trated under reduced pressure to about 3 ml. The yellow solid was isolated by filtration and vacuum dried for 12 hr. Then it was dissolved in 25 ml. of water and the solution was stirred for 0.5 hr. The solution was neutralized to pH 6 with 1 N sulfuric acid. Benzene (20 ml.) was added and the mixture was stirred for 15 min. The benzene layer was separated and evaporated to dryness under reduced pressure. Tropolone sublimed from the residue at 30° (0.1 μ).

Mass spectral analyses showed no increase in the deuterium content of tropolone over that of the natural abundance. The infrared spectrum run as a potassium chloride pellet (1 mg./300 mg. of KCl) on the Perkin-Elmer 21 infrared spectrophotometer showed no C–D absorption.

Acknowledgment. We are indebted to Mr. A. Biddle for the X-ray data.

Olefin Coordination Compounds of Rhodium. II. The Mechanism of Ethylene Dimerization

Richard Cramer

A four-step cyclic mechanism is proposed for the rhodium chloride catalyzed dimerization of ethylene to linear butenes: (a) protonation of a bis(ethylene)rhodium(I) complex to an ethylrhodium(III) compound; (b) the rate-determining rearrangement of this compound to a butylrhodium(III) complex; (c) collapse of the latter to butene and rhodium(I); and (d) coordination of ethylene to provide the initial bis(ethylene)rhodium(I) complex.

Introduction

Discovery of ferrocene and of Ziegler–Natta polymerization catalysts have aroused widespread interest in organometallic chemistry. Subsequent theoretical and synthetic developments have encouraged a prevalent opinion that it will be possible to detail the mechanisms of many syntheses that involve hydrocarbon, hydride, or carbonyl coordination compounds of transition metals as intermediates. This paper reports a study of such a reaction, namely, the rhodium chloride catalyzed dimerization of ethylene to linear butenes. Because of the tractability of the intermediates in polar media at easily accessible temperatures and pressures, it has been possible to isolate most of the steps that constitute a proposed mechanism. This mechanism includes and further elucidates some characteristic reactions of coordination chemistry: (1) the reversible oxidation of rhodium(I) by a protonic acid to give a rhodium(III) hydride; (2) an insertion of coordinated olefin between an alkyl group and the metal ion to which it is attached, a reaction which may be the chain-growth step of Ziegler polymerization; (3) the labilization of hydrogen in rhodium(III) alkyl and olefin complexes; and (4) the critical importance of appropriate auxiliary ligands to the catalytic effectiveness of rhodium.

The rhodium-catalyzed dimerization of ethylene has been described by Alderson, Jenner, and Lindsey.[1] It is run conveniently at 40°, in alcohol with 0.1 mole

% "rhodium trichloride trihydrate,"[2] based upon ethylene, and with ethylene supplied at one to several hundred atmospheres. Although a mixture of linear butenes is obtained, the initial product is probably 1-butene. There is very little higher hydrocarbon; the yield of butenes is greater than 99% based upon consumed ethylene.[3]

Discussion

The proposed reaction cycle for the synthesis of 1-butene is summarized in Figure 1. It is supported by a variety of interlocking physical and chemical evidence relating to the intermediates and to the individual reactions. A brief over-all description will be given followed by a detailed discussion of the individual steps.

A bis(ethylene) complex of monovalent rhodium (A) is rapidly converted by reaction with HCl into an ethylrhodium(III) compound (B). B rearranges by a slow, rate-determining chain-growth reaction, giving a n-butylrhodium(III) complex (D). D decomposes rapidly through loss of HCl to give a 1-butene complex of monovalent rhodium (E). Coordinated 1-butene and solvent in E are rapidly displaced by ethylene reforming the initial rhodium(I) complex A. At high ethylene pressures and in ethanol solutions above about 0.1 M in HCl, most of the rhodium in the reaction system is in the form of the ethylrhodium complex B waiting to go through the rate-determining insertion or chain-growth step (eq. 4, Figure 1), but at ethylene pressures near 1 atm., B dissociates extensively, rapidly, and reversibly to ethylene and the ethylrhodium(III) complex C.

The rates of the steps may be classified by noting the temperatures at which they can be studied. Reaction

(1) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, in press; T. Alderson, U. S. Patent 3,013,066 (1961).

(2) "Rhodium trichloride trihydrate" is a noncrystalline, water-soluble solid with approximate composition RhCl$_{3.3}$(H$_2$O)$_{2.3}$. Material used in this work was purchased from Engelhard Industries.

(3) Ethylene is also dimerized cleanly with a cobalt–aluminum catalyst (G. Hata, *Chem. Ind.* (London), 223 (1965)), but large amounts of ethylene are converted to higher olefins by a CH$_3$TiCl$_3$·CH$_3$AlCl$_2$ catalyst (H. Bestian, *et al.*, *Angew. Chem. Intern Ed. Engl.*, **2**, 32 (1963)).

$$\text{"Rh}^{III}\text{Cl}_3\cdot 3\text{H}_2\text{O"} \qquad\qquad \text{C}_2\text{H}_4 + [\text{C}_2\text{H}_5\text{Rh}^{III}\text{Cl}_3]^{2-}$$
$$\text{C}$$

$$\text{C}_2\text{H}_4 \downarrow (1a) \qquad\qquad\qquad +s\uparrow \qquad \downarrow \overset{-s}{(3)}$$

$$\text{L}_2\text{Rh}^{I}(\text{C}_2\text{H}_4)_2 \xrightarrow[\text{(1b)}]{\text{H}^+ + \text{Cl}^-} [\text{Cl}_2\text{Rh}^{I}(\text{C}_2\text{H}_4)_2]^- \xrightarrow[\text{(2)}]{+\text{H}^+ +\text{Cl}^-} [\text{C}_2\text{H}_5\text{Rh}^{III}\text{Cl}_3(\text{C}_2\text{H}_4)\text{s}]^-$$
$$\text{A} \qquad\qquad\qquad\qquad\qquad \text{B}$$

$$\text{C}_2\text{H}_4 \uparrow (6) \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \overset{(4)}{s}$$

$$[\text{Cl}_2\text{Rh}^{I}\text{s}(\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2)]^- \xrightarrow[\text{(5)}]{-\text{H}^+ - \text{Cl}^-} [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Rh}^{III}\text{Cl}_3\text{s}_2]^-$$
$$\text{E} \qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{D}$$

$$\text{L}_2 = \text{acetylacetonyl or } (\text{C}_2\text{H}_4)_2\text{Rh} \overset{\displaystyle Cl}{\underset{\displaystyle Cl}{\diamond}}$$
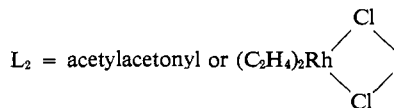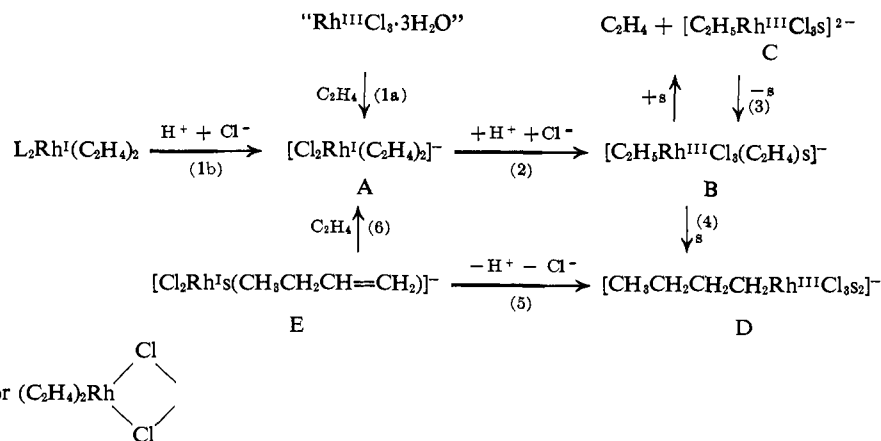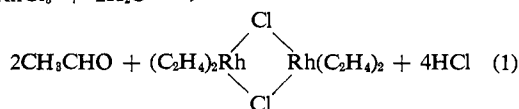
s = solvent

Figure 1. Mechanism for 1-butene synthesis.

2 occurs in alcohol at moderate speed at $-20°$ and is inconveniently slow at $-35°$. Reaction 3 has been examined in the range -15 to $-35°$. Reaction 4 is slow at $+10°$ and, for some experimental work, may be neglected at $-10°$. Reaction 5 has certainly been observed at $-25°$; there is no experimental evidence on its low temperature limit. Reaction 6 is probably very fast at $-50°$.

There is some uncertainty regarding the ligand "s" in the formulas of Figure 1 and in the discussion which follows. It will be assumed that compounds of rhodium(I) are four-coordinate and of rhodium(III), six-coordinate. "s" stands for solvent (usually ethanol), H_2O, or Cl^-, and enough are used to satisfy coordination-number bookkeeping.

All the rhodium complexes proposed as intermediates are anions. This is consistent with the fact that if ethylene is dimerized in a cyclohexane–water medium, rhodium is found only in the aqueous phase.[4]

Activation of "Rhodium Trichloride Trihydrate" (Eq. 1a and 1b, Figure 1). When ethylene is dimerized near atmospheric pressure with rhodium introduced as "rhodium trichloride trihydrate," there is an induction period of about 30 min. (Table IV). During this time ethylene is absorbed slowly and "RhCl$_3\cdot$3H$_2$O" is converted to an active catalyst. It has been reported[5] that ethylene and "RhCl$_3\cdot$3H$_2$O" give acetaldehyde and a sparingly soluble rhodium(I) complex, [(C$_2$H$_4$)$_2$RhCl]$_2$, in a reaction (eq. 1) resembling Smidt's[6] palladium chloride catalyzed synthesis of acetaldehyde from ethylene. Although [(C$_2$H$_4$)$_2$RhCl]$_2$ itself is not a catalyst, its solutions in alcoholic HCl dimerize ethylene without an induction period, so it is chemically closer to a catalyst species then "RhCl$_3\cdot$3H$_2$O."

$$6\text{C}_2\text{H}_4 + 2\text{RhCl}_3 + 2\text{H}_2\text{O} \longrightarrow$$
$$2\text{CH}_3\text{CHO} + (\text{C}_2\text{H}_4)_2\text{Rh}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{\diamond}}\text{Rh}(\text{C}_2\text{H}_4)_2 + 4\text{HCl} \quad (1)$$

Another compound of rhodium(I), bis(ethylene)rhodium acetylacetonate,[7] acacRh(C$_2$H$_4$)$_2$, is often a more convenient source of rhodium catalyst than [(C$_2$H$_4$)$_2$RhCl]$_2$ since it is more soluble. N.m.r. experiments show that acetylacetonyl is displaced instantly when HCl is added to acacRh(C$_2$H$_4$)$_2$ in ethanol, and the resulting solution catalyzes 1-butene synthesis immediately.

