$Ru(CO)_2Cl_4^{2-}$ was found to exhibit no catalytic activity for the hydration of acetylenes or for the exchange of D_2 with H_2O.

Formation of Ruthenium Carbonyl Complexes during the Hydration of Acetylenes. A common feature of the ruthenium(III) chloride catalyzed hydrations of acetylene and substituted acetylenes described earlier[4] was the tendency of the rate to decrease with time until the reaction ultimately ceased. For acetylene itself this decrease was relatively gradual, the rate falling to about half its initial value after 24 hr (at 50°); for methylacetylene and ethylacetylene the decline in catalytic activity was much more rapid.

The decrease in rate, in each case, was accompanied by a change in the color of the ruthenium complex, the initially orange-brown solution turning first green and finally yellow. In every case the spectrum of the final solution, which was catalytically inactive, corresponded to that of $Ru(CO)_2Cl_4^{2-}$, and evaporation of this solution yielded $(NH_4)_2Ru(CO)_2Cl_4$.[16] The spectrum of the intermediate green solution corresponded to that of $Ru(CO)(H_2O)Cl_4^{2-}$ which, as shown above, was itself a catalyst, although a less efficient one than ruthenium(III) chloride, for the acetylene hydration reaction.

Several experiments were performed with a view to elucidating the origin of the formation of these ruthenium carbonyl complexes during the hydration reactions. The principal products of hydration, acetaldehyde, acetone, and methyl ethyl ketone (from acetylene, methylacetylene, and ethylacetylene, respectively), were ruled out as precursors by showing that they did not react with either ruthenium(III) or ruthenium(II) chlorides under N_2 at 80° over a period of 48 hr. Furthermore, the rates of the ruthenium(III)-catalyzed hydration reactions were found to be unaffected by the addition of these hydration products in large excess. The hydration of ethylacetylene was found to be accompanied by the formation of ethane and methane, the former in an amount corresponding approximately to the amount of ruthenium(III) initially present and the latter in about one-tenth of this amount. No free CO was detected.

These experiments are insufficient to establish the mechanism of the formation of the ruthenium carbonyl complexes which accompanies the hydration of acetylenes and which is at present not understood. Decarbonylation of an intermediate or a by-product of the hydration or (less likely) of impurities present in the acetylenes all constitute possible mechanisms. In related studies it was found[17] that ruthenium(II) chloride in aqueous solution rapidly decarbonylates formic acid to form $Ru^{II}(CO)$. Some indication of formation of $Ru^{II}(CO)$ by decarbonylation of formaldehyde (but not of acetic acid or ethanol) also was obtained. A number of other examples of the formation of metal carbonyl complexes (including complexes of Ru^{II}, Os^{II}, Rh^{I}, and Ir^{I}) by decarbonylation of organic compounds have recently been reported and possible mechanisms of these reactions discussed.[18-22] These reactions are, at best, only partially understood and further work is needed to elucidate them.

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[16] The decrease, with time, of the catalytic activity of ruthenium(II) chloride for the hydrogen transfer reactions of allyl alcohol observed by J. K. Nicholson and B. L. Shaw, *Proc. Chem. Soc.*, 282 (1963), may similarly be due to the formation of catalytically inactive ruthenium carbonyl complexes.

[17] J. Halpern and A. L. W. Kemp, *J. Am. Chem. Soc.*, **88**, 5147 (1966).

[18] J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964).

[19] L. Vaska, *J. Am. Chem. Soc.*, **86**, 1943 (1964).

[20] A. Rusina and A. A. Vlcek, *Nature*, **206**, 295 (1965).

[21] M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129 (1966).

[22] R. H. Prince and K. A. Raspin, *ibid.*, 156 (1966).

The Decarbonylation of Formic Acid by Ruthenium(II) Chloride[1]

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Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637. *Received June 30, 1966*

Abstract: Ruthenium(II) chloride was found to react with formic acid in aqueous hydrochloric acid solution to form $Ru(CO)(H_2O)Cl_4^{2-}$ according to the reaction $RuCl_4^{2-} + HCOOH \longrightarrow Ru(CO)(H_2O)Cl_4^{2-}$. This paper describes a kinetic study of this reaction in which the dependence of the rate on the concentrations of ruthenium(II), formic acid, hydrogen ion, and chloride ion, as well as on the temperature, was examined. The results suggest that the reaction proceeds through a stepwise mechanism in which the initial step involves the dissociation of a chlororuthenate(II) complex.

