low phosphite coordination numbers, either for electronic or steric reasons, and ready formation of unsaturated species. The low selectivity for, e.g., 1-alkenes was ascribed to high rates of isomerization. The reversible metal–alkyl reaction is much faster for these catalysts than for $Rh_4(CO)_{12}$ [3]. Since their introduction [1] "bulky" phosphites have found widespread application [4]. We have now studied the complex formed from rhodium hydrido carbonyl and tri(*o*-t-butylphenyl) phosphite by *in situ* high pressure NMR and IR techniques. Cyclooctene was chosen as the substrate




Scheme 1

because it remains unchanged upon isomerization and yields only one hydroformylation product.

The hydrogenation step of rhodium acyl complexes in the hydroformylation cycle (Scheme 1) has for some time been the subject of controversy [5]. As indicated in Scheme 1, formation of the aldehyde from the acyl complex can occur in two ways: (1) via reaction with rhodium hydride and concomitant formation of a metal dimer, and (2) via reaction with dihydrogen with or without the intermediacy of an acyl dihydride complex. While most steps of the Heck–Breslow [6] mechanism have been well documented by model reactions or direct observation, it has been observed that "our knowledge of dihydrogen activation in hydroformylation is still very unsatisfactory, and further research is necessary to clarify this point" [7]. Stoichiometric reactions for cobalt and model complexes with molybdenum are consistent with the dimeric pathway [8,9]. For the cobalt catalyst evidence has been presented for both mechanisms [6,10–12], with the dihydrogen mechanism favored more recently. The reaction with dihydrogen can proceed by two mechanisms: (a) hydrogenolysis of the acyl–metal bond ($\sigma$-bond metathesis), and (b) oxidative addition of dihydrogen followed by reductive elimination of the aldehyde product. Ruthenium acyl complexes undergo a direct reaction with dihydrogen to form aldehydes via a mechanism involving hydrogenolysis [13]. For the iridium analogue of a rhodium hydroformylation catalyst the oxidative addition of dihydrogen has been experimentally verified and the kinetics of the reductive elimination have been studied [14]. On the other hand, a recent theoretical study lends support to the feasibility of a hydrogenolysis pathway with the intermediacy of a cobalt $\eta^2$-$H_2$ complex [15]. For an active rhodium catalyst no proof for either mechanism, via dihydrogen or rhodium hydride, has as yet been provided, although most authors seem intuitively to prefer reaction of dihydrogen by an oxidative addition mechanism. The special properties of the "bulky" phosphite catalyst enabled us to

Table 1

Reaction conditions for high pressure measurements

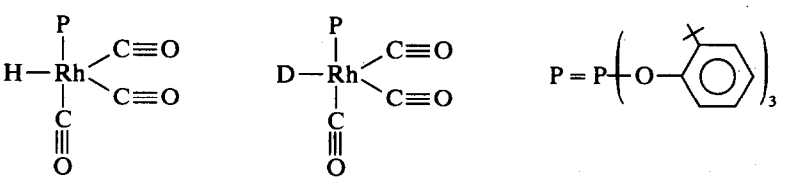
| Exp. no. | Cyclohexane (ml) | Cyclooctene (ml) | Temp. (°C) | $p(CO)$ (bar) | $p(H_2)$ (bar) | $p(D_2)$ (bar) |
|---|---|---|---|---|---|---|
| 1 | 20 | – | 60 | 10 | 10 | – |
| 2 | 20 | – | 60 | 10 | – | 10 |
| 3 | 18 | 2 | 60 | 10 | 10 | – |
| 4 | 18 | 2 | 60 | 10 | – | 10 |
| 5 | – | 20 | 60 | 10 | – | 10 |
| 6 | – | 20 | 40 | 15 | – | 5 |
| 7 | – | 20 | 40 | 15 | 2.5 | 2.5 |

[Rh(COD)acac] = 4 mmol/l, [phosphite]/[Rh(COD)acac] = 15.

distinguish between the two major pathways. Evidence has been obtained for the reaction between dihydrogen and the rhodium acyl intermediate in a truly catalytic system, and thus we can exclude a bimetallic reaction as the aldehyde-forming step for this catalyst.