We have not succeeded in isolating a salt of the anion [Cl$_2$Rh(C$_2$H$_4$)$_2$]$^-$ (A, Figure 1). Spectrophotometric experiments, which are discussed later, point to its existence in dilute solution, but upon concentration in the presence of bulky cations these solutions yield either sparingly soluble [(C$_2$H$_4$)$_2$RhCl]$_2$ (eq. 2) or a trivalent rhodium compound and metallic rhodium by disproportionation.

$$2\text{M}[(\text{C}_2\text{H}_4)_2\text{RhCl}_2] \longrightarrow (\text{C}_2\text{H}_4)_2\text{Rh}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{\diamond}}\text{Rh}(\text{C}_2\text{H}_4)_2 + 2\text{MCl} \quad (2)$$

Oxidation of Rhodium and Formation of an Ethylrhodium Complex (Eq. 2, Figure 1). In Ziegler catalysis of ethylene polymerization, the transition metal catalyst is obtained by alkylation of, for example, a titanium halide with an aluminum alkyl.[8] In rhodium-catalyzed ethylene dimerization, the rhodium alkyl is formed by reaction of HCl with an ethylene complex of rhodium(I). Evidence supporting the existence of ethylrhodium complexes was found in n.m.r. experiments conducted below $-10°$. Reaction of HCl with [(C$_2$H$_4$)$_2$RhCl]$_2$ in CD$_3$OD gives a solution with an n.m.r. absorption characteristic of CH$_3$ in an ethyl group (Figure 2a). The absorption ascribed to CH$_2$ of this ethyl group appears to be obscured by absorption of coordinated ethylene. However, the solution of an analogous ethylrhodium compound obtained when π-C$_5$H$_5$Rh(C$_2$H$_4$)$_2$ in chloroform is treated with gaseous HCl at $-60°$ has n.m.r. absorptions clearly attributable to protons of π-C$_5$H$_5$, coordinated C$_2$H$_4$, and a C$_2$H$_5$ group (Figure 2b).

$$\pi\text{-C}_5\text{H}_5\text{Rh}^{I}(\text{C}_2\text{H}_4)_2 + \text{HCl} \longrightarrow \pi\text{-C}_5\text{H}_5\text{Rh}^{III}(\text{C}_2\text{H}_4)\text{Cl} \quad (3)$$
$$|$$
$$\text{C}_2\text{H}_5$$

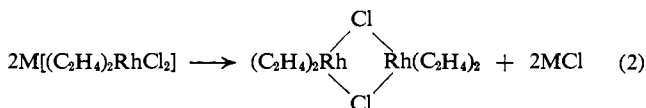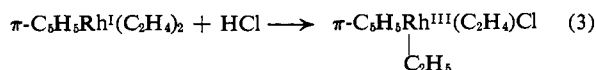Both solutions are stable for hours at $-20°$, but at $-10°$ new absorptions begin to appear in the n.m.r. spectra

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(4) It is possible to dimerize ethylene in chloroform solution by an apparently nonionic reaction. To do this π-C$_5$H$_5$Rh(C$_2$H$_4$)$_2$ is supplied as catalyst. A series of equations involving nonionic rhodium complexes may be written which parallel those of Figure 1 except that π-C$_5$H$_5$ takes the place of Cl$_2$ in formulas A and E and of Cl$_2$s in formulas B, C, and D. In ethanol reaction is not quite so fast with π-C$_5$H$_5$Rh-(C$_2$H$_4$)$_2$ as with an equivalent amount of acacRh(C$_2$H$_4$)$_2$.

(5) R. Cramer, *Inorg. Chem.*, 1, 722 (1962).

(6) J. Smidt, *et al.*, *Angew. Chem.*, 71, 176 (1959).

(7) R. Cramer, *J. Am. Chem. Soc.*, 86, 217 (1964).

(8) P. Cossee, *J. Catalysis*, 3, 80 (1964).
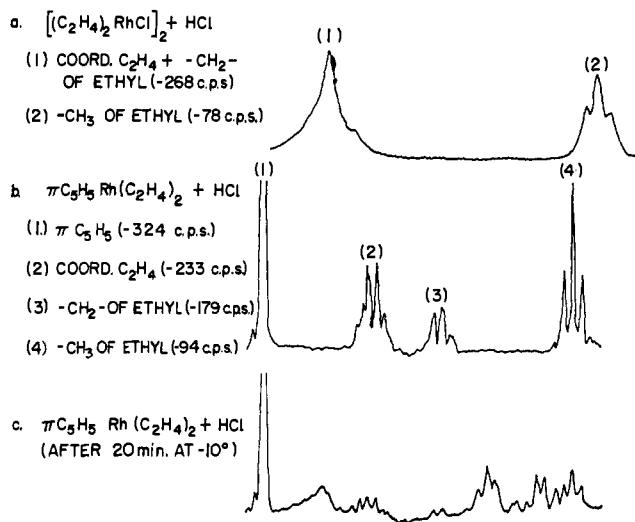
Figure 2. N.m.r. spectra of ethylrhodium compounds.

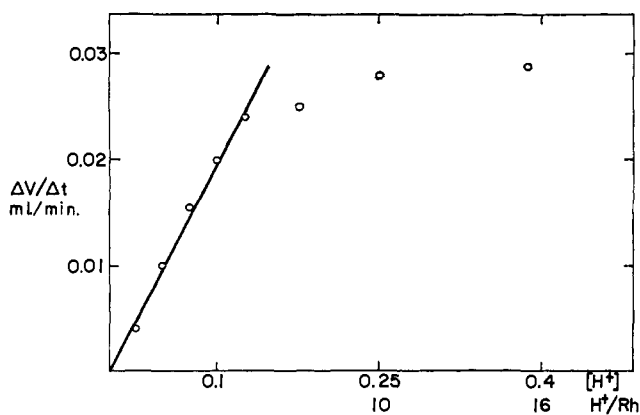a. $[(C_2H_4)_2RhCl]_2 + HCl$
  (1) COORD. $C_2H_4 + -CH_2-$
     OF ETHYL (-268 c.p.s)
  (2) $-CH_3$ OF ETHYL (-78 c.p.s.)

b. $\pi C_5H_5 Rh(C_2H_4)_2 + HCl$
  (1) πC_5H_5 (-324 c.p.s.)
  (2) COORD. C_2H_4 (-233 c.p.s)
  (3) $-CH_2-$OF ETHYL (-179 cps)
  (4) $-CH_3$ OF ETHYL (-94 c.p.s)

c. $\pi C_5H_5 Rh (C_2H_4)_2 + HCl$
  (AFTER 20 min. AT -10°)

Figure 4. Effect of [Rh] on ethylene dimerization.

Figure 3. Effect of [H⁺] on ethylene dimerization.
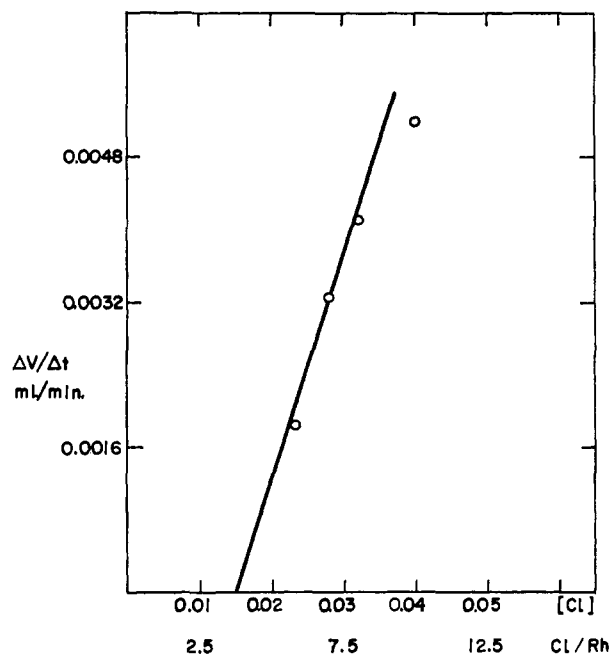
Figure 5. Effect of [Cl⁻] on ethylene dimerization.

and after about 20 min. these are strong blurred signals to which no definite assignment may be given (Figure 2c).

It is often possible to deduce the composition of the activated complex for a rate-determining reaction step from kinetic studies and if, as proposed, the rate-determining step is rearrangement of an unstable intermediate, then the intermediate should have the same composition as the activated complex. Accordingly, we examined the manner in which the rate of ethylene dimerization responds to changes in the concentration of the various species in the reaction system. These experiments and spectrophotometric studies suggest the formula $[C_2H_5Rh^{III}Cl_3(C_2H_4)s]^-$ for the product from HCl and either $[(C_2H_4)_2RhCl]_2$ or $acacRh(C_2H_4)_2$.