We have previously reported[2] that the chlorocarbonylruthenate(II) complexes, $Ru(CO)(H_2O)Cl_4^{2-}$ and $Ru(CO)_2Cl_4^{2-}$ (hereafter designated $Ru^{II}(CO)$ and $Ru^{II}(CO)_2$, respectively), which can also be prepared by direct reaction between CO and ruthenium(II) chloride, are formed as by-products of the ruthenium(III) chloride catalyzed hydration of acetylenic compounds in aqueous HCl solution, presumably by decarbonylation of one of the organic intermediates or by-products of the hydration reaction. In an at-

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[1] This work was supported by grants from the National Science Foundation and from the Petroleum Research Fund, administered by the American Chemical Society.

[2] J. Halpern, B. R. James, and A. L. W. Kemp, *J. Am. Chem. Soc.*, **88**, 5142 (1966).

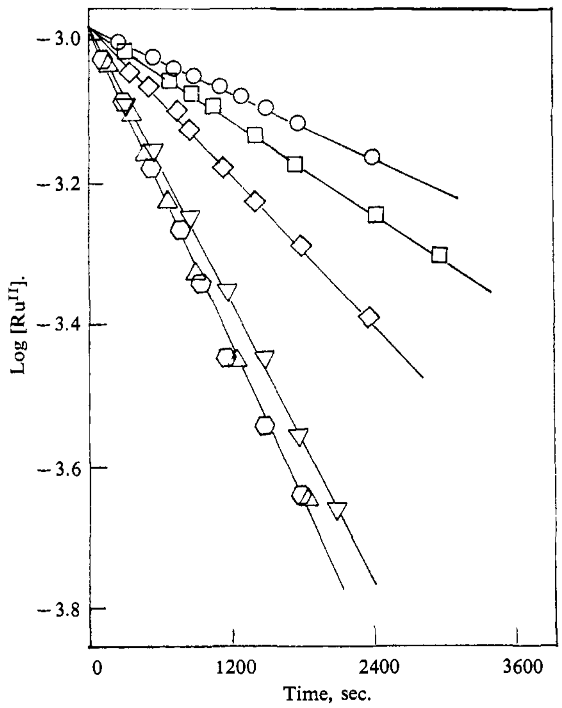

Figure 1. Typical rate plots for reaction 1 showing dependence of k' on the HCOOH concentration (60.1°, 8.3×10^{-4} *M* Ru^{II}, 2.9 *M* HCl). [HCOOH]: ○, 0.023 *M;* □, 0.040 *M;* ◇, 0.080 *M;* ▽, 0.28 *M;* ⌀, 0.82 *M;* △, 1.42 *M.*

tempt to gain some insight into the origin of these carbonyl complexes we attempted to decarbonylate various simple organic compounds with ruthenium(II) chloride. This resulted in the observation that in aqueous HCl solution ruthenium(II) chloride reacts readily with formic acid to form Ru^{II}(CO) according to reaction 1. The kinetics of this reaction were

$$\mathrm{RuCl_4^{2-} + HCOOH \longrightarrow Ru(CO)(H_2O)Cl_4^{2-}} \qquad (1)$$

examined in some detail and the results are reported in this paper.

The study of the decarbonylation of organic compounds by transition metal complexes which form stable carbonyl derivatives has attracted considerable interest in recent years and a number of other examples of such reactions have been reported although not fully elucidated. These include the decarbonylation of a variety of compounds including alcohols and aldehydes by complexes of Ru^{II}, Os^{II}, Rh^{I}, and Ir^{I}.[3-8]

Experimental Section

Ruthenium(II) chloride was generated by reduction of Johnson Matthey Specpure ammonium aquochlororuthenite in aqueous HCl solution with titanium(III) chloride as previously described.[9] The titanium(III) was always in at least tenfold excess in order to ensure complete reduction to ruthenium(II). Provided that this excess was maintained or exceeded, the spectrum of the ruthenium(II) chloride solution and the kinetic behavior were found to be independent of the titanium concentration.

