

# Hydrogenation of Cyclohexene, Catalyzed by $\text{CoH}_3(\text{PPh}_3)_3$ ; Kinetics and Possible Mechanism

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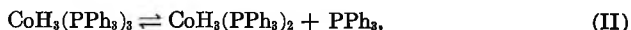
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At 40°C, the rate of hydrogenation of cyclohexene, catalyzed by  $\text{CoH}_3(\text{PPh}_3)_3$ , is described by Eq. (I).

$$-\frac{d[\text{S}]}{dt} = k'[\text{A}_0][\text{S}] \frac{[\text{H}_2]^{3/2}}{1 + (k''[\text{H}_2]^{3/2})} \cdot \frac{1}{(1 + k'''[\text{P}])^2} \quad (\text{I})$$

where  $[\text{A}_0]$ ,  $[\text{S}]$ ,  $[\text{H}_2]$  and  $[\text{P}]$  are the concentrations of catalyst, cyclohexene, hydrogen and triphenylphosphine, respectively, in solution. Equation (I) shows that triphenylphosphine is an inhibitor for the hydrogenation reaction.

Infrared measurements indicate that  $\text{PPh}_3$  does not retard the hydrogen-deuterium exchange between the catalyst and the gas phase. The conclusion is that  $\text{PPh}_3$  inhibits the addition of cyclohexene by displacing equilibrium (II),



to the left, and that both hydrogen and cyclohexene have separate sites on the catalytic active species of the compound.

## INTRODUCTION

The best investigated triphenylphosphine-transition metal hydrogenation catalyst to date is  $\text{RhCl}(\text{PPh}_3)_3$  (1, 2). Essential for this catalyst is the activation of one hydrogen molecule into two hydride ligands. The active species is considered to be the octahedral complex  $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2\text{So}$ , where So is a solvent molecule, which temporarily occupies a phosphine site. Another type of homogeneous hydrogenation catalyst is  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$  (3). The active species of the compound,  $\text{IrH}(\text{CO})(\text{PPh}_3)_2\text{So}$ , is in equilibrium with  $\text{IrH}_3(\text{CO})(\text{PPh}_3)_2$ , so that the rate of hydrogenation decreases with increasing hydrogen pressure and triphenylphosphine concentration. Consequently, on this catalyst, the activation of olefins occurs on a vacant phosphine site in competition with hydrogen and triphenylphosphine.

In this paper we report on the kinetics

of the hydrogenation of cyclohexene with  $\text{CoH}_3(\text{PPh}_3)_3$  as a homogeneous catalyst and we give a possible mechanism. It has already been reported that  $\text{CoH}_3(\text{PPh}_3)_3$  is a homogeneous catalyst for the hydrogenation of cyclohexene (4) and ethylene (5). However, these papers contain few kinetic data and do not deal with extensive kinetic studies of the hydrogenation of olefins with  $\text{CoH}_3(\text{PPh}_3)_3$ .

The structure of  $\text{CoH}_3(\text{PPh}_3)_3$  is most likely to be octahedral with two hydride ligands in *trans* positions (11). This structure is supported by that of the analogous complex  $\text{IrH}_3(\text{PPh}_3)_3$  (12), which exists in two isomeric configurations. The *cis*-form (one Co-H stretching vibration at 2075  $\text{cm}^{-1}$  in the ir spectrum) and the *trans*-form (two Co-H stretching modes at 2130 and 1750  $\text{cm}^{-1}$ ). It has already been shown that  $\text{CoH}_3(\text{PPh}_3)_3$  is able to exchange hydride ligands with other molecules (e.g.,  $\text{N}_2$ ) (6, 7). Therefore, the main question

of our investigation has been to enquire which ligand dissociates from the coordinatively saturated complex in order to create a site for cyclohexene activation. We may ask whether it is a hydride ligand, in view of the easy exchange with  $N_2$ , CO, etc., or a phosphine ligand, by analogy with the above-mentioned hydrogenation catalysts.

#### EXPERIMENTAL METHODS

**Materials.** Commercial benzene, ether and cyclohexene (Merck AG) were distilled off from a sodium-lead alloy, in order to remove nitrogen, oxygen, water and, in the case of cyclohexene, hydroquinone. The hydrogen was purified by diffusion through Pd. Deuterium (Noury-Baker chemicals), cobalt(III) acetylacetonate (Merck AG) and triphenylphosphine (Merck AG) were used without purification. Tri-*n*-butylphosphine (Merck AG) was degassed before use.