The rate of ethylene dimerization varies with the concentration of H⁺, Cl⁻, ethylene, and rhodium. When the rate is restricted by severely reducing the concentration of one of these reactants, there is a linear dependence of the rate on the concentration of that species. Extrapolation shows that as the concentration of H⁺ or rhodium is reduced, the rate does not approach zero until the concentration of the restricting species drops to zero (Figures 3 and 4). However, extrapolation of the plot of rate vs. [Cl⁻] indicates that ethylene does not dimerize if the Cl⁻/Rh ratio is below about 3 (Figure 5). These results imply that limited chloride

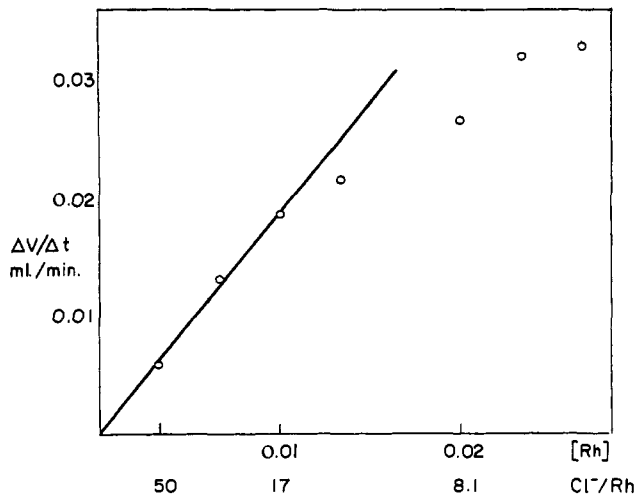ion coordinates strongly with rhodium when added to an acidified solution of $acacRh(C_2H_4)_2$, but the product is catalytically inactive. More chloride converts part of the rhodium to an active catalyst species.

Reaction of $acacRh(C_2H_4)_2$ with ethanolic HCl is accompanied by a color change from yellow to orange-red which can reasonably be attributed to the oxidation of rhodium(I) to rhodium(III) and the formation of a six-coordinate complex with chloride ligands.[9] Spectrophotometry confirms the conclusions concerning the chloride stoichiometry of catalyst activation that were reached on the basis of kinetic studies. The spectra of the solutions resulting when an equivalent of HCl gas is added (in increments of 0.2 equiv.) to a 0.005 M solution of $acacRh(C_2H_4)_2$ in ethanolic sulfuric acid have an isosbestic point at 421 mμ. Accordingly, the solution is believed to contain only two species over that range of Cl⁻/Rh ratios. One is $acacRh(C_2H_4)_2$ and the other

(9) C. K. Jørgensen, Acta Chem. Scand., 10, 500 (1956).

is believed to be $[(C_2H_4)_2RhCl]_2$ which precipitates when higher concentrations of $acacRh(C_2H_4)_2$ are employed (eq. 4).

$$2acacRh(C_2H_4)_2 + 2HCl \longrightarrow [(C_2H_4)_2RhCl]_2 + 2C_5H_8O_2 \quad (4)$$
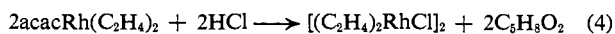
When more HCl is added incrementally, the isosbestic at 421 mμ is replaced by one at 463 mμ which persists as the Cl$^-$/Rh ratio increases from 1.07 to 4.3. Again, the solution appears to contain only two species. Since the absorbance of the solution at other wave lengths (e.g., 520 mμ) increases with added Cl$^-$ in a manner consistent with eq. 5, it is proposed the two species are $[(C_2H_4)_2RhCl]_2$ and $[(C_2H_4)_2RhCl_2]^-$. The consistency is demonstrated by the small variation in
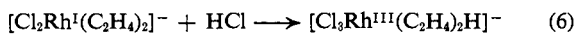
$$[(C_2H_4)_2RhCl]_2 + 2Cl^- \rightleftharpoons 2[(C_2H_4)_2RhCl_2]^- \quad (5)$$
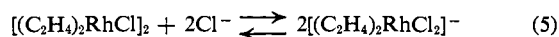
values for the equilibrium constant for eq. 5 calculated from the absorbance of solutions covering a 25-fold change in [Cl$^-$] (Table VI).

When more than 4.3 equiv. of HCl are added, the isosbestic at 463 mμ disappears and the absorbance of the solution increases at all wave lengths over the range 300 to 600 mμ. However, since the kinetic experiments showed that the rate of ethylene dimerization increases linearly with [Cl$^-$] above a Cl$^-$/Rh ratio of about 3, it appears that a trichloro complex is being formed in ethanol solution as the Cl$^-$/Rh ratio is increased from 4.3:1 to 50:1. Absorption in the longer wave lengths of the visible region is relatively weak during coordination of the first two chloride ions. A red color is not developed until the final stage when the third chloride coordinates and Rh(I) is oxidized by HCl to Rh(III).

The trichloro ion whose rearrangement leads to chain growth is formulated as $[C_2H_5RhCl_3(C_2H_4)s]^-$ because (a) its electronic spectrum and the composition of the complex left after dissociation of ethylene (see below) correspond to a compound of rhodium(III); (b) linear dependence of the rate of ethylene dimerization on rhodium concentration indicates a mononuclear complex[10]; (c) n.m.r. absorption shows coordinated ethylene and ethyl groups; (d) kinetics and spectrophotometry indicate each rhodium ion has three chloride ligands; (e) since rhodium(III) compounds are generally six-coordinate a solvent molecule is included.

Related experimental work[11] suggests that the addition of HCl to rh^I-(CH=CH$_2$)[12] to give rh^{III}-CH$_2$CH$_3$ (eq. 2, Figure 1) involves an unstable intermediate which might be a rhodium hydride via eq. 6 and 7. The

$$[Cl_2Rh^I(C_2H_4)_2]^- + HCl \longrightarrow [Cl_3Rh^{III}(C_2H_4)_2H]^- \quad (6)$$

$$[Cl_3Rh^{III}(C_2H_4)_2H]^- \xrightarrow{s} [C_2H_5Rh^{III}Cl_3(C_2H_4)s]^- \quad (7)$$

chemistry of other coordination compounds indicates that a hydride might be anticipated under these conditions. Formation of metal hydrides by protonation of complexes having π-bonded ligands appears to be a general reaction.[13] More specifically, Sacco and Ugo

have reported[14] the addition of HCl to $[Rh(Ph_2PCH_2$-$CH_2PPh_2)_2]Cl$, while Vaska and DiLuzio[15] have described the addition of HCl to $IrCl(CO)(Ph_3P)_2$; both reactions are analogs of the oxidation summarized in eq. 6. The formation of metal alkyls by addition of a metal hydride to an olefin is also an established reaction[16a,b] which has been proposed[16c] frequently as a step in transition metal catalyzed syntheses.[17]

Numerous fruitless attempts, including experiments at $-70°$, were made to detect an unstable rhodium hydride through its characteristic n.m.r. absorption.[18a,b] Consequently, a rhodium hydride, if it is an intermediate, may not be present in substantial concentration.

Formation of the ethylrhodium complex B (eq. 2, Figure 1) is reversible. At $-24°$ there is virtually no insertion reaction (eq. 4, Figure 1) and, if a solution of $acacRh(C_2H_4)_2$, C_2H_4, and DCl in CH_3OD is stirred at $-24°$ for 12 hr., the C_2H_4 is converted into a mixture of deuterated ethylenes. It is suggested that the reactions are summarized by eq. 8-11. Repetition of

$$acacRh^I(C_2H_4)_2 + D^+ + Cl^- \longrightarrow [CH_2DCH_2Rh^{III}Cl_3(C_2H_4)s]^- \quad (8)$$

$$[CH_2DCH_2Rh^{III}Cl_3(C_2H_4)s]^- \longrightarrow [(CHD=CH_2)(C_2H_4)Rh^ICl_2]^- + Cl^- + H^+ + s \quad (9)$$

$$C_2H_4 + [(CHD=CH_2)(C_2H_4)Rh^ICl_2]^- \longrightarrow C_2H_3D + [(C_2H_4)_2Rh^ICl_2]^- \quad (10)$$

$$[(C_2H_4)_2Rh^ICl_2]^- + D^+ + Cl^- \xrightarrow{s} [CH_2DCH_2Rh^{III}Cl_3(C_2H_4)s]^- \quad (11)$$

reactions 10 and 11 with deuterated ethylene instead of C_2H_4 in reaction 10 would eventually produce C_2D_4.

Necessity for Halide in Ethylene Dimerization. Synthesis of 1-butene occurs only in the presence of Cl$^-$, Br$^-$, or I$^-$. It fails when H_2SO_4, CH_3COOH, HNO_3, or CF_3COOH are used instead of HCl or when urea, dimethyl sulfoxide, bis(n-propyl) sulfide, or triphenylphosphine are used with H_2SO_4.[19] The n.m.r. spectrum of a CD_3OD solution which was 0.4 M in $acacRh(C_2H_4)_2$ and 1 M in H_2SO_4 showed that, at $25°$, the rhodium complex was unchanged in 3 hr. After 24 hr. acetylacetone was displaced and absorptions corresponding to CH_3CH_2rh had appeared. These were essentially unchanged after a week at $25°$. The results indicate that halide is involved both in formation of $C_2H_5Rh^{III}(C_2H_4)$ and in its rearrangement. Only traces of butene were formed by heating acacRh-$(C_2H_4)_2$ with methanolic H_2SO_4 and ethylene at 500 atm. (150°). A unique activity of chloride-containing

(10) A referee has pointed out that the concentration of a tight dimer would also be linear with rhodium concentration, so the ion might be formulated $[C_2H_5RhCl_3(C_2H_4)]_2$.
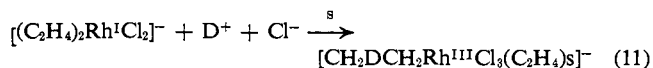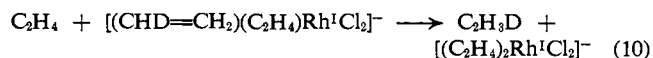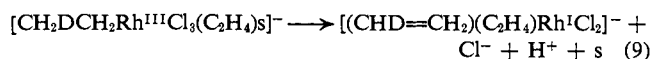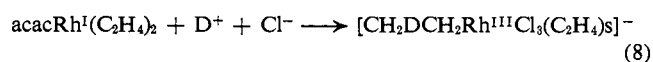
(11) R. Cramer, unpublished results.

(12) "rh" signifies a rhodium atom and one coordination bond: cf. H. H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, p. 219.

(13) A. Davison, W. McFarland, L. Pratt, and G. Wilkinson, J. Chem. Soc., 3653 (1962).