The reaction (1) of ruthenium(II) chloride with formic acid was followed by measuring the decrease in the absorbance of the solution at 680 mμ where ruthenium(II) chloride absorbs strongly (ϵ 750, attributed to $RuCl_4^{2-}$ [10]) and $Ru(CO)(H_2O)Cl_4^{2-}$ is essentially transparent.[2] Since ruthenium(II) is readily oxidized by oxygen, the reactions were conducted under an atmosphere of pure nitrogen. Samples were withdrawn periodically by means of a hypodermic syringe and transferred through a serum cap to a spectrophotometer cell (also nitrogen filled) for spectral analysis. The spectral measurements were made with a Beckman DU spectrophotometer.

Reagent grade formic acid was redistilled before use. Hydrochloric acid and other chemicals were of reagent grade. Deaerated distilled water was used for the preparation of all solutions.

Results and Discussion

When a solution of ruthenium(II) chloride (≈0.02 *M*) in 3 *M* HCl containing an equimolar or excess concentration of formic acid was maintained under nitrogen for 1 hr at 70°, the color of the solution changed from deep blue to green. The absorption spectrum of the final solution corresponded to that of $Ru(CO)(H_2O)Cl_4^{2-}$ [2] at a concentration equal to that of the original concentration of ruthenium(II) chloride. Evaporation of the solution yielded a residual solid whose infrared spectrum corresponded to that of $(NH_4)_2Ru(CO)(H_2O)Cl_4$. No gas was evolved during the reaction implying the absence of any catalytic decomposition of formic acid (to CO or H_2). It is thus concluded that the stoichiometry of the reaction, when expressed in terms of $RuCl_4^{2-}$ (which is believed to be the principal chlororuthenate(II) complex present[10]) as the reactant, is represented by eq 1. Above 3 *M* Cl$^-$ the absorbance of ruthenium(II) chloride solutions decreased significantly with increasing Cl$^-$ concentration suggesting that higher chlororuthenate(II) complexes were accumulating and presumably also contributing to reaction with formic acid to form $Ru(CO)(H_2O)Cl_4^{2-}$.

Examination of the spectrum of the solution during the intermediate stages of the reaction revealed only contributions from ruthenium(II) chloride and $Ru(CO)(H_2O)Cl_4^{2-}$ with no indication of intermediate or by-product ruthenium species.

The kinetic experiments were generally conducted with the initial formic acid concentration in at least 20-fold excess over the concentration of ruthenium(II). Under these conditions it was found that the reaction always exhibited pseudo-first-order kinetic behavior in accord with the rate law

$$-d[\mathrm{Ru^{II}}]/dt = d[\mathrm{Ru^{II}(CO)}]/dt = k'[\mathrm{Ru^{II}}] \qquad (2)$$

Typical first-order rate plots are depicted in Figure 1.

Values of k', determined from the slopes of first-order rate plots such as those in Figure 1, are listed in Table I and are seen to be substantially independent of the initial Ru^{II} concentration. The kinetic dependence on the HCOOH concentration, also depicted in Figure 2, is seen to approximate first order at low HCOOH concentrations but to approach zero order (*i.e.*, a limiting rate) as the HCOOH concentration is increased. The form of this dependence (Figure 2), and the inverse dependence of k' on the Cl$^-$ concentration (at both low and high HCOOH concentration) are similar to the kinetic behavior previously observed[9] for the formation of a ruthenium(II)-ethylene complex, under similar conditions, by reaction 3. This suggests

$$\mathrm{Ru^{II} + C_2H_4 \longrightarrow Ru^{II}(C_2H_4)} \qquad (3)$$

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(3) R. H. Prince and K. A. Raspin, *Chem. Commun.*, 156 (1966).

(4) J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 3466 (1964).

(5) J. Chatt and B. L. Shaw, *Chem. Ind.* (London), 290 (1961).

(6) A. Rusina and A. A. Vlcek, *Nature*, **206**, 295 (1965).

(7) M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 130 (1966).

(8) L. Vaska, *J. Am. Chem. Soc.*, **86**, 1943 (1964).

(9) J. Halpern and B. R. James, *Can. J. Chem.*, **44**, 495 (1966).