The catalyst was prepared under hydrogen pressure, by reducing 6 g of cobalt(III) acetylacetonate and 20 g of triphenylphosphine in 150 ml dry, oxygen-free diethyl ether, with 7 ml tri-*i*-butylaluminum. Before the addition of the tri-*i*-butylaluminum the mixture had to be cooled in an ice bath. The reaction solution was allowed to stand overnight, warming up slowly from 0°C to room temperature. Yellow crystals of  $CoH_3(PPh_3)_3$  were formed and filtered off. The collected crystals were washed with

cold diethyl ether, dried and dissolved in freshly distilled, dry and nitrogen-free benzene. This catalyst solution was stored in a buret under hydrogen pressure.

**Apparatus.** The hydrogenation reactions were carried out in a glass reactor. All connections to the reactor, which might contact the used chemicals or its vapors, were of the greaseless type. The storage burets for the catalyst solution, benzene and cyclohexene were equipped with Teflon membrane valves and connected to the reactor by means of greaseless ball and socket joints. All parts of the apparatus were carefully kept at constant temperature, within 0.1°C. The entire apparatus was leakproof. The regulating manometer, an oil-filled U-tube, was equipped with a photo electric sensor, which opened the bottom valve of the oil storage vessel as soon as the pressure in the reactor system fell below the reference value, so that the reaction was carried out under constant pressure. The reference pressure of the oil manometer was adjusted by bringing the reference vessel on the desired pressure. This pressure could be read on the mercury manometer. A scheme of the hydrogenation apparatus is given in Fig. 1.

The ir measurements were carried out in a similar apparatus to the kinetic experiments. A loop containing a pump and an ir cell was placed on the reactor, such that

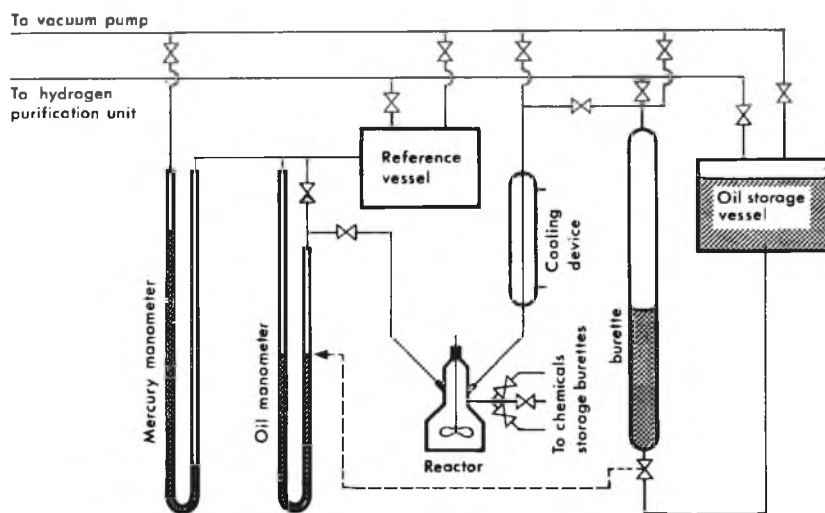


FIG. 1. Hydrogenation apparatus.

the reactor contents were pumped through the cell continuously. So, at any desired moment, a spectrum of the reaction mixture could be taken. All parts of the pump which might contact the reaction liquid were constructed from Teflon and all necessary metal parts in the ir cell were made of stainless steel, in order to avoid corrosion by the reaction liquid.

**Experimental procedure.** The desired amount of catalyst solution (10 ml) was introduced into the reactor from a storage buret through a stainless steel connection tube (i.d.  $\frac{1}{8}$  in.). This catalyst solution was diluted to the desired concentration with distilled benzene which had been stored under hydrogen. The mixture was allowed to warm up in the reactor during 15 min under stirring. Finally, the cyclohexene was added, and that was considered to be the starting point of the hydrogenation reaction. The progress of the reaction could be read on the gas buret by following the hydrogen volume decreasing at constant pressure. The reproducibility of the kinetic measurements was better than  $\pm 5\%$ .

### RESULTS

The effect of the variables (catalyst concentration, cyclohexene concentration, hydrogen pressure and triphenylphosphine concentration) on the rate of hydrogenation has been measured. In the following figures, the rate of hydrogenation has been plotted as a function of these variables. The rate of hydrogenation was obtained from the tangent in the plot of hydrogen uptake against time at zero time. We have made measurements at only one temperature ( $40 \pm 0.1^\circ\text{C}$ ).