(14) A. Sacco and R. Ugo, ibid., 3274 (1964).

(15) L. Vaska and J. W. DiLuzio, J. Am. Chem. Soc., 83, 2784 (1961); 84, 679 (1962).

(16) (a) E. O. Fischer and H. Werner, Z. Chem., 2, 180 (1962); (b) J. Chatt and B. L. Shaw, J. Chem. Soc., 5080 (1962); (c) H. W. Sternberg and I. Wender, 5th International Conference on Coordination Chemistry, London, 1959; Special Publication No. 13, The Chemical Society, London, 1959, p. 51.

(17) It should be mentioned that a stable hydridodiolefin complex of iridium(III), [IrHCl$_2$(cycloocta-1,5-diene)]$_2$, has been prepared by S. D. Robinson and B. L. Shaw (Tetrahedron Letters, 1301 (1964)). This compound might have been expected to rearrange via eq. 7.

(18) (a) W. P. Griffith and G. Wilkinson, J. Chem. Soc., 2757 (1959); (b) R. D. Gillard and G. Wilkinson, ibid., 3594 (1963); J. A. Osborn, R. D. Gillard, and G. Wilkinson ibid., 3168 (1964).
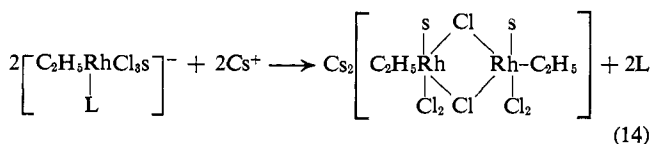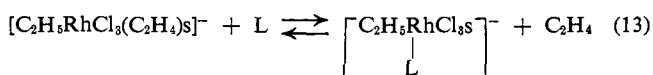
(19) Ethylene does not dimerize in a system containing acacRh-$(C_2H_4)_2$, H_2SO_4, and any of the ions CN$^-$, N$_3^-$, NO$_2^-$, or SCN$^-$. However, since insoluble rhodium compounds precipitate from these mixtures, an inherent catalytic activity may be obscured by extremely low catalyst concentration.

transition metal catalysts has been noted for other reactions, such as ruthenium-catalyzed olefin hydrogenation[20a] or acetylene hydration[20b] and rhodium-catalyzed butadiene polymerization.[20c] It may be unrecognized in other reactions since chloride is a ubiquitous component of many transition metal catalyst systems. The specific activity of halide in ethylene dimerization may arise (at least in part) from its ability to function as an electron transferring bridge between rhodium(I) and H^+. In that case the rate of hydride formation would depend on the concentration

$$rh^I: \ + \ Cl-H \longrightarrow H:rh^{III}-Cl \tag{12}$$
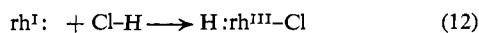
of molecular hydrogen chloride or, equivalently, the product $[H^+][Cl^-]$. It is observed that catalyst activation is impeded by solvents which favor ionization of HCl. Reaction in methanol of 0.1 M HCl with 0.001 M acacRh(C_2H_4)$_2$ requires about 4 hr. at $-20°$, but when HCl gas is added to a frozen 0.001 M acacRh-(C_2H_4)$_2$-chloroform solution, reaction is complete when the chloroform thaws ($-63°$). Differences in reactivity of sparingly soluble [(C_2H_4)$_2$RhCl]$_2$ with HCl in various media are ambiguous because the rate of physical solution may be a controlling factor. However, it may be noted that, at 25°, [(C_2H_4)$_2$RhCl]$_2$ reacts slowly with 0.1 M ethanolic HCl but not perceptibly with aqueous HCl that is more dilute than 4 M. The rate of dissolution in 8 M aqueous HCl is at least 20 times as fast as in 4 M aqueous HCl.

Dissociation of [$C_2H_5RhCl_3(C_2H_4)$]$^-$ (Eq. 3, Figure 1). Although rearrangement of [C_2H_5Rh(C_2H_4)Cl$_3$s]$^-$ by an insertion reaction is very slow below $-15°$, the ion is not stable at that temperature but loses ethylene. This dissociation of ethylene is reversible, and the extent to which it occurs depends on the partial pressure of ethylene and the temperature. If ethylene is pumped from a solution of [(C_2H_4)$_2$RhCl]$_2$ in 1 M methanolic HCl, an ethylrhodium complex may be precipitated as a cesium salt which is stable at 25° even when exposed to air. The presence of an ethyl group is established by infrared absorption and by the formation of approximately 1 mole of ethane per rhodium atom when the salt is warmed with aqueous HCl.[21] Elemental analyses conform acceptably with values calculated for Cs[$C_2H_5RhCl_3(H_2O)$].[22] The reactions involved are summarized in eq. 13 and 14. L is included in eq.

$$[C_2H_5RhCl_3(C_2H_4)s]^- + L \ \rightleftharpoons \ \left[\begin{array}{c} C_2H_5RhCl_3s \\ | \\ L \end{array} \right]^- + C_2H_4 \tag{13}$$

$$2\left[\begin{array}{c} C_2H_5RhCl_3s \\ | \\ L \end{array} \right]^- + 2Cs^+ \longrightarrow Cs_2 \left[\begin{array}{c} s \quad Cl \quad s \\ \diagdown / \diagdown / \\ C_2H_5Rh \qquad Rh-C_2H_5 \\ | \diagup \diagdown / | \\ Cl_2 \ Cl \ Cl_2 \end{array} \right] + 2L \tag{14}$$

13 for bookkeeping reasons and seems most likely to be a solvent molecule. L does not appear to be Cl^- or H_2O because the extent of dissociation of coordinated ethylene from [$C_2H_5RhCl_3(C_2H_4)$s]$^-$ is not appreciably greater in 2 M HCl than in 1 M HCl or when water is added to the mixture.

On the assumption that L may be ignored (i.e., does not exist or its concentration is effectively constant), equilibrium constants were measured for eq. 13 from the composition of equilibrated solutions of acacRh(C_2H_4)$_2$ and HCl in ethanol at -15, -25, and $-35°$. In each experiment equilibrium was approached from both directions, first in an ethylene-free system and then after a measured excess of ethylene was introduced. The values in Table I are the mean of the two values for K found in each experiment. The equilibrium constant at $-25°$ was confirmed by measuring the rates of the forward and reverse reactions of eq. 13.

Table I. Equilibrium Constants for the Reaction
[$C_2H_5RhCl_3(C_2H_4)$s]$^-$ $\rightleftharpoons$ [$C_2H_5RhCl_3$s]$^-$ + C_2H_4

Temp., °C.	K, mole l.$^{-1}$
-15	0.111, 0.096
-25	0.087, 0.085, 0.080, 0.085[a]
-35	0.058, 0.053, 0.061

[a] Ratio of rate constants for forward and reverse reactions.

If, using data from Table I, log K is plotted against $1/T$ and the curve extrapolated, it is estimated that, at 30°, K will have a value of about 0.35. This indicates that in 1 M ethanolic HCl under 1 atm. of ethylene ([C_2H_4] $\approx$ 0.08 M), the ratio [$C_2H_5RhCl_3$s]$^-$/[C_2H_5-RhCl$_3$(C_2H_4)s]$^-$ is about 4 or the ethylene complex is about 80% dissociated. Accordingly, the concentration of [$C_2H_5RhCl_3(C_2H_4)$s]$^-$ and, consequently, the rate of its rearrangement have a nearly linear dependence on the ethylene concentration. This conforms with kinetic measurements.[23]

The rates of dissociation of ethylene from [C_2H_5Rh-(C_2H_4)Cl$_3$s]$^-$ at -15, -25, and $-35°$ are reported in Table II. These results correspond to an activation energy for dissociation of 19.5 kcal./mole and, by extrapolation, a rate constant of 3.5 sec.$^{-1}$ at 30°. On the basis of the extrapolated equilibrium constant, the reverse rate constant is about one-fourth as large or 1 sec.$^{-1}$.

Table II. Rate Constants for Dissociation of [$C_2H_5RhCl_3(C_2H_4)$s]$^-$

Temp., °C.	k, sec.$^{-1}$ × 10^4
-15	10.0, 10.1, 10.3
-25	2.50
-33.3	0.38, 0.45
-35	0.35

(20) (a) J. Halpern, J. F. Harrod, and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961); (b) J. Halpern, B. R. James, and A. L. W. Kemp, *ibid.*, **83**, 4097 (1961); (c) R. E. Rinehart, H. P. Smith, H. S. Witt, and H. Romeyn, Jr., *ibid.*, **84**, 4145 (1962).

(21) The cesium salt is not sufficiently soluble for n.m.r. examination. However, n.m.r. absorption of solutions prepared from [(C_2H_4)$_2$RhCl]$_2$ and HCl and which have been freed of ethylene provide further evidence of a C_2H_5 group attached to rhodium. In CD_3OD solution the spectrum has two absorptions, a smeared triplet centered at -1.2 p.p.m. (tetramethylsilane, external standard) and a broad absorption centered at -4.5 p.p.m. In H_2O solution the absorptions are located at -1.1 and -5.0 p.p.m. The ratio of the integrated areas is $^3/_2$.

(22) Water is believed to have been introduced with the methanolic HCl in which it is formed on storage along with CH_3Cl and CH_3OCH_3.

(23) A mechanism involving addition of [$C_2H_5Rh^{III}Cl_3s$]$^-$ to uncoordinated ethylene is not excluded by these results since it would have the same first-order dependence on ethylene and rhodium as rearrangement of [$C_2H_5RhCl_3(C_2H_4)$s]$^-$. Since olefin exchange is much faster than insertion, it is not possible to distinguish these possibilities by tracer experiments as was done for CO insertion in $CH_3Mn(CO)_5$ by Coffield, Kozikowski, and Closson, Abstracts of Papers, International Conference on Coordination Chemistry, London, April 6–11, 1959, Paper No. 26.

