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Substitution Reactions of (Acetonitrile)chlorobis(triphenylphosphine)rhodium(I) in Benzene

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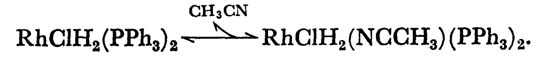
Synopsis. The kinetics of the substitution reactions of $\mathrm{RhCl(NCCH_3)(PPh_3)_2}$ in benzene was studied at 20 °C by the stopped-flow method under anaerobic conditions. The following mechanism was proposed:

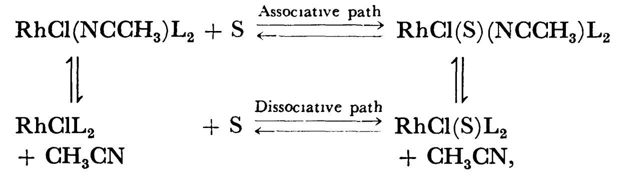


$$\mathrm{RhCl(C_2H_4)(PPh_3)_2} \overset{\mathrm{H_2}}{\rightleftarrows} \mathrm{RhClH_2(C_2H_4)(PPh_3)_2} \overset{\mathrm{C_2H_4}}{\rightleftarrows}$$
$$\mathrm{RhClH_2(PPh_3)_2} \overset{\mathrm{CH_3CN}}{\rightleftarrows} \mathrm{RhClH_2(NCCH_3)(PPh_3)_2}.$$

In a previous paper we reported a kinetic study of a series of substitution reactions of Wilkinson's complex, showing that the substitution reaction, $\mathrm{RhCl(C_2H_4)(PPh_3)_2+H_2+PPh_3 \rightleftarrows RhClH_2(PPh_3)_3+C_2H_4}$, proceeds faster than the dissociation of $\mathrm{C_2H_4}$ from $\mathrm{RhCl(C_2H_4)(PPh_3)_2}$ as well as that of $\mathrm{H_2}$ from $\mathrm{RhClH_2(PPh_3)_3}$.[1)] The results suggest an associative mechanism involving dihydrido-ethylene complex $\mathrm{RhClH_2(C_2H_4)(PPh_3)_2}$ as a reaction intermediate, though it cannot be detected spectrophotometrically. In the present study, the substitution reaction of (acetonitrile)chlorobis(triphenylphosphine)rhodium(I) was investigated in comparison with that of chlorotris(triphenylphosphine)rhodium(I). The reaction was carried out in benzene at 20 °C.

Equilibria. The equilibrium constants $K=[\mathrm{RhClH_2(NCCH_3)L_2}]/[\mathrm{RhCl(NCCH_3)L_2}][\mathrm{H_2}]$ and $K'=[\mathrm{RhCl(C_2H_4)L_2}][\mathrm{CH_3CN}]/[\mathrm{RhCl(NCCH_3)L_2}][\mathrm{C_2H_4}]$ were estimated from the measurements at $[\mathrm{CH_3CN}]=$ 1.0, 1.9, and 3.8 mol dm^{-3} to be 2.5×10^4 mol^{-1} dm^3 and 3.4×10^2, respectively. The equilibrium constant for the substitution $K''=[\mathrm{RhClH_2(NCCH_3)L_2}][\mathrm{C_2H_4}]/[\mathrm{RhCl(C_2H_4)L_2}][\mathrm{H_2}][\mathrm{CH_3CN}]\equiv K/K'$ was evaluated to be 74 mol^{-1} dm^3. The values of these equilibrium measurements indicate that hydrogen forms the final product $\mathrm{RhClH_2(NCCH_3)L_2}$, but $\mathrm{C_2H_4}$ cannot form the final product $\mathrm{RhCl(C_2H_4)(NCCH_3)L_2}$. In the case of $\mathrm{C_2H_4}$, substitution of $\mathrm{CH_3CN}$ in $\mathrm{RhCl(NCCH_3)L_2}$ occurred to form a square planar complex $\mathrm{RhCl(C_2H_4)L_2}$. The results may explain the low catalytic activity of Wilkinson's complex in acetonitrile solutions. The acetonitrile molecule competes with the olefin in the coordination to the central rhodium atom, as suggested by Schrock and Osborn.[3)]