Figure 2 shows that the rate of hydrogenation is proportional to the catalyst concentration. The correlation of the rate of hydrogenation with the cyclohexene concentration is also linear to a fair approximation, but extrapolation to zero cyclohexene concentration gives an almost negligible positive intercept with the rate axis (see Fig. 3).

The dependence of the rate on the hydrogen pressure shows a strong saturation

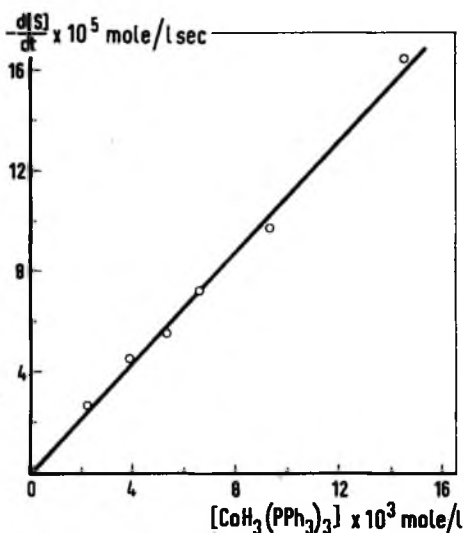


FIG. 2. Rate of hydrogenation as a function of the catalyst concentration.  $[S] = 1.65$  mole/liter;  $P_{\text{H}_2} = 896$  mm Hg;  $T = 40^\circ\text{C}$ ; volume of reaction mixture, 50 ml.

effect (Fig. 4). This dependence is described (see Fig. 5) by:

$$-\frac{d[S]}{dt} = \frac{P_{\text{H}_2}^{3/2}}{c_4 + c_5 P_{\text{H}_2}^{3/2}}$$

Added triphenylphosphine has a strong retardation effect on the hydrogenation. The dependence of the rate of hydrogenation on the added triphenylphosphine concentration is described by (Fig. 6):

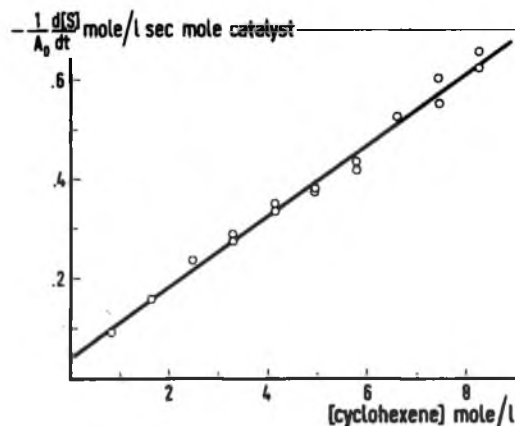


FIG. 3. Rate of hydrogenation as a function of the cyclohexene concentration.  $[A_0] = 8.3 \times 10^{-3}$  mole/liter;  $P_{\text{H}_2} = 896$  mm Hg;  $T = 40^\circ\text{C}$ ; volume of reaction mixture, 60 ml.

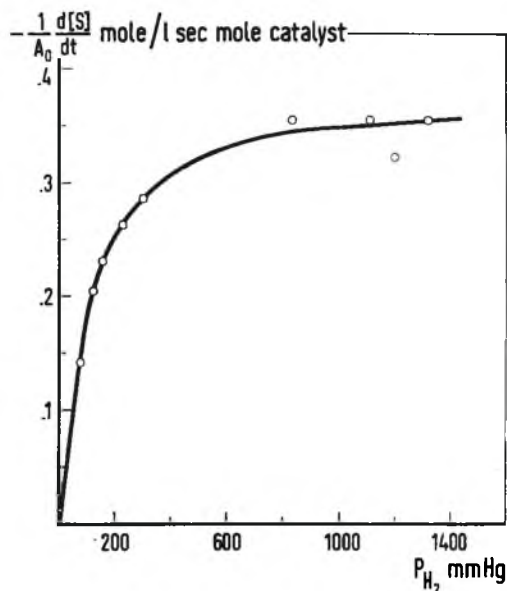


FIG. 4. Rate of hydrogenation as a function of the hydrogen pressure.  $[A_0] = 8.3 \times 10^{-3}$  mole/liter;  $[S] = 4.12$  mole/liter;  $T = 40^\circ\text{C}$ ; volume of reaction mixture, 60 ml.