## Results and discussion

The structure of the rhodium aryl phosphite complex under 20 bar $H_2/CO$ pressure was deduced from $^{31}P$ NMR, $^1H$ NMR, and IR spectroscopic data. The IR spectrum shows three peaks at 2093, 2045 and 2016 $cm^{-1}$, respectively (exp. 1, Table 1). When the $H_2/CO$ (1:1) gas mixture is replaced by $D_2/CO$ (1:1) the absorptions at 2093 and 2045 $cm^{-1}$ shift to 2086 and 2033 $cm^{-1}$, respectively (exp. 2, Table 1). Similar deuterium shifts were reported by Vaska [16] (for H/D–$Rh(CO)(PPh_3)_3$) and Wilkinson et al. [17] (for H/D–$Rh(CO)_2(PPh_3)_2$. The absorption at 2016 $cm^{-1}$ retains its position. None of the three absorption bands can be ascribed to a Rh–D vibration, so at least three carbonyl groups must be present. Monitoring of the spectra during the reactions proves that all three carbonyl bands belong to one complex, since the relative intensity of the bands do not change as the reaction proceeds. The $^1H$ NMR spectrum shows a hydride doublet ($\delta = -9.80$ ppm, $J$(H–Rh or P) = 2.7 Hz). It is not clear whether the hydride couples with the rhodium or the phosphorus nucleus. The $^{31}P$ NMR spectrum reveals a doublet at 132.1 ppm, $J$(P–Rh) = 234, which shifts to 132.2 ppm when $D_2/CO$ is used instead of $H_2$. Structure **1a** (under $H_2/CO$) and structure **1b** (under $D_2/CO$) are consistent with these data.



**(1a)** **(1b)**

By use of a high pressure infrared cell (Fig. 1) the progress of the hydroformylation reaction could be monitored. Under hydroformylation conditions, i.e. when

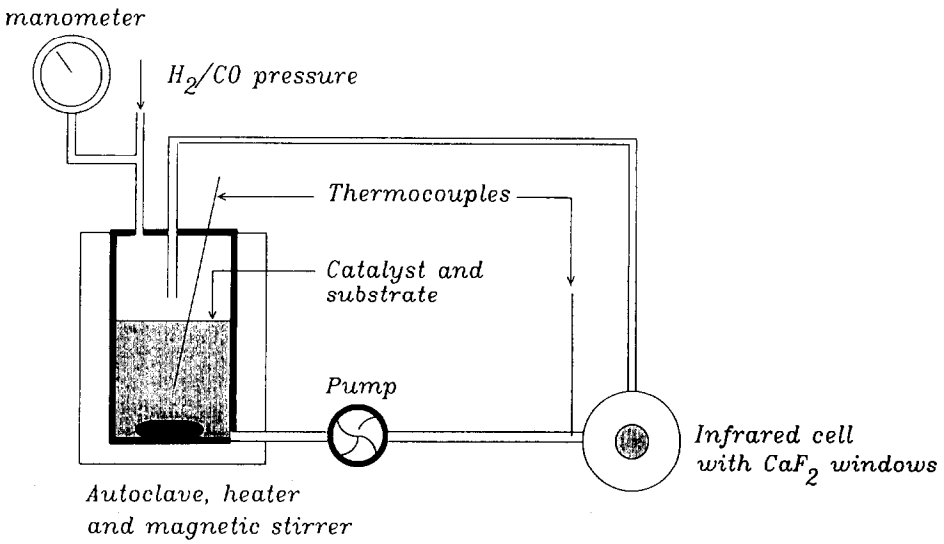
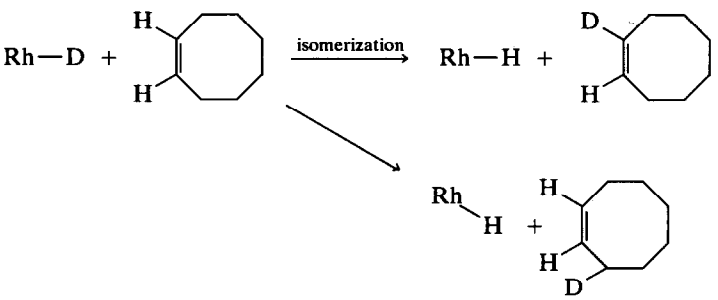



Fig. 1. Schematic drawing of high pressure infrared cell with autoclave and pump.

cyclooctene is added, the main rhodium species is still complex **1a** (exp. 3, Table 1).