Kinetics. *Addition Reactions*: The addition of molecular hydrogen to $\mathrm{RhCl(NCCH_3)L_2}$ and the substitution of the acetonitrile in $\mathrm{RhCl(NCCH_3)L_2}$ complex by ethylene was found to proceed through both associative and dissociative paths based on the kinetic measurements:



$$\begin{array}{ccc}
\mathrm{RhCl(NCCH_3)L_2} + \mathrm{S} & \xrightleftharpoons{\text{Associative path}} & \mathrm{RhCl(S)(NCCH_3)L_2} \\
\Updownarrow & & \Updownarrow \\
\mathrm{RhClL_2} \quad + \mathrm{S} & \xrightleftharpoons{\text{Dissociative path}} & \mathrm{RhCl(S)L_2} \\
+ \mathrm{CH_3CN} & & + \mathrm{CH_3CN},
\end{array}$$

where S denotes hydrogen or ethylene. Though no accurate values could be obtained, the rate constant of the associative addition of hydrogen to $\mathrm{RhCl(NCCH_3)L_2}$, k, was estimated to be *ca.* 1.4×10^2 mol^{-1} dm$^3\cdot$s^{-1} from the addition rate of hydrogen obtained by extrapolating $[\mathrm{CH_3CN}]$ to infinity. The value lies between that for $\mathrm{RhClL_3}$ (4.8 mol^{-1} dm^3 s^{-1} at 25 °C) and that for $\mathrm{RhClL_2}$ ($>7\times10^4$ mol^{-1} dm^3 s^{-1} at 25 °C).[4)] The rate constant of the dissociation of hydrogen from $\mathrm{RhClH_2(NCCH_3)L_2}$ is calculated to be 5.6×10^{-3} s^{-1} from k and K. The rate constant of the dissociation of $\mathrm{C_2H_4}$ from $\mathrm{RhCl(C_2H_4)L_2}$ was reported to be 0.4 s^{-1}.[1)] The results indicate that the dissociation rates of $\mathrm{H_2}$ from $\mathrm{RhClH_2(NCCH_3)L_2}$ and $\mathrm{C_2H_4}$ from $\mathrm{RhCl(C_2H_4)L_2}$ are much lower than the rate of the substitution, $\mathrm{RhCl(C_2H_4)L_2+H_2+CH_3CN \rightleftharpoons RhClH_2(NCCH_3)L_2+C_2H_4}$ (*vide infra*).

Substitution Reactions: Upon mixing a solution of $\mathrm{RhClH_2(NCCH_3)L_2}$ with a solution containing $\mathrm{C_2H_4}$, or a solution of $\mathrm{RhCl(C_2H_4)L_2}$ with a solution containing $\mathrm{H_2}$ and $\mathrm{CH_3CN}$, the spectrum of the solution rapidly turned to that of an equilibrium mixture of $\mathrm{RhClH_2(NCCH_3)L_2}$ and $\mathrm{RhCl(C_2H_4)L_2}$. Since no hydrogenation of the coordinated $\mathrm{C_2H_4}$ was observed during the course of measurement,[5)] the observed process should be expressed by

$$\mathrm{RhCl(C_2H_4)L_2} + \mathrm{H_2} + \mathrm{CH_3CN} \rightleftharpoons \mathrm{RhClH_2(NCCH_3)L_2} + \mathrm{C_2H_4}.$$

Figure 1 gives the dependence of k_{obsd} for the above reaction on $[\mathrm{CH_3CN}]$. The observed rate constant is larger than the dissociation rate constant of $\mathrm{C_2H_4}$ from $\mathrm{RhCl(C_2H_4)L_2}$ and that of $\mathrm{H_2}$ from $\mathrm{RhClH_2(NCCH_3)L_2}$, suggesting the existence of an associative intermediate. Increase in k_{obsd} with decreasing $[\mathrm{CH_3CN}]$ suggests that, in the substitution reaction, the dihydrido complex $\mathrm{RhClH_2(NCCH_3)L_2}$ is activated by the dissociation of $\mathrm{CH_3CN}$ molecule, as in the case of the dissociation of a $\mathrm{PPh_3}$ molecule from Rh-

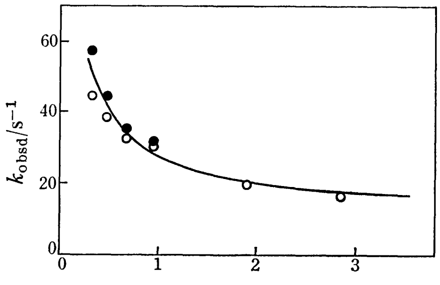


Fig. 1. The dependence of k_{obsd} on $[\mathrm{CH_3CN}]$ for the reactions, $\mathrm{RhCl(C_2H_4)L_2+H_2+CH_3CN}$ (○) and $\mathrm{RhClH_2(NCCH_3)L_2+C_2H_4}$ (●). $[\mathrm{Rh}]=1.0\times10^{-4}$, $[\mathrm{H_2}]=1.4\times10^{-3}$, and $[\mathrm{C_2H_4}]=7.5\times10^{-2}$ mol dm^{-3}. At 500 nm and 20 °C.