$$-\frac{d[S]}{dt} = \frac{1}{c_6[P] + c_5}$$

Combining the results of the measured separate influences of the variables on the rate of hydrogenation, the following expression results:

$$-\frac{d[S]}{dt} = c_1 c_2 [A_0][S] \frac{[H_2]^{3/2}}{c_3 [H_2]^{3/2} + c_4} \cdot \frac{1}{c_6 [P] + c_5}$$

which may be rewritten as:

$$-\frac{1}{[A_0]} \frac{d[S]}{dt} = \frac{(c_1 c_2 / c_4 c_5) [S] [H_2]^{3/2}}{1 + (c_3 c_6 / c_4 c_5) [H_2]^{3/2} [P] + c_3 / c_4 [H_2]^{3/2} + c_6 / c_5 [P]} \quad (1)$$

The ir spectra have also been measured. The spectrum of  $\text{CoH}_3(\text{PPh}_3)_3$  shows two bands, due to Co-H stretching vibrations. In a solution of benzene, we measured the positions of these bands at 1930 and 1750  $\text{cm}^{-1}$ . The bending mode was located at 760  $\text{cm}^{-1}$ . After exposure to deuterium, all three bands disappeared and only two new bands appeared, at 1265 and 565  $\text{cm}^{-1}$ , respectively. The spectra were recorded under reaction conditions, by circulating the reaction liquid through the cell continuously.

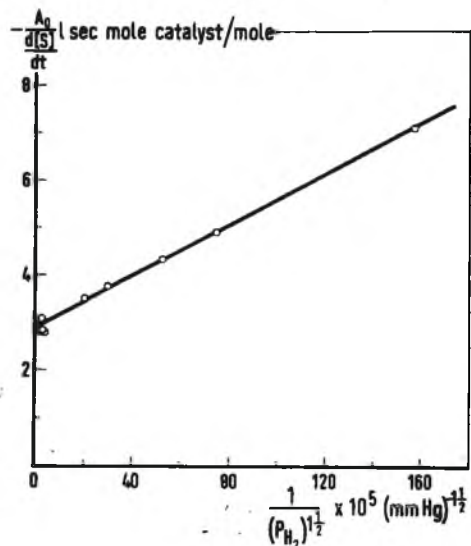


FIG. 5. Plot of the reciprocal rate of hydrogenation against  $(1/P_{H_2})^{3/2}$ .

The spectrum of the solvent was subtracted by placing a variable ir cell containing benzene in the reference beam of the spectrophotometer. The observed change from hydride to deuteride ligands was very rapid. The catalyst was deuterated within 3 min, so that a dynamic equilibrium must exist between the hydrides in the complex and the hydrogen in the gas phase. No retardation of this  $\text{H}_2$ - $\text{D}_2$  exchange was observed after addition of free triphenylphosphine or tri-*n*-butylphosphine, although these latter compounds are effective inhibitors for the catalytic hydrogenation of cyclohexene.

When using  $\text{PBU}_3$ , a simultaneous shift of both Co-H stretching modes was observed. With a sixfold excess of  $\text{PBU}_3$ , with respect to  $\text{CoH}_3(\text{PPh}_3)_3$ , the positions of these bands were 1920 and 1720  $\text{cm}^{-1}$ , which are the band positions of the Co-H stretching modes in  $\text{CoH}_3(\text{PBU}_3)_3$ .

#### DISCUSSION

In view of the observed inhibition of the hydrogenation by free triphenylphosphine, the first step in the mechanism is most

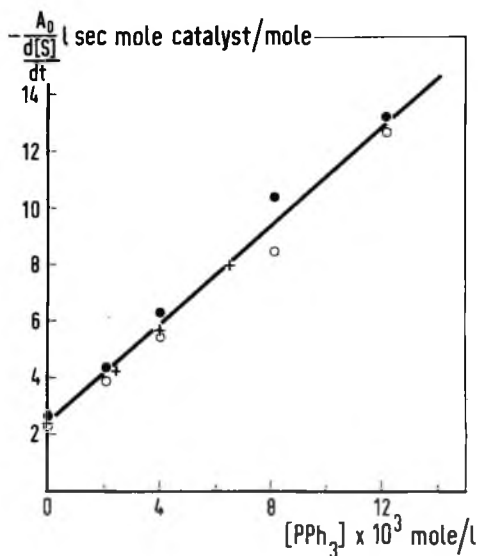
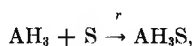
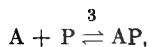
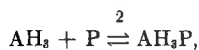
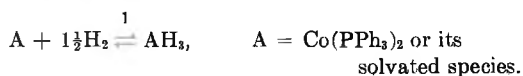