In a reaction under $D_2/CO$ atmosphere only the deuteride complex **1b** is present. After addition of the alkene, the deuteride complex is rapidly transformed to the hydride complex **1a** (exp. 4, Table 1). Van Leeuwen and Roobeek found that under hydroformylation conditions a very fast isomerization reaction takes place, and this accounts for the rapid formation of rhodium hydride (eq. 1).



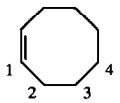

(1)

A reaction carried out under $D_2/CO$ yielded partially deuterated cyclooctene and cyclooctane carboxaldehyde after 23 percent conversion (exp. 5, Table 1). The products are analyzed by GLC-MS and $^{13}C$ NMR. From the degree of deuteration the extent of productive isomerization can be calculated. Productive isomerization takes place 8 times faster than the hydroformylation reaction. Once the deuteride in the rhodium complex is replaced by a hydride, further isomerizations are not productive. The distribution of deuterium atoms along all carbons in cyclooctene (Table 2) indicates that non-productive isomerization does, indeed, take place. Thus, the actual rate of isomerization is an order of magnitude higher than the rate of productive isomerization. The isomerization reaction is at least an order of magnitude faster than the hydroformylation.

Table 2

Distribution of deuterium in the cyclooctene ring determined by $^{13}C$ NMR spectroscopy

| | $C_1$ | $C_2$ | $C_3$ | $C_4$ |
|---|---|---|---|---|
| % deuteration | 19 | 9 | 8 | 7 |




The reaction mixture from experiment 4 was analyzed after 23% conversion. From GLC-MS data it was found that 1.8 mol/mol deuterium atoms were incorporated in cyclooctene and 1.4 mol/mol in cyclooctanecarboxaldehyde. This is in agreement with the NMR data.

During a hydroformylation reaction under $D_2/CO$ atmosphere only the rhodium hydride complex **1a** is present in the reaction mixture. The competing reaction that would transform Rh–H **1a** into **1b** turns out to be relatively slow (eq. 2):

$$Rh{-}H + D_2 \xrightarrow{\text{slow}} Rh{-}D + HD \qquad (2)$$

This allows the possibility of distinguishing between the two possible mechanisms of hydrogenation, I and II, simply by analyzing the hydroformylation product:

$$\text{I: } Rh{-}\underset{\underset{O}{\|}}{C}{-}R + Rh{-}H \xrightarrow{\text{dimerization}} Rh{-}Rh + H{-}\underset{\underset{O}{\|}}{C}{-}R \qquad (3)$$

$$\text{II: } Rh{-}\underset{\underset{O}{\|}}{C}{-}R + D_2 \xrightarrow[\text{or } \sigma\text{-bond metathesis}]{\text{oxidative addition}} Rh{-}D + D{-}\underset{\underset{O}{\|}}{C}{-}R \qquad (4)$$

In mechanism I a hydrogenated aldehydic carbon is formed, whilst reaction via mechanism II yields a deuterated aldehydic group.

The mechanism of hydrogenation in the catalytic cycle was studied by carrying out the above described hydroformylation reaction under $D_2/CO$ (exp. 6, Table 1), taking advantage of the fast isomerization reaction (eq. 1) which rapidly transforms complex **1b** into **1a**. To make the deuterium sink as large as possible the cyclooctene concentration was as high as possible, i.e. cyclooctene was used as solvent.

From in situ IR (D–CO–R, 1722 $cm^{-1}$, H–CO–R, 1733 $cm^{-1}$) and $^{13}C$ NMR analysis we found that 60 percent of the cyclooctane carboxaldehyde was deuterated at the aldehyde group after a reaction time of 20 min. Plots of the yields of the two products versus time showed that initially the percentage of deuterated aldehyde was higher (Fig. 2).