It is interesting to compare the stability and lability of ethylene complexes of rhodium(I) and rhodium(III). acacRh(C$_2$H$_4$)$_2$ is more stable but exchanges ethylene far faster than [C$_2$H$_5$Rh(C$_2$H$_4$)Cl$_3$s]$^-$. A similar stability–lability relationship was proposed by Brault, Thorsteinson, and Basolo for carbonyls of mono- and trivalent rhodium.[24]

Cs$_2$[C$_2$H$_5$RhCl$_3$[(H$_2$O)]$_2$ dissolves in 8 M aqueous HCl at 25° to give relatively stable orange-pink solutions. In acid-free water, the salt gives yellow solutions which deposit metallic rhodium within 10 sec. at 25°. The color suggests initial aquation of the chlorido complex (which is much faster than usual for rhodium(III) chlorido compounds,[9] probably as a consequence of rhodium(I) catalysis[25]) followed by reduction of rhodium(III) through oxidation of the ethyl group to C$_2$H$_4$ and H$^+$. Orange solutions of the cesium salt in 4 M aqueous LiCl persist for several minutes before reduction to metallic rhodium. No metal was deposited from solutions in concentrated aqueous CF$_3$COOH, H$_2$SO$_4$, or HF.

The Insertion Reaction (Eq. 4, Figure 1). The insertion reaction is the rate-determining step of ethylene dimerization. This is supported by two arguments: (1) all the other proposed reaction steps (or their analogs) were shown to be much faster than the overall reaction, and (2) the n.m.r. spectrum of [C$_2$H$_5$RhCl$_3$-(C$_2$H$_4$)$_2$s]$^-$ changes at, but not below, the temperature at which dimerization of ethylene occurs.[26]

Rate constants for 1-butene synthesis over the temperature range 10 to 50° and in ethanol solution 1.00 M in HCl and 0.67 M in Rh are given in Table III and are

Table III. Rate Constants for Ethylene Dimerization

Temp., °C.	$10^4 k$, sec.$^{-1}$
10	0.350, 0.371
30	2.67, 2.79
50	16.8, 16.9, 17.9

summarized by the equation $k = 7.4 \times 10^8$ exp $(-17.2/RT)$. From a value of E_a of 17.2 kcal. and the specific rate constant at 30° of 2.73×10^{-4} sec.$^{-1}$, the thermodynamic parameters of the activated state at 30° were calculated[27] to be: $\Delta H^* = 16.6$ kcal. mole^{-1}, $\Delta F^* = 22.7$ kcal. mole^{-1}, and $\Delta S^* = -20.1$ cal. mole^{-1} deg.$^{-1}$. These values refer to an insertion (or chain growth) reaction of ethylene (eq. 15). Since

$$[C_2H_5Rh(C_2H_4)Cl_3s]^- \longrightarrow [C_2H_5CH_2CH_2RhCl_3s]^- \quad (15)$$
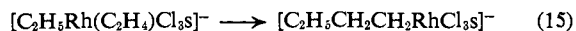
the rates of ethylene dimerization in ethanol and water are nearly equal,[28] it appears that an entering ligand does not "push" ethylene into insertion.

(24) A. T. Brault, E. M. Thorsteinson, and F. Basolo, *Inorg. Chem.*, **3**, 770 (1964).
(25) R. D. Gillard, J. A. Osborn, and G. Wilkinson, *Proc. Chem. Soc.*, 284 (1964); J. V. Rund, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 658 (1964).
(26) It may be noted that compounds of the type [R$_2$Pd^{II}(diene)] (G. Calvin and G. E. Coates, *J. Chem. Soc.*, 2008 (1960)) and [R$_2$Pt^{II}(diene)] (C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, **2**, 1255 (1963)) have been prepared. There is no report of an insertion of the diene ligand between metal and an alkyl ligand.
(27) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 195–199.
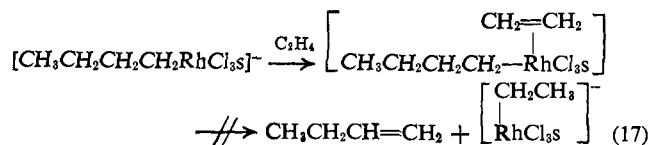(28) Ethylene dimerization has been studied only in alcohols (methanol or ethanol) and water. In other media (glyme, diglyme, THF,

It is interesting to compare these values with those found by Calderazzo and Cotton[29] for the insertion of CO into methylmanganese pentacarbonyl (eq. 16):

$$CH_3Mn(CO)_5 + CO \longrightarrow CH_3COMn(CO)_5 \quad (16)$$
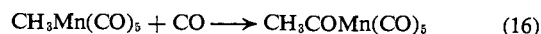
$\Delta H^* = 14.2$ kcal. mole^{-1}, $\Delta F^* = 20.6$ kcal. mole^{-1}, and $\Delta S^* = -21.1$ cal. mole^{-1} deg.$^{-1}$.

Release of Butene and Reduction of Rhodium(III) (Eq. 5, Figure 1). The final step in ethylene dimerization is formation of 1-butene by the decomposition of butylrhodium(III) anion (D, Figure 1). This reaction might be pictured as an intramolecular hydrogen transfer to yield an ethylrhodium(III) compound (eq. 17) which could be expected to become an intermediate

$$[CH_3CH_2CH_2CH_2RhCl_3s]^- \xrightarrow{C_2H_4} \left[\begin{array}{c} CH_2{=}CH_2 \\ | \\ CH_3CH_2CH_2CH_2{-}RhCl_3s \end{array} \right]$$
$$\xcancel{\longrightarrow} CH_3CH_2CH{=}CH_2 + \left[\begin{array}{c} CH_2CH_3 \\ | \\ RhCl_3s \end{array} \right]^- \quad (17)$$

in a catalyst cycle involving reactions similar to those discussed earlier. But an examination of rhodium-catalyzed isomerization of 1-butene furnishes strong evidence that this does not occur.

It was mentioned that much of the initially formed 1-butene isomerizes to 2-butene. The results of a study[71] of this isomerization are incompatible with a transfer of hydrogen such as that indicated in eq. 17. Instead they suggest that for every molecule of 1-butene converted to 2-butene a rhodium atom is oxidized from rhodium(I) to rhodium(III) by reaction with a proton and then reduced back to rhodium(I).[30] The isomerization results are explicable by a mechanism which involves the step summarized by eq. 18. Since

$$\overset{rh^{III}{-}Cl}{CH_3CH_2CHCH_3} \longrightarrow \overset{rh^I}{CH_3CH{=}CHCH_3} + HCl \quad (18)$$
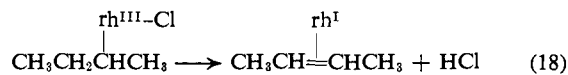
isomeration is very fast under conditions of 1-butene synthesis and since it may be considered the microscopic reverse of reaction 2 of Figure 1, it is proposed as the mechanism by which 1-butene is released. The absence of higher olefins in the ethylene dimerization product is consistent with identical mechanisms for release of butenes in synthesis and isomerization. Isomerization (measurable at −25°) is much faster than insertion. Therefore, every step of isomerization (and, specifically, olefin release) is much faster than insertion. Accordingly, it would be expected that 1-butene would be released before a second molecule of ethylene could be coordinated and inserted.

Coordination of Ethylene to Give Bis(ethylene)-rhodium(I) Dichloride. Regeneration of the Catalyst

nitrobenzene) a tarry second phase separates which contains most of the rhodium. The rate of ethylene dimerization is approximately the same in alcohol and water although exact comparisons cannot be made. Thus, the activity of H$^+$, Cl$^-$, and C$_2$H$_4$ are not the same in alcohol and aqueous solutions at the same concentration. From the operational point of view, in ethanol the partial pressure of HCl and the correction for C$_2$H$_5$Cl formation become an increasing problem as the [HCl] increases above 1 M. But aqueous reaction systems in which HCl is as dilute as 1 M are unstable and deposit metallic rhodium shortly after reaction starts. The following comparison, which may be a valid one, pertains to reactions run at 30° with 0.1 g. of [(C$_2$H$_4$)$_2$RhCl]$_2$ as catalyst: in 1 M ethanolic HCl, $\Delta \log p/\Delta t = 2.65 \times 10^5$ sec.$^{-1}$; in 8 M aqueous HCl, $\Delta \log p/\Delta t = 2.55 \times 10^5$ sec.$^{-1}$.
(29) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 1962).
(30) R. D. Gillard and G. Wilkinson (*J. Chem. Soc.*, 3594 (1963)) have proposed an analogous reduction of rhodium in [Rh^{III}(py)$_4$HCl]$^+$ by oxidation of H$^-$ to H$^+$.

(*Eq. 6, Figure 1*). Prompt conversion of $[Cl_2Rh^Is-(CH_3CH_2CH=CH_2)]^-$ to $[Cl_2Rh(C_2H_4)_2]^-$ is expected on the basis of both thermodynamic and kinetic evidence. The extent of ethylene dissociation from acac-$Rh(C_2H_4)_2$ dissolved in ethanol is quite small[7] although the rate of ethylene exchange is possibly faster[7,31] than any of the steps which have been proposed for ethylene dimerization. This is also true in 0.5 M ethanolic LiCl. Since in coordination to Rh(I), ethylene is favored by a factor of about 10^3 over 1-butene,[32] 1-butene will be rapidly displaced from $[Cl_2Rh^Is(CH_3CH_2CH=CH_2)]^-$ to give $[Cl_2Rh(C_2H_4)_2]^-$ for a new reaction cycle.

Experimental Section

Induction Period with "$RhCl_3 \cdot 3H_2O$" Catalyst. The apparatus, operable at 6 atm., comprised a flask with stirrer in a thermostated bath, a gas buret, a manometer, and a cylinder of ethylene. The flask containing 0.1 g. of "$RhCl_3 \cdot 3H_2O$", 5 ml. of ethanol, and 1 ml. of aqueous HCl of appropriate concentration was chilled to $-80°$, evacuated, and purged with ethylene. It was then heated to $50.0 \pm 0.1°$ and pressured with ethylene to 5 atm. The rate of ethylene absorption varied with [HCl] as shown in Table IV.