(10) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

Table I. Kinetic Data for Reaction 1 at 60°

$[Ru^{II}] \times 10^3$, M	[HCOOH], M	[HCl], M	[LiCl], M	$k' \times 10^4$, sec^{-1}
0.28	0.57	2.9	0.0	9.52
0.44	0.57	2.9	0.0	8.95
0.83	0.57	2.9	0.0	9.18
1.7	0.57	2.9	0.0	8.90
2.1	0.57	2.9	0.0	8.85
0.83	0.040	2.9	0.0	2.58
1.7	0.040	2.9	0.0	2.56
0.83	0.023	2.9	0.0	1.74
0.83	0.067	2.9	0.0	3.75
0.83	0.080	2.9	0.0	4.16
0.83	0.17	2.9	0.0	6.04
0.83	0.28	2.9	0.0	7.67
0.83	0.41	2.9	0.0	8.00
0.83	0.85	2.9	0.0	8.75
0.83	1.10	2.9	0.0	8.80
0.83	1.40	2.9	0.0	8.84
0.83	0.57	2.9	0.6	8.11
0.83	0.57	2.9	1.0	7.26
0.83	0.57	2.9	1.4	7.61
0.83	0.57	2.9	1.8	5.93
0.83	0.57	2.9	2.6	4.30
0.83	0.57	2.9	3.1	3.34
0.83	0.57	1.6	0.0	10.8
0.83	0.57	1.6	0.7	11.1
0.83	0.57	1.6	1.6	9.9
0.83	0.067	3.0	0.4	2.82
0.83	0.067	3.0	1.3	2.23
0.83	0.067	3.0	2.3	1.25
0.83	0.067	3.0	3.0	0.63

a mechanism similar to that proposed for the latter reaction, namely a stepwise mechanism in which the first step involves the dissociation of a chlororuthenate(II) complex.

$$Ru^{II}Cl_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru^{II}Cl_{n-1} + Cl^- \tag{4}$$

$$Ru^{II}Cl_{n-1} + HCOOH \xrightarrow{k_2} Ru^{II}(CO) \tag{5}$$

Assuming the steady state approximation for the intermediate $Ru^{II}Cl_{n-1}$ this mechanism yields the rate law

$$\frac{d[Ru^{II}(CO)]}{dt} = \frac{k_1k_2[Ru^{II}Cl_n][HCOOH]}{k_{-1}[Cl^-] + k_2[HCOOH]} \tag{6}$$

Therefore, at constant $[Cl^-]$ and [HCOOH], and assuming $[Ru^{II}] \simeq [Ru^{II}Cl_n]$

$$k' = k_1k_2[HCOOH]/(k_{-1}[Cl^-] + k_2[HCOOH]) \tag{7}$$

whence

$$\frac{[HCOOH]}{k'} = \frac{[HCOOH]}{k_1} + \frac{k_{-1}[Cl^-]}{k_1k_2} \tag{8}$$

The linear plot of $[HCOOH]/k'$ *vs.* [HCOOH] in Figure 2 is in accord with this and yields the values $k_1 = 1.0 \times 10^{-3}$ sec^{-1} and $k_{-1}[Cl^-]/k_2 = 1 \times 10^2$ M (at 3 M HCl). The corresponding values, determined under approximately the same conditions, for reaction 3 are 3.4×10^{-3} sec^{-1} and 2.8×10^{-3} M, respectively.[9] While the two values of k_1 are of the same order, the discrepancy between them is larger than is readily explained by the small differences in conditions involved in the comparison. The difference of a factor of some 3×10^4 in the two values of k_{-1}/k_2, reflecting the relative reactivities of C_2H_4 and HCOOH toward the $Ru^{II}Cl_{n-1}$ intermediate, is in the expected direction.