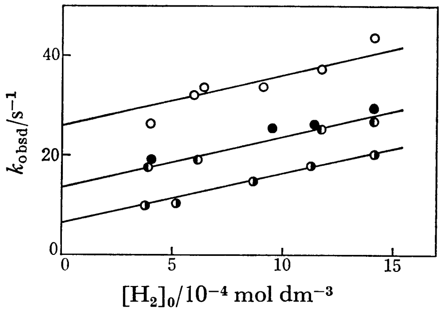


Fig. 2. The dependence of k_{obsd} on $[H_2]$, $[C_2H_4]$, and $[CH_3CN]$ for the reaction $RhCl(C_2H_4)L_2+H_2+CH_3CN$. The plot of k_{obsd} *vs.* $[H_2]$. $[Rh]=1.0\times10^{-4}$ mol dm^{-3}. $[C_2H_4]=7.5\times10^{-2}$ (○,◑,◑) or 3.8×10^{-2} (●) mol dm^{-3}. $[CH_3CN]=0.5$ (○,●), 1.0 (◐), or 1.9 (◑) mol dm^{-3}. At 500 nm and 20 °C.

ClH_2L_3.[1)] Figure 2 shows the dependence of k_{obsd} on $[H_2]$, $[C_2H_4]$, and $[CH_3CN]$ for the reaction of $RhCl(C_2H_4)L_2$ with H_2 and CH_3CN. From Fig. 2 the k_{obsd} is expressed as

$$k_{obsd} = k[H_2] + k'\frac{[C_2H_4]}{[CH_3CN]}. \qquad (1)$$

The following mechanism is proposed for the substitution reaction:

$$\begin{aligned} &RhCl(C_2H_4)L_2 + H_2 + CH_3CN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RhClH_2(C_2H_4)L_2 \\ &\quad + CH_3CN \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RhClH_2L_2 + C_2H_4 + CH_3CN \overset{K_3}{\rightleftharpoons} \\ &\quad RhClH_2(NCCH_3)L_2 + C_2H_4. \end{aligned}$$

The steady-state approximation to $RhClH_2(C_2H_4)L_2$ and $RhClH_2L_2$ leads to

$$k_{obsd} = \frac{k_1k_2}{k_{-1}+k_2}[H_2] + \frac{k_{-1}k_{-2}}{(k_{-1}+k_2)K_3}\cdot\frac{[C_2H_4]}{[CH_3CN]}. \qquad (2)$$

From Fig. 2, the values of $k_1k_2/(k_{-1}+k_2)$ and $k_{-1}k_{-2}/(k_{-1}+k_2)K_3$ are determined to be 9.6×10^3 mol^{-1} dm$^3\cdot$s^{-1} and 1.7×10^2 s^{-1}, respectively. The value of $k_1k_2/(k_{-1}+k_2)$ agrees with that obtained previously (7.8×10^3 mol^{-1} dm^3 s^{-1}).[1)]

The uni-molecular activation step $RhCl(C_2H_4)L_2 \rightarrow Rh^*Cl(C_2H_4)L_2$ as observed in the case of $RhClL_3$,[1)] was not observed in the present study. This would be interpreted as suppression of the reaction by acetonitrile. The proposed mechanism also suggests that the effect of acetonitrile on the catalytic activity of Wilkinson's complex is due to the formation of a catalytically inactive species $RhClH_2(NCCH_3)L_2$, the fraction of which is determined by the value of K''.

Experimental

A solution of $RhCl(NCCH_3)(PPh_3)_2$ was prepared by dissolving $RhCl(C_2H_4)(PPh_3)_2$ in oxygen-free benzene containing acetonitrile.[6)] The coordinated ethylene was easily replaced by acetonitrile, leaving a pure $RhCl(NCCH_3)(PPh_3)_2$ in the solution.

$RhCl(C_2H_4)(PPh_3)_2$ was prepared from $RhCl(PPh_3)_3$ and ethylene. Benzene and acetonitrile were distilled. Commercial hydrogen and ethylene were used without further purification. Concentration and purity were determined by gas chromatography with a molecular sieve 5A.

All the measurements were carried out at 20±0.2 °C in oxygen-free benzene. The equilibrium of the reaction was measured with a Hitachi EPS-3T spectrophotometer. The kinetic measurements were made using a Union Giken RA-1300 stopped-flow apparatus under anaerobic conditions.

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