Table IV. Induction Period in 1-Butene Synthesis

[HCl], M	Induction period,[a] min.	Subsequent rate,[b] ml./min.	Color of solution
0.46	13	0.000	Yellow[c]
0.79	20	0.090	Yellow
1.97	36	0.287	Red

[a] Time to absorb 6 ml. of ethylene required to reduce $RhCl_3 \cdot 3H_2O$. [b] Of ethylene absorption. [c] Contained precipitate of $[(C_2H_4)_2RhCl]_2$.

N.m.r. Experiments Supporting Formation of an Ethylrhodium Compound. N.m.r. spectra were taken with a Varian HR 60 instrument equipped with a Varian Model V-4340 variable temperature probe accessory. An n.m.r. tube chilled in liquid nitrogen was charged with 0.08 g. of $[(C_2H_4)_2RhCl]_2$, 0.4 ml. of CD_3OD, 0.01 ml. of tetramethylsilane (TMSi), 25 ml. of HCl gas, and 15 ml. of ethylene, evacuated, and sealed. After several hours at $-33°$ the complex had dissolved, and the spectrum was recorded at $-30°$. It is reproduced in Figure 2.

In another experiment, a cooled, evacuated tube containing 0.04 g. of π-$C_5H_5Rh(C_2H_4)_2$, 0.4 ml. of $CHCl_3$, 0.01 ml. of TMSi, and 10 ml. of HCl gas was warmed to $-60°$ and the spectrum recorded at that temperature (Figure 2b). It did not change in 2 hr. at $-20°$ but was decidedly different after 20 min. at $-10°$ (Figure 2c).

Kinetics of Ethylene Dimerization. Ethylene dimerization was followed by the change of pressure accompanying reaction. Two types of apparatus were employed.

1. Experiments in Warburg Apparatus. The effect of [Rh], [Cl⁻], or [H⁺] was studied in a Warburg apparatus,[33] a standardized manometric device em-

ployed routinely in biochemical studies. A set of concurrent experiments yielded a set of differential values for the rate of ethylene absorption. Flasks with three compartments were used, and standardized ethanol solutions of H⁺ (as HCl or H_2SO_4), Cl⁻ (as HCl or LiCl), and Rh⁺ (as acacRh(C_2H_4)₂) were pipetted into separate compartments. The flasks were then attached to their manometers and cooled to $-80°$ while the manometers were immobilized by freezing the bottoms at $-80°$. The reactors were purged by alternately evacuating and pressuring with ethylene, finally leaving them filled with ethylene. They were then warmed to room temperature; the pressure which developed was relieved from time to time by "cracking" a stopcock to allow excess ethylene to escape. After a group of reactors containing mixtures differing only in the concentration of one of the reactants had been charged in this manner, they were positioned in the thermostated bath for 5 min. to allow the unmixed reactants to come to $30 \pm 0.1°$. Then reactants were mixed, and the reaction was followed in the usual way[33] as 10 to 20% of the ethylene dimerized.

The effect of rhodium concentration was measured in solutions which were 0.33 M in both H⁺ and Cl⁻ and varied from 0.0033 to 0.026 M in acacRh(C_2H_4)₂. In Figure 3, values of $\Delta V/\Delta t$ are plotted against [acacRh(C_2H_4)₂] to a value of 0.01 M (corresponding to a Cl/Rh mole ratio of 17). At high [acacRh(C_2H_4)₂] (low Cl/Rh ratio), the rate appears to be limited by the amount of Cl⁻ available for coordination to rhodium as well as by the amount of rhodium in the system.

The effect of hydrogen ion concentration was examined in ethanol which was 0.33 M in Cl⁻, 0.026 M in acacRh(C_2H_4)₂, and varied from 0.026 to 0.52 M in H⁺. Results are summarized in Figure 4 in which $\Delta V/\Delta t$ is plotted against the hydrogen ion concentration to a H⁺/Rh ratio of 5. Beyond that point, acid concentration had little effect on the rate of ethylene dimerization.

The influence of chloride ion concentration is illustrated by Figure 5. The reaction solutions were 0.33 M in H⁺ and 0.0033 M in acacRh(C_2H_4)₂, and the concentration of Cl⁻ covered the range 0.008 to 0.040 M. There was no measurable ΔV until the Cl⁻/Rh mole ratio had reached 6. Above this ratio, $\Delta V/\Delta t$ increased linearly with [Cl⁻] through a Cl/Rh ratio of 10. Extrapolation to $\Delta V/\Delta t = 0$ indicates no reaction at a Cl⁻/Rh ratio of about 3.

The Warburg apparatus was also used to study the effect of auxiliary ligands on ethylene dimerization. Separate compartments of reaction flasks were charged with ethanol solutions of H_2SO_4, acacRh(C_2H_4)₂, and the ligand to be evaluated, and the procedure described earlier was employed. Each ligand was examined at five or more concentrations with ligand/Rh ratios from 1:1 to 20:1. The rates of dimerization with Br⁻ and I⁻ are five and ten times, respectively, those with Cl⁻. No reaction occurred in systems containing urea, dimethyl sulfoxide, bis(*n*-propyl) sulfide, tris(*n*-butyl)phosphine, NaCN, $NaNO_2$, NaN_3, and NaSCN; the last four precipitated rhodium compounds from the reaction mixture.

2. Experiments to Measure Temperature Dependence of Reaction Rate. Apparatus for studying the effect

(31) R. Cramer, *Inorg. Chem.*, **4**, 445 (1965).
(32) R. Cramer, unpublished results.
(33) W. W. Umbreit, *et al.*, "Manometric Techniques," Burgess Publishing Co., Minneapolis, Minn., 1957.
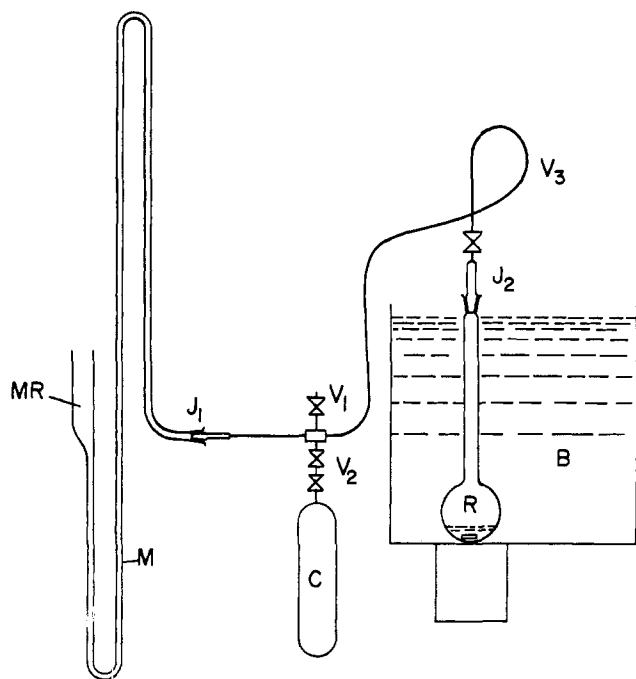
Figure 6. Apparatus for ethylene dimerization.

of ethylene concentration and temperature on ethylene dimerization is shown in Figure 6. It consisted of (1) a reaction flask, R, with a magnetic stirrer, contained in a constant temperature bath, B, controlled to ±0.01° and (2) an open-end manometer, M, of 1-mm. i.d. capillary tubing with a mercury reservoir, MR, made of 30-mm. i.d. tubing. These pieces of glass equipment were attached by ground-glass joints, J, to glass–"Kovar" connectors soldered to a manifold of $^1/_{16}$-in. o.d. copper tubing. The manifold was also connected to a cylinder of ethylene and a pump. Hoke bellows valves, V, were attached to the manifold by compression fittings.

Rates were measured by the following procedure. A flask, R, of suitable capacity was charged with ethanolic hydrogen chloride. The solution was chilled to −80°, and [(C₂H₄)₂RhCl]₂ was introduced.[34] R was sealed to J_2 with a thermoplastic polyphenylene ether resin. With R at −80°, the system was alternately evacuated and pressured with ethylene to purge the reaction mixture of air. Finally, R was evacuated and immersed in B and stirred until [(C₂H₄)₂RhCl]₂ dissolved (1 to 3 min.). Ethylene was admitted through V_2 to a pressure of about 1100 mm. The mercury level in M was measured by a cathetometer, generally at 10-min. intervals. Experiments were run for 2–72 hr. When a temperature of 10° was required, B was loaded with a solid carbon dioxide–acetone slush and a water-filled 1-gal. dewar flask in B served as the reaction bath. The temperature was controlled to 10.0 ± 0.1°.

3. Calculations. The system comprised a gas phase (ethylene, butenes, ethanol vapor, HCl gas, and, at 50°, a significant amount of ethyl chloride from reaction of ethanol and HCl) and a liquid phase (all the components of the gas phase and the rhodium catalyst). It was assumed that the partial pressures of

(34) When C₅H₅Rh(C₂H₄)₂ was used as catalyst, the reaction mixture was prepared and kept under nitrogen until R was sealed to J₂.

ethanol and HCl are constant throughout the reaction and that the partial pressures of the olefins and ethyl chloride are related to their concentration through Henry's law. The value of ΔF for conversion of ethylene to butene[35] is so large ($K \approx 10^{11}$) that ethylene dimerization may be considered unidirectional. Accordingly, a plot of log ($P_{inst} - P_\infty$) against t would be linear for a first-order reaction[36] where P_{inst} is the total pressure of the system at time t and P_∞ is the pressure when all the ethylene has dimerized.

P_∞ was obtained empirically. Most experiments were run until the pressure change was 1–5 mm./hr. Gas chromatographic analysis of the residual gas showed that >98% of the ethylene had dimerized, and the rate was becoming diffusion controlled. In these systems the measured pressure had approached P_∞. A value for P_∞ was obtained by subtracting 10 mm. from the measured pressure when the rate of pressure change was reduced to 1 mm./hr.

In experiments at 50° correction was made for accumulating ethyl chloride using empirical values found for $\Delta P_{C_2H_5Cl}/\Delta t$ by heating solutions of ethanolic HCl. Typical values for 30.00 ml. of reaction solution in a 180-ml. reaction flask are 1.42 (1 M HCl) and 3.07 mm./hr. (2 M HCl).