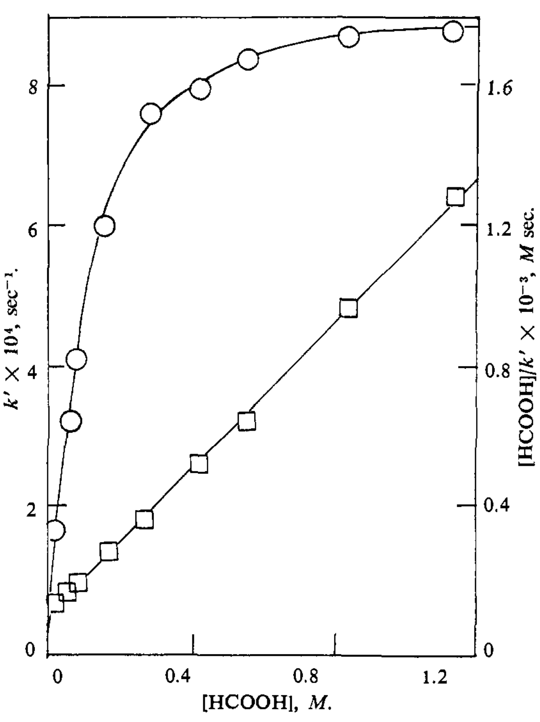

Figure 2. Dependence of k' on the concentration of HCOOH at 60.1°, 2.9 M HCl: ○, k'; □, $[HCOOH]/k'$.

The inverse dependence of k' on the Cl^- concentration, reflected in the data in Table I, is qualitatively in accord with the proposed mechanism but, unfortunately, just as in the case of reaction 3, two circumstances preclude the quantitative testing of the Cl^- dependence predicted by eq 8. These are (a) the significant variations in ionic strength which accompany the variation of the Cl^- concentration due to failure to find a suitably inert anion to substitute for Cl^-, (ClO_4^-, for example, is rapidly reduced by Ru^{II}) and (b) the effect of varying the Cl^- concentration on the distribution of ruthenium(II) chloride complexes. As previously noted, spectral measurements indicate a marked decrease ($\simeq$50%) in the absorbance (presumably due to $RuCl_4^{2-}$) at 680 mμ, when the Cl^- concentration is increased from 3 to 6 M implying the formation of higher chlororuthenate(II) complexes. Unfortunately, the complexing equilibria involved have not thus far been elucidated.

Measurements of the temperature dependence of k' over the range 50–65° (Table II), at a constant HCOOH concentration (0.57 M) sufficiently high that $k' \simeq k_1$, yielded the activation parameters $\Delta H^* = 23.5$ kcal/mole, $\Delta S^* = -5$ eu. These parameters are in good agreement with the corresponding values of 22.8 kcal/mole and -4 eu, respectively, previously determined for k_1 from measurements on reaction 3.[9]

Mention should be made of another mechanism which is also consistent with the observed kinetic dependence on the HCOOH concentration. This involves a preequilibrium step (9) in which a ruthenium(II)–formic acid complex is formed, followed by a rate-determining rearrangement (10) to product, *i.e.*

$$\mathrm{Ru^{II}Cl}_n + \mathrm{HCOOH} \overset{K}{\rightleftharpoons} \mathrm{Ru^{II}(HCOOH)Cl}_{n-1} + \mathrm{Cl}^- \qquad (9)$$

$$\mathrm{Ru^{II}(HCOOH)Cl}_{n-1} \xrightarrow{k_3} \mathrm{Ru^{II}(CO)} \qquad (10)$$

Under the prevailing conditions where [HCOOH] >> [$\mathrm{Ru^{II}}$] this yields a rate law

$$\frac{\mathrm{d[Ru^{II}(CO)]}}{\mathrm{d}t} = \frac{k_3K[\mathrm{Ru^{II}}]_0[\mathrm{HCOOH}]}{[\mathrm{Cl}^-] + K[\mathrm{HCOOH}]} \qquad (11)$$

(where $[\mathrm{Ru^{II}}]_0 = [\mathrm{Ru^{II}Cl}_n] + [\mathrm{Ru^{II}(HCOOH)Cl}_{n-1}]$), which is the same form as the rate law (6) derived for the earlier mechanism. However, since the spectrum of a ruthenium(II) chloride solution was found to be unaffected by addition of HCOOH up to concentrations (≥ 1 *M*) corresponding to the limiting zero-order region, this interpretation would require that the spectrum of $\mathrm{Ru^{II}(HCOOH)Cl}_{n-1}$ be identical with that of $\mathrm{Ru^{II}Cl}_n$, a condition which is considered unlikely. For this reason, as well as the parallel with the reaction between $\mathrm{Ru^{II}}$ and ethylene, the earlier interpretation involving the dissociation mechanism is strongly favored.