This result excludes mechanism I. During the reaction only the rhodium hydride complex **1a** is present. Thus the formation of 60 percent of the deuterated aldehyde cannot be accounted for in terms of mechanism I. The formation of 40 percent of hydrogenated aldehyde, however, does not exclude mechanism II. Analysis of the gas mixture revealed that substantial amounts of HD and $H_2$ were present; these can be formed in the solution by exchange reactions (eqs. 5 and 6)

$$Rh{-}H + D_2 \rightleftharpoons Rh{-}D + HD \quad \text{and further,} \qquad (5)$$

$$Rh{-}H + HD \rightleftharpoons Rh{-}D + H_2 \qquad (6)$$

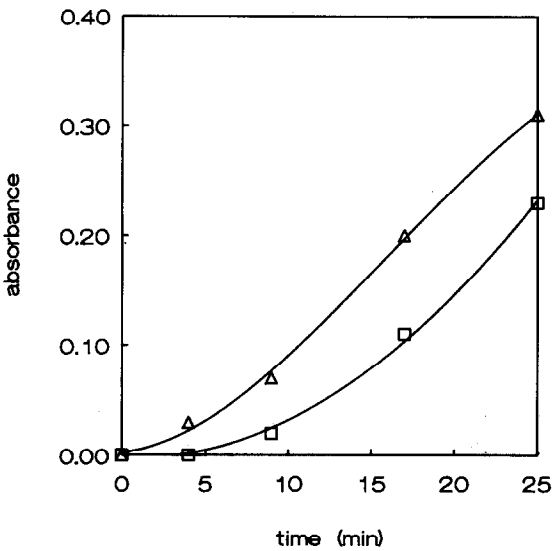



Fig. 2. Formation of deuterated and hydrogenated cyclooctane carboxaldehyde during a hydroformylation reaction under $D_2$/CO atmosphere (exp. 6, Table 1). The IR absorbance for D–CO–R (△, 1722 $cm^{-1}$) and H–CO–R (□, 1733 $cm^{-1}$) were measured during the hydroformylation reaction. The mixture was also analyzed by $^{13}C$ NMR spectroscopy after the reaction.

This will make possible the formation of aldehydes with a hydrogenated aldehyde group via mechanism II. In the high pressure infrared apparatus (Fig. 1) the liquid/gas interface is small, and gas movement from and to the solution will be slow. This means that though the absolute amount of HD and $H_2$ in the system is quite low, the concentrations in solution can be high. Furthermore, due to the isotope effect, $H_2$ and HD are more reactive than $D_2$. This is illustrated by a similar experiment as that described above but with equal amounts of $H_2$ and $D_2$ ($p = 20$ bar, $CO:H_2:D_2 = 15:2.5:2.5$) (exp. 7, Table 1). Only aldehydes with hydrogenated aldehyde groups are formed. The isotope effect favors the formation of hydrogenated aldehyde groups. Hence due to mass transfer limitations, formation of $H_2$ and HD as the reaction proceeds, and kinetic isotope effects, the yield of deuterated aldehyde is only 60 percent.

We conclude that the aldehyde formation does not occur via a dimerization reaction (mechanism I). The reaction involves direct attack of dihydrogen (mechanism II). We cannot distinguish between an oxidative addition or a $\sigma$-bond metathesis mechanism.

## Experimental

*Materials*

*(i) Tri(o-t-butylphenyl)phosphite.* $PCl_3$ (33.6 ml, 0.38 mol) was added dropwise to 200 ml of *o*-t-butylphenol (1.3 mol) at 50 °C. The mixture was then stirred overnight at 160 °C. The product was purified by vacuum distillation and recrystallized from n-hexane. Yield 70%, $^{31}P$ NMR, $CDCl_3$, $\delta$ 130.22 ppm; $^1H$ NMR, $CDCl_3$, $\delta$ 1.37 (s, 9H, t-butyl), 6.9–7.4 (m, 4H, aromatic).

*(ii) Rhodium (1,5-cyclooctadiene) 2,4-pentadionate (Rh(COD)acac).* This was prepared as described previously [18,19].

*(iii) Cyclooctene.* Cyclooctene was freed from hydroperoxides by percolation through aluminium oxide (neutral).