Since the gas phase acts as a reservoir to replace ethylene consumed in the liquid phase, the rate of pressure change depends upon the volume of the gas phase as well as the rate at which ethylene is converted into 1-butene. To correct for the arbitrary ethylene increment from the gas phase, the observed rate was divided by the fraction of ethylene in the liquid phase. The distribution of ethylene between gas and liquid was calculated from the solubility of ethylene in the reaction medium[37] and the volume of the reaction system.

A plot of log ($P - P_\infty$) *vs.* t is shown in Figure 7 for an experiment in which 30.00 ml. of 1 M ethanolic HCl and 0.390 g. of [(C₂H₄)₂RhCl]₂ (2 mmoles of Rh) were employed at 50° using a 181.4-ml. reaction flask. The slope of the line drawn to fit the points is 9.98 × 10⁻³ min.⁻¹. The liquid phase contains 30.00 × 1.65 (=49.5) ml. of ethylene. The gas phase is 166.9 ml. Consequently, the fraction of ethylene in the liquid phase is 0.228 so the rate constant for ethylene dimerization in ethanol which is 1.00 M in HCl and 0.067 M in Rh is k = 2.30 × 9.98 × 10⁻³/(0.228 × 60) = 1.68 × 10⁻³ sec.⁻¹.

Four duplicate experiments gave values for k of 1.65, 1.69, 1.75, and 1.79 × 10⁻³ sec.⁻¹. This corresponds to a mean of 1.71 × 10⁻³ sec.⁻¹ with a sample standard deviation of 0.06 × 10⁻³ sec.⁻¹.

The results of other kinetic experiments are summarized in Table V. About 200 were run covering a wider range of conditions than those reported in Table V

(35) J. E. Kilpatrick, *et al.*, *J. Res. Natl. Bur. Std.*, **36**, 610 (1946).
(36) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 1st Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 28.
(37) The Oswald solubility coefficient, *l*, of ethylene in ethanolic HCl of various concentrations was measured at the pertinent temperatures.

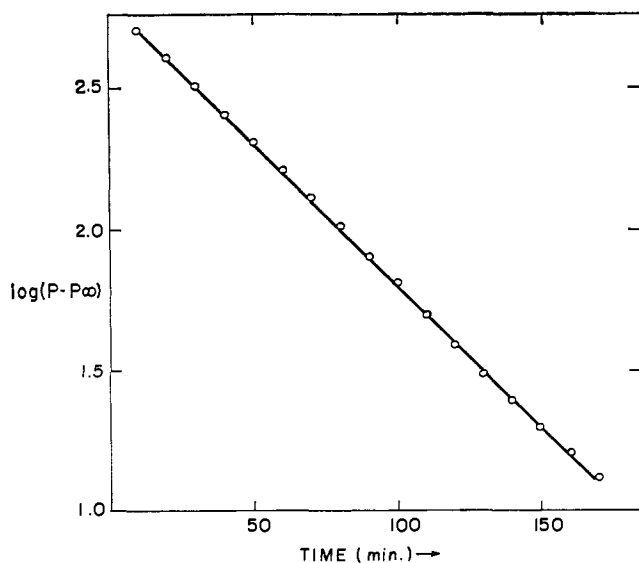| [HCl], | l for ethylene in ethanolic HCl | | |
M	10°	30°	50°
0	2.87	2.30	1.84
0.5	2.65	2.08	1.71
1.0	2.51	1.98	1.65
2.0	2.29	1.81	1.52
4.7		1.44	1.16

Figure 7. Rate of ethylene dimerization.

and the results of all conform to a reaction that is first order in ethylene. This includes experiments in large reactors which initially contained 90 mole % nitrogen or butene.

A plot of log k vs. $1/T$ using values from Table V gives a rate expression $k = 7.4 \times 10^8 \exp(-17.2/RT)$.

Table V. Rate Constants for Ethylene Dimerization

Temp., °C.	[HCl], M	[Rh], M	$k \times 10^4$ sec.$^{-1}$
50	1.00	0.067	16.5, 16.8, 16.9, 17.5, 17.9
30	2.00	0.067	3.14
30	1.00	0.067	2.79, 2.67
30	0.50	0.067	2.51
30	0.10	0.067	1.56
30	1.00	0.033	1.97
30	1.00	0.0167	1.24
30	1.00	0.0067	0.540
10	1.00	0.067	0.350, 0.371

Experiments in Table V in which the concentration of HCl or rhodium catalyst was adjusted show changes in k that parallel results with the Warburg apparatus.

Spectrophotometric Study of Addition of HCl to acacRh(C_2H_4)_2. A Cary Model 11 spectroscope was used in conjunction with a cell (Figure 8) consisting of a conventional 1-cm. cylindrical cell with quartz windows (C) cemented with polyphenylene ether resin to a mixing reservoir, R. The cell was charged with solid acacRh(C_2H_4)_2 and swept with nitrogen. Three milliliters of 0.5 M H_2SO_4 in ethanol (enough to fill C, only) was added under nitrogen, and a hypodermic cap, S_2, was attached to R. Next R was filled with ethylene through a hypodermic needle inserted in S_2, and the cap S_1 was attached. Increments of Cl$^-$ were introduced (as HCl gas) by a hypodermic syringe inserted in S_1 or S_2. The apparatus was inverted several times after each addition of HCl (to dissolve the added HCl and to keep the solution of rhodium complexes saturated with ethylene) and the spectrum was recorded. The reaction solution equilibrated during mixing and did not change in 0.5 hr.
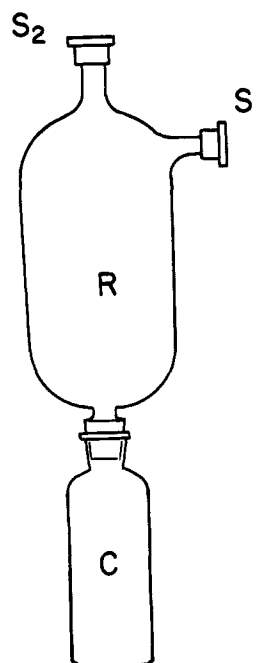

Figure 8. Cell for spectrophotometric studies.

Addition of 0.015 mmole of HCl to 0.015 mmole of acacRh(C_2H_4)_2 in 3 ml. of ethanolic H_2SO_4 appears to give a solution of [(C_2H_4)_2RhCl]_2 with a molar absorptivity (at 520 mμ) of 88; 0.049 mmole more of HCl appears to be just enough to convert it to [(C_2H_4)_2-RhCl_2]$^-$ with a molar absorptivity (at 520 mμ) of 79.

By measuring the absorbance at 520 mμ of solutions following the addition of each increment of the final 0.049 mmole of HCl, equilibrium constants were calculated for the reaction

$$[(C_2H_4)_2RhCl]_2 + 2Cl^- \rightleftharpoons 2[(C_2H_4)_2RhCl_2]^-$$
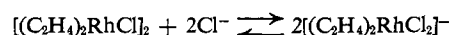
Results are summarized in Table VI.

Rhodium-Catalyzed Exchange of Hydrogen between C_2H_4 and CH_3OD. A heavy-walled glass tube containing a magnetic stirrer was charged with 0.02 g. of acacRh(C_2H_4)_2 (0.1 mmole) and 2 ml. of CH_3OD (67 mmoles of D). The tube was chilled in liquid nitrogen, evacuated, and further charged with 25 ml. of DCl gas and 80 ml. of C_2H_4 (3.2 mmoles). The tube was sealed, and the contents were stirred for 13 hr. at $-23°$. The gas was analyzed by mass spectroscopy. It contained 77.5% C_2H_4, 17.5% C_2H_3D (0.56 mmole of D), 3.5% $C_2H_2D_2$, and 1.5% C_2HD_3.

Dissociation of [$C_2H_5RhCl_3(C_2H_4)s$]$^-$. Preliminary experiments showed that displacement of ethylene from [$C_2H_5RhCl_3(C_2H_4)s$]$^-$ dissolved in ethanolic HCl is extensive enough at -15 to $-35°$ to produce a measurable vapor pressure increment. The apparatus shown in Figure 9 was used to measure equilibrium rate constants. It consisted of a manometer made of 1-mm. i.d. capillary tubing, a gas buret, and a reaction flask, F, containing a magnetic stirrer. These components were connected with capillary stopcocks and tubing. The reaction flask F was immersed to the joint G in a dewar flask containing either (experiments at -15 to $-25°$) acetone whose temperature was kept within 0.2° of the nominal temperature by occasional

Table VI. Equilibrium Constant for $[(C_2H_4)_2RhCl]_2 + 2Cl^- \rightleftharpoons 2[(C_2H_4)_2RhCl_2]^-$

Added Cl⁻, mmole	Absorbance (520 mμ)	Concn.ᵃ of $[(C_2H_4)_2RhCl]_2$, M	Concn.ᵇ of $[(C_2H_4)_2RhCl_2]^-$, M	Concn.ᶜ of Cl⁻, M	K^d
0.0012	0.225	0.00243	0.00014	0.00026	1.19
0.0090	0.280	0.00164	0.00172	0.00128	1.10
0.0170	0.322	0.00105	0.00290	0.00277	1.04
0.0330	0.370	0.00036	0.00428	0.00672	1.13

ᵃ (0.395 − absorbance)/70. ᵇ 0.005 − 2(concentration of $[(C_2H_4)_2RhCl]_2$). ᶜ Added Cl⁻/3 − concentration of $[(C_2H_4)_2RhCl_2]^-$. ᵈ (Concentration of $[(C_2H_4)_2RhCl_2])^2$(concentration of $[(C_2H_4)_2RhCl]_2)^{-1}$(concentration of Cl⁻)⁻².