Table II. Temperature Dependence of *k′*

Temp, °C	*k′*,[a] sec^{-1}
50.5	3.06
54.5	4.74
57.5	6.75
60.1	9.18
62.6	11.7
65.2	15.7

[a] Determined for 8.3 × 10^{-4} *M* $\mathrm{Ru^{II}}$, 0.57 *M* HCOOH, 2.9 *M* HCl.

The detailed mechanism of the decarbonylation step is not revealed by these experiments. In related experiments it was found that under similar conditions to those used in the experiments with formic acid, $\mathrm{Ru^{II}(CO)}$ is also formed by reaction of ruthenium(II) chloride with formaldehyde, *i.e.*

$$\mathrm{Ru^{II}} + \mathrm{H_2CO} \longrightarrow \mathrm{Ru^{II}(CO)} + \mathrm{H_2} \qquad (12)$$

It is of interest that the first-order rate constant of this reaction measured at a high $\mathrm{H_2CO}$ concentration (0.68 *M*) was 1.0 × 10^{-3} sec^{-1} (at 60° in 3 *M* HCl), *i.e.*, the same as the limiting rate constant (k_1) of reaction 1 at high HCOOH concentration.

Under the same conditions it was found that ruthenium(II) chloride did not decarbonylate or otherwise react with acetic acid, acetone, acetaldehyde, ethanol, or ethylene glycol. Thus, decarbonylation, at least under acidic conditions, appears to occur readily only when breaking of C–H, but not C–C, bonds is involved. Other workers have reported the decarbonylation of alcohols and aldehydes by chloro(diethylphenylphosphine)ruthenium(II) complexes in the presence of base, to yield $\mathrm{Ru(CO)Cl_2(PEt_2Ph)_3}$ along with alkanes and alkenes, respectively.[3,4] The decarbonylation of various organic compounds including dimethylformamide, aldehydes, and acyl chlorides by rhodium salts with formation of the stable rhodium(I) carbonyl complex, $\mathrm{Rh(CO)Cl(PPh_3)_2}$, has also been reported.[5-7] The detailed mechanisms of these and related decarbonylation reactions remain to be elucidated.

Homogeneous Catalysis of the Hydrogenation of Olefinic Compounds by Ruthenium(II) Chloride[1]

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Contribution from the Departments of Chemistry, University of Chicago, Chicago, Illinois 60637, and University of British Columbia, Vancouver, British Columbia, Canada. Received June 30, 1966

Abstract: The homogeneous catalytic hydrogenation of maleic and fumaric acids to succinic acid in aqueous solution, using ruthenium(II) chloride as catalyst, is described. The catalytic mechanism apparently involves formation of a ruthenium(II)–olefin complex which reacts homogeneously with hydrogen to form succinic acid. The rate law for the reaction in each case is thus $k[\mathrm{H_2}][\mathrm{Ru^{II}(olefin)}]$. The values of k at 80° in 3 *M* HCl and the corresponding activation parameters are: for maleic acid, $k = 2.3 \pm 0.1\ M^{-1}\ \mathrm{sec}^{-1}$, $\Delta H^* = 14$ kcal/mole, $\Delta S^* = -17$ eu; for fumaric acid, $k = 3.6 \pm 0.6\ M^{-1}\ \mathrm{sec}^{-1}$, $\Delta H^* = 17$ kcal/mole, $\Delta S^* = -8$ eu. Tracer studies using $\mathrm{D_2}$ and $\mathrm{D_2O}$ reveal that the hydrogen atoms which add to the double bond originate from the solvent rather than the hydrogen gas. The hydrogenation of fumaric acid in $\mathrm{D_2O}$ yields predominantly DL-2,3-dideuteriosuccinic acid indicating that the addition is stereospecifically *cis*. Ruthenium(II) complexes of nonactivated olefins containing isolated double bonds are not reduced by hydrogen but do catalyze the exchange of $\mathrm{D_2}$ with $\mathrm{H_2O}$. A mechanism which accommodates all these observations is proposed. Some equilibrium measurements on the complex formation between ruthenium(II) and olefins also are reported.

The study of the catalytic reactions of transition metal complexes, including homogeneous catalytic hydrogenation, has attracted extensive interest in recent years.[5] Numerous complexes have been found, among them complexes of ruthenium(II),[6] platinum(II),[7]

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(5) For a review see J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965).