FIG. 6. Plot of the reciprocal rate of hydrogenation against the added triphenylphosphine concentration.  $[S] = 4.12$  mole/liter;  $P_{H_2} = 896$  mm Hg;  $T = 40^\circ\text{C}$ ;  $[A_0]$ , resp., (+)  $4.18 \times 10^{-3}$  mole/liter, (O)  $8.37 \times 10^{-3}$  mole/liter, (●)  $16.73 \times 10^{-3}$  mole/liter; volume of reaction mixture, 60 ml.

likely to be the dissociation of one  $\text{PPh}_3$  ligand. The kinetic data suggest that the addition of cyclohexene to the catalyst is the rate-limiting step under the experimental conditions of this investigation. Therefore, the following mechanism is proposed.



which gives expression (2):

$$-\frac{1}{[A_0]} \frac{d[S]}{dt} = \frac{k_r K_1 [H_2]^{3/2} [S]}{1 + K_1 [H_2]^{3/2} + K_1 K_2 [H_2]^{3/2} [P] + K_3 [P]} \quad (2)$$

Equation (2) is identical in form to the experimental expression (1). Comparison of Eqs. (1) and (2) gives the result that

$K_2$  and  $K_3$  are equal. This means that the addition of free  $\text{PPh}_3$  to the complex is independent of the presence of hydride ligands.

In view of the fact that all three hydride ligands are involved in the mechanism, the nature of A has to be either  $\text{Co}(\text{PPh}_3)_2$  (I), or  $\text{Co}(\text{PPh}_3)_3$  (II), or the solvated species of I or II.  $\text{Co}(\text{PPh}_3)_3$  is less favorable, because this would imply that cyclohexene is activated on a coordinatively saturated compound. So we conclude that A has to be  $\text{Co}(\text{PPh}_3)_2$ , or, more likely, its solvated species. Although the experimental Eq. (1) gives a fair description of the rate of hydrogenation as a function of the added  $\text{PPh}_3$  concentration, the phosphine contribution from the dissociated complex has been neglected. With small additions of  $\text{PPh}_3$  this effect will be significant. Allowance for the dissociated  $\text{PPh}_3$  can be made as follows:

A balance over the  $\text{PPh}_3$  concentrations gives:

$$[P] = [P_a] + [A_0] \frac{1 + K_1 [H_2]^{3/2}}{1 + K_1 [H_2]^{3/2} + (K_1 K_2 [H_2]^{3/2} + K_3) [P]}, \quad [P_a] = \text{added } \text{PPh}_3. \quad (3)$$

If we assume that also in this case  $K_2$  and  $K_3$  are not very different and therefore suppose them to be equal, Eq. (3) simplifies to:

$$[P] = \frac{1}{2}([P_a] - 1/K_2) + \frac{1}{2}\{([P_a] - 1/K_2)^2 + 4/K_2([P_a] + [A_0])\}^{1/2}. \quad (4)$$

Substitution of Eq. (4) into Eq. (2) gives a very good approximation of the rate of hydrogenation on the added amount of  $\text{PPh}_3$ . From the slope and intercept in Fig. 5 the numerical value for  $K_1$  has been calculated. The required solubilities of hydrogen in benzene were taken from the data reported by Cook, Hanson and Alder (8). The value for  $K_2$  has been calculated from Eqs. (2) and (4) with the aid of an iterative computer program. The plot of the rate of hydrogenation against the total triphenylphosphine concentration is given in Fig. 7.