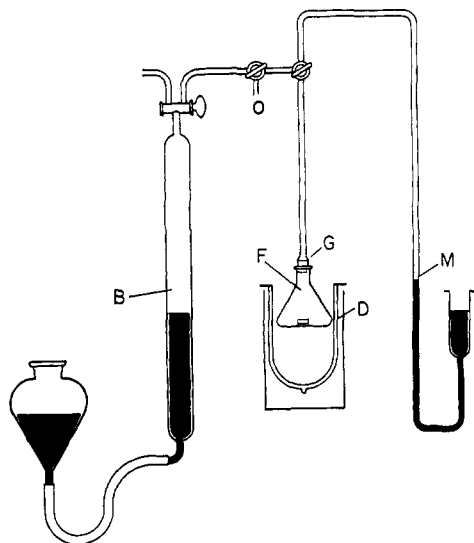addition of solid carbon dioxide or (experiments at −33.3°) liquid ammonia.

Figure 9. Apparatus for measuring dissociation of [C₂H₅RhCl₃-(C₂H₄)s].

The amount of ethylene liberated at −15, −25, or −33.3° was measured by reference to empirical graphs relating pressure to the volume of ethylene in the system at these temperatures. Plots of volume of ethylene in the system vs. pressure were linear over the temperature and pressure range (<700 mm.) that was studied. The amount of ethylene required to saturate the solutions at a partial pressure of 760 mm. was found by extrapolation and, since the volume of free space and solution was known, the concentration of ethylene in saturated 1 M ethanolic HCl could be calculated (0.168 M, −15°; 0.222 M, −25°; 0.268 M, −33.3°).

To measure the dissociation pressure, F was charged with 5.00 ml. of 1.00 M ethanolic HCl and chilled in liquid nitrogen; 0.129 g. (0.5 mmole) of acacRh(C₂H₄)₂ was added. F was attached to G, the system was evacuated, and the mercury level in the manometer was measured. F was then immersed in a constant-temperature bath and pressure readings were taken periodically until the rate of pressure change was less than 1 mm./hr. The pressure is that of ethylene and ethanolic HCl. Assuming that the added rhodium compound does not affect the solubility of ethylene nor the vapor pressure of ethanolic HCl, the partial pressure of ethylene and its concentration in the liquid phase can be calculated from the empirical graphs described earlier. Since the rate is slow (ca. 1.5 hr.

for completion at −15° or 16 hr. at −35°), two modifications were made to ensure equilibration. (a) After apparent equilibration, a measured increment of ethylene was introduced from the gas buret. The reaction was then reversed as part of the introduced ethylene became coordinated to rhodium and another value for the equilibrium constant was calculated for the new ethylene concentration. (b) In measurements at −33.3°, reaction was allowed to proceed at −15° until an amount of ethylene corresponding approximately to equilibrium at −33.3° was released. The equilibration was completed at −33.3°. The concentration of each of the species can be calculated from the amount of complex charged and the amount of ethylene released assuming that the reaction is given by the equation

$$[C_2H_5Rh(C_2H_4)Cl_3s]^- \rightleftharpoons [C_2H_5RhCl_3s]^- + C_2H_4$$
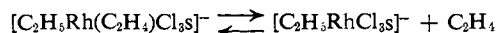
Rate of Displacement of Ethylene from $[C_2H_5RhCl_3-(C_2H_4)s]^-$. By making frequent measurements of the pressure during the displacement of ethylene from $[C_2H_5RhCl_3(C_2H_4)s]^-$, data were collected for calculating the rate of the reaction.

Calculations. The reaction was treated as an example of the type $A \underset{k'}{\overset{k}{\rightleftharpoons}} B + C$.[38] The rate of such a reaction is given by the expression

$$\ln\left(\frac{A_0^2 - A_eA_t}{(A_t - A_e)A_0}\right) = k\left(\frac{A_0 + A_e}{A_0 - A_e}\right)t$$

where A is the concentration of $[C_2H_5RhCl_3(C_2H_4)s]$ (A_0, initial; A_e, equilibrium; A_t at the time of observation). A_e and A_t were calculated from A_0 and the partial pressure of ethylene in the system. Plots of $\log (A_0^2 - A_eA_t)/[(A_t - A_e)A_0]$ vs. t were nearly linear for 90% of the reaction. For a number of experiments at lower temperatures, calculations were also made for the first 20% of the reaction assuming an irreversible reaction $(\ln (A_0 - A_t) = kt)$. These plots of $\log A_t$ vs. t give values for k that are close to those for the more complex expression.

Rate of Coordination of Ethylene to $[C_2H_5RhCl_3s]^-$. Using the apparatus of Figure 9, 0.129 g. of acacRh(C₂H₄) (0.50 mmole) was treated with 5.00 ml. of 1.00 M HCl in ethanol at −15°, and the evolved ethylene was removed using the gas buret as a Toepler pump. As 12.3 ml. of gas (0.50 mmole) was collected, the rate of gas evolution decreased rapidly. The reaction solution was chilled to −25°, and the ethylene which had been evolved was added. The course of reaction was followed by observing the rate at which the pressure dropped.

To calculate the rate constant, a bimolecular reaction was assumed. The reverse reaction was ignored and

(38) See ref. 36, p. 173.

$(1/[C_2H_4]_{initial} - 1/[C_2H_4]_t)$ was plotted against t. Because the reaction is reversible, the points fit a curved line. A tangent drawn to the curve for the first 5 min. of reaction (approximately the first 10% of reaction) has a slope corresponding to a rate of 0.0028 l. mole^{-1} sec.$^{-1}$. In conjunction with an average value of 2.38×10^{-4} sec.$^{-1}$ for the rate constant for ethylene displacement at $-25°$, this gives a value for K of $(2.38 \times 10^{-4})/(2.8 \times 10^{-3}) = 0.085$, which agrees closely with values between 0.080 and 0.087 from the composition of equilibrated mixtures (Table I).

Synthesis and Isolation of $Cs_2[C_2H_5RhCl_3(H_2O)]_2$. A flask containing 20 ml. of 1 M HCl in methanol was chilled in liquid nitrogen, and 1 g. of $[(C_2H_4)_2RhCl]_2$ was added. The flask was attached to a high vacuum apparatus and held at -18 to $-24°$ as ethylene was distilled from the reaction into a trap chilled by liquid nitrogen. After 3 hr., reaction was complete as indicated by (a) complete dissolution of $[(C_2H_4)_2RhCl]_2$ and (b) constant pressure over the reaction mixture. Then a solution of 1 g. of CsCl in 75 ml. of 0.4 M HCl in methanol was added. A rose-colored salt separated and this was filtered and washed with methanol and ether before it was exposed to the air. It weighed 1.6 g.

Anal. Calcd. for $CsC_2H_7ORhCl_3$: Cs, 34.14; C, 6.17; H, 1.82; Rh, 26.43; Cl, 27.33. Found: Cs, 35.3; C, 6.01; H, 0.74; Rh, 24.72; Cl, 28.06.

The infrared spectrum (KBr wafer) had absorptions at 3.37, 3.44, 3.53 (saturated C–H stretch), and 2.91 μ (O–H stretch).

$Cs_2[C_2H_5RhCl_3(H_2O)]_2$ (0.1 g., 0.13 mmole) was warmed with 10 ml. of aqueous 8 M HCl to 90° for 10 min. The evolved gas (5 ml., 0.2 mmole) was identified as ethane from its mass spectrum.

Effect of Medium on the Reaction of HCl with π-$C_5H_5Rh(C_2H_4)_2$. (a) *Ethanol.* Glass tubes (30 × 300 mm.) were charged under nitrogen with 15 ml. of 0.001 M π-$C_5H_5Rh(C_2H_4)_2$ in oxygen-free ethanol and chilled in liquid nitrogen. To each tube was added 1.5 ml. of 1 M HCl in ethanol, and the tubes were evacuated, charged with 15 ml. of ethylene, and sealed. One tube was warmed to 25° for 10 min. to permit reaction and provide a color standard. Other tubes were held at -20, -28, and $-35°$. After 13 hr. the tubes at $-20°$ nearly matched the blank by visual comparison, while tubes at $-28°$ were much lighter and those at $-35°$ had scarcely changed.

(b) *Chloroform.* Similar tubes were charged with 15 ml. of 0.001 M π-$C_5H_5Rh(C_2H_4)_2$ in deoxygenated, alcohol-free chloroform, chilled in liquid nitrogen, and evacuated. To each was added 10 ml. of HCl gas and 50 ml. of C_2H_4 and the tubes were sealed. As they were warmed, the characteristic color of protonated rhodium complex appeared immediately as the chloroform melted.

The Addition of Acylcobalt Carbonyls to α,β-Unsaturated Carbonyl Compounds. 1-Acyloxy-π-allylcobalt Tricarbonyl Derivatives

Richard F. Heck

Acylcobalt tetracarbonyls and alkylcobalt tetracarbonyls react with α,β-unsaturated aldehydes or ketones to form 1-acyloxy-π-allylcobalt tricarbonyls. These complexes are conveniently isolated in the form of their crystalline monotriphenylphosphine derivatives, 1-acyloxy-π-allylcobalt dicarbonyl triphenylphosphines.

Introduction

Additions of Grignard reagents, lithium alkyls, and other nontransition metal alkyls to α,β-unsaturated carbonyl compounds are well known. Similar reactions of transition metal alkyls, however, are not. Numerous examples of the reduction of α,β-unsaturated carbonyl compounds by transition metal hydrides have been reported. These reductions probably involve addition reactions of the metal hydrides, but the mechanisms are not well understood because intermediate products cannot be isolated. Some light is shed upon these reductions and related reactions by the discovery that acylcobalt carbonyls will add to α,β-

unsaturated carbonyl compounds to give new isolable organocobalt complexes. The preparation and identification of these new complexes is the subject of this paper.

Results

Acylcobalt tetracarbonyls react in a few hours at room temperature with α,β-unsaturated aldehydes and ketones, evolving a mole of gas and producing new complexes with carbonyl absorption bands at about 1765, 2005, and 2070 cm.$^{-1}$. Alkylcobalt tetracarbonyls react similarly, but more rapidly and without gas evolution, to produce the same products. These products react with excess triphenylphosphine at 25° to evolve a mole of carbon monoxide per mole of complex and form easily isolable, yellow to orange crystalline derivatives of the new complexes. The infrared spectra, properties, analyses, and, in one case, the n.m.r. spectrum indicate that the isolated products are 1-acyloxy-π-allylcobalt dicarbonyl triphenylphosphine de-