*Procedure for hydroformylations*

*(i) Apparatus*

For high pressure infrared measurements during hydroformylation reactions a 50 ml stainless steel autoclave equipped with a Morgan 55-DS plunger pump with timing relay TR-2 and a high pressure infrared cell with $CaF_2$ windows (cut off below 1000 $cm^{-1}$) was used (Fig. 1). The apparatus can be heated and is thermostated. The pressure was determined with a mechanical manometer. Spectra were collected on a Digilab FT 50 infrared spectrometer.

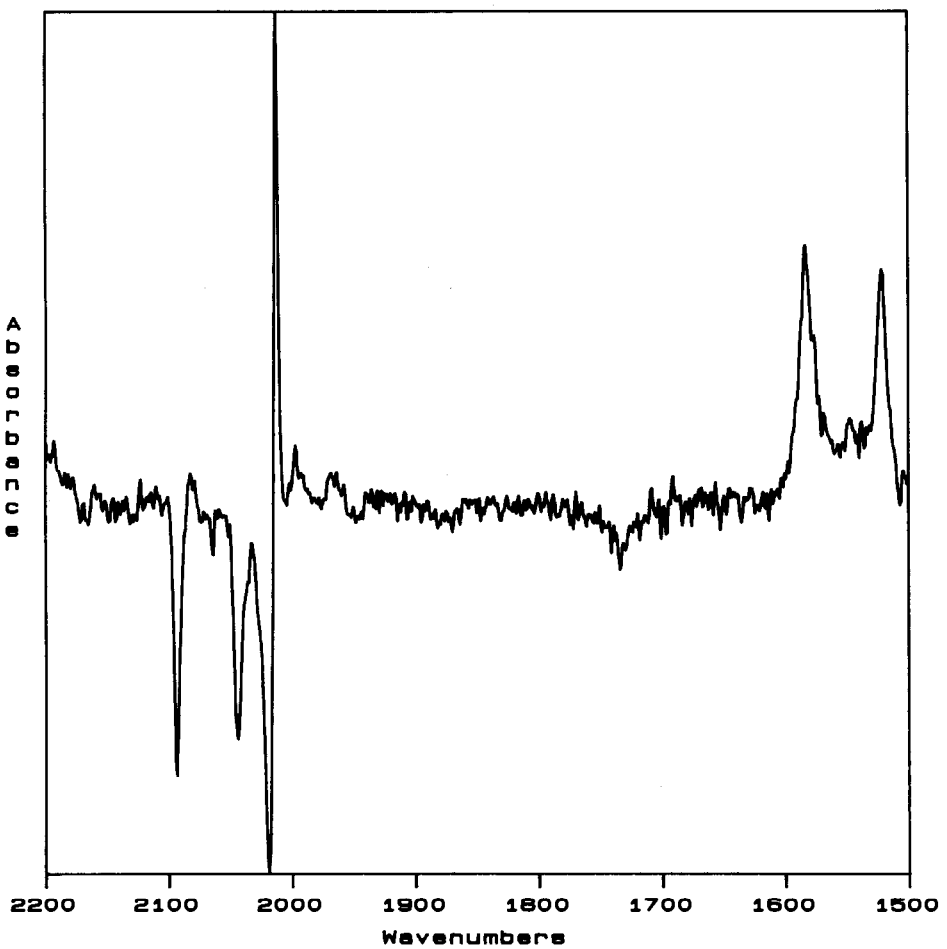



Fig. 3. Absorption spectrum of rhodium complex at 20 bar $CO/H_2$ (exp. 1, Table 1) after 15 minutes (peaks down). The initial spectrum (after 10 seconds) is used as reference (peaks up).

*(ii) Experimental*

The autoclave was charged with 20 ml of solvent, pressurized with the desired gas mixture, and heated. The IR spectrum was recorded. The apparatus was then depressurized, the phosphite added, the system pressurized and the IR spectrum recorded. The rhodium(COD)acac complex was added, and the IR spectrum was recorded every two minutes for one hour. By using the solvent and phosphite spectra as the references, a spectrum of only the rhodium complex(es) was obtained. Spectra collected at various times can be used to make plots of the absorption against time (Fig. 3).

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