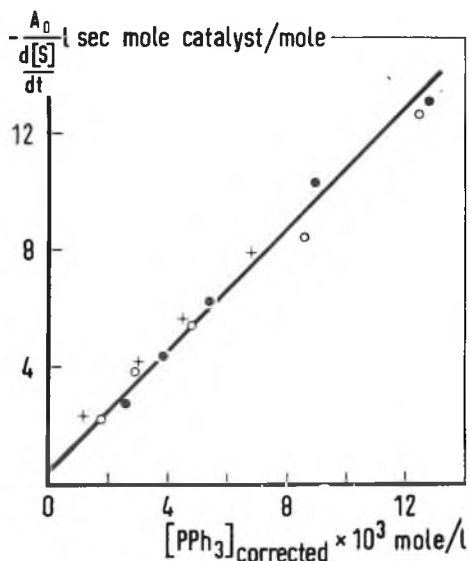
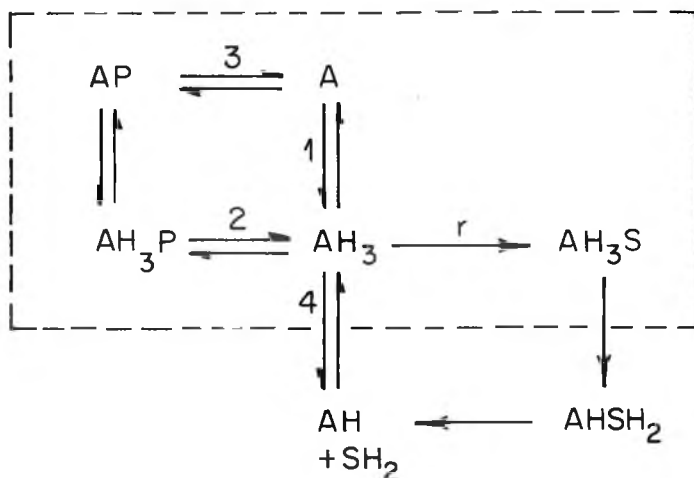


FIG. 7. As Fig. 6, but  $\text{PPh}_3$  concentration corrected for the contribution from the catalyst dissociation.

The resulting values for  $K_1$ ,  $K_2$ ,  $K_3$  and  $k_r$  are shown in Table 1.

Although Eq. (2) describes our kinetic results fairly well, the proposed mechanism is not fully complete, because it does not include a catalytic cycle. A better mechanism is:



which gives expression (5).

$$-\frac{1}{[A_0]} \frac{d[S]}{dt} = \frac{k_r K_1 [H_2]^{3/2} [S]}{(1 + K_1 [H_2])^{3/2} + (K_1/K_4) [H_2]^{1/2} + K_1 K_2 [H_2]^{3/2} [P] + K_3 [P]} \quad (5)$$

TABLE 1

Constant	Unit	Numerical value
$K_1$	(liters/mole) <sup>3/2</sup>	140
$K_2$	liters/mole	2260
$K_3$	liters/mole	2260
$k_r$	liters/mole sec	0.031

If  $K_4 \gg K_1 [H_2]^{1/2}$ , Eq. (5) simplifies to (2), which is the rate expression of the framed part of the mechanism.

Computer calculations show that this simplification is not fully allowed, because fits of  $-[A_0]/(d[S]/dt)$  vs  $(1/P_{H_2})^n$  give the best linear plot for  $n = 1.4$ . However, our experimental data to date are not sufficient for solving this problem in detail. In a later paper we shall give a more detailed mechanism, based on more kinetic data. Also the mechanism of insertion of the activated cyclohexene in the Co-H bond is not clear, because our experiments do not give information about it.

The ir spectra confirm the results obtained from the kinetic measurements. When adding free  $\text{PBu}_3$  to a solution of  $\text{CoH}_3(\text{PPh}_3)_3$ , a shift of both bands due to Co-H stretching modes was seen. This shift

was complete after addition of a sixfold ex-

cess of  $\text{PBu}_3$  with respect to  $\text{CoH}_3(\text{PPh}_3)_3$ . Then the band positions were 1920 and 1720  $\text{cm}^{-1}$ , which are the locations of the Co-H stretching modes in  $\text{CoH}_3(\text{PBu}_3)_3$  (9). A similar exchange of the phosphine ligands has been published by Yamamoto *et al.* (10) for the closely related complex  $\text{CoHN}_2(\text{PPh}_3)_3$ . The observed exchange supports the assumption that there is a dynamic equilibrium between the phosphine ligands and the free phosphine in the solution. On the other hand, the  $\text{H}_2$ - $\text{D}_2$  exchange was not inhibited by a tenfold excess of free phosphine. So the conclusion is that free phosphine inhibits the addition of cyclohexene to the catalyst, but not the activation of hydrogen to hydride. This then confirms the assumption that cyclohexene is activated on a phosphine site, which is probably temporarily occupied by a benzene molecule, while the sites occupied by hydride ligands cannot be occupied by cyclohexene or phosphine.

In the proposed mechanism the essential step is the dissociation of a complex molecule into the active form of the catalyst and one  $\text{PPh}_3$  ligand. This phenomenon has also been observed with other homogeneous hydrogenation catalysts [e.g.,  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ ]. A discrepancy is observed with the hydrogen pressure dependence of the rate of hydrogenation for  $\text{CoH}_3(\text{PPh}_3)_3$  and  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ . The participation of three hydride ligands, following from our kinetic data, has not been reported before.

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