Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Lewis Acid Influenced Ethylene Hydrogenation by Rhodium(I) Complexes

STEVEN H. STRAUSS and DUWARD F. SHRIVER*

Received June 5, 1978

Ethylene hydrogenation at subatmospheric pressures in benzene at 20 °C was catalyzed by $RhCl(PPh_3)_3$, $RhH(PPh_3)_3$, and $RhH(PPh_3)_4$ with and without added Lewis acids ($AlPh_3$, $AlEt_3$, $AlClEt_2$, $AlCl_3$, BMe_3, BF_3, BCl_3, $SnCl_4$, AsF_5, and $Yb(\eta^5\text{-}C_5H_5)_3$). For the system $RhCl(PPh_3)_3 + AlEt_3$ a rapid Cl/Et metathesis produces $RhH(PPh_3)_3$, which is 39 times more active than $RhCl(PPh_3)_3$ under our conditions. A mechanism for hydrogenation catalysis by $RhH(PPh_3)_3$, which differs from that proposed for catalysis by $RhCl(PPh_3)_3$, is presented. The major catalytic path is the addition of ethylene to $RhH(PPh_3)_3$ to form $RhH(C_2H_4)(PPh_3)_3$, which rapidly rearranges to $Rh(C_2H_5)(PPh_3)_3$. This rhodium–ethyl complex reacts with hydrogen to produce ethane and to regenerate $RhH(PPh_3)_3$. A second path involving an ortho-metalated intermediate was discovered but was found to be kinetically insignificant. Although a phosphine dissociation equilibrium is believed to be required for catalysis by $RhH(PPh_3)_4$, the equilibrium could not be shifted toward the more active $RhH(PPh_3)_3$ by adding a Lewis acid. Phosphorus-31 NMR data demonstrate that phosphine dissociation from $RhH(PPh_3)_4$ is much more rapid than the rate-determining step for ethylene hydrogenation.

Introduction

The addition of Lewis acids to soluble transition-metal complexes can lead to a homogeneous catalyst that is more active or more selective than either component alone. Lewis acid influenced catalysis includes systems that are important commercially and those that are useful synthetically in the laboratory. Examples can be found from many of the major catalytic reactions of olefins, such as isomerization,[1] hydrogenation,[2–4] oligomerization,[5] and metathesis,[6] and also include specific reactions such as the production of adiponitrile from butadiene and hydrogen cyanide[7,8] and the stereospecific dimerization of norbornadiene to Binor-S.[9,10] In some cases the Lewis acid is necessary for any catalytic activity to be observed (most olefin metathesis catalysts are in this category) and in other cases it enhances the activity or alters the selectivity of complexes that are catalysts in the absence of the acid.

There has been much speculation about the mechanisms by which Lewis acids influence catalytic systems. It is believed that the influences will arise from the known[11] interactions of Lewis acids with metal complexes: addition to the metal center (reaction 1), addition to a coordinated ligand (reaction 2), ligand abstraction (reaction 3), oxidative addition (reaction 4), and metathesis (reaction 5). In addition, a Lewis acid–substrate interaction might possibly lead to an activated substrate. However, in the work cited above, no serious attempts were made to elucidate the mechanisms of the observed influences.

$$L_nM + A \rightarrow L_nM\text{–}A \qquad (1)$$

$$L_nM + A \rightarrow L_{n-1}M\text{–}L\text{–}A \qquad (2)$$

$$L_nM + A \rightarrow L_{n-1}M + L\text{–}A \qquad (3)$$

$$L_nM + A\text{–}Z \rightarrow L_nM(A)(Z) \qquad (4)$$

$$L_nM\text{–}Y + A\text{–}Z \rightarrow L_nM\text{–}Z + A\text{–}Y \qquad (5)$$

Some degree of coordinative unsaturation is necessary for homogeneous catalytic reactions which involve the addition of substrates to the metal center. Reaction 3 would provide a mechanism for increased coordinative unsaturation, and in certain systems this might lead to enhanced rates. A report in the literature[2b] in which Lewis acid enhanced rates are attributed to ligand abstraction lacks specific evidence for this interaction.

In 1975 our initial attempts to induce ligand abstraction in a catalytic system with added Lewis acids were reported.[4] It is known that the homogeneous hydrogenation of olefins catalyzed by $RhClP_3$ (P = triphenylphosphine) involves a phosphine dissociation equilibrium (reaction 6) producing a

$$RhClP_3 \rightleftharpoons RhClP_2 + P \qquad (6)$$

small concentration of the coordinatively unsaturated complex $RhClP_2$, the most active species under catalytic conditions.[12–14] It was hoped that a suitable Lewis acid might form an adduct with free triphenylphosphine, displacing reaction 6 to the right and producing a higher concentration of the active species, which would be manifested as a higher rate of olefin hydrogenation. However, no evidence for phosphine abstraction was found with the Lewis acids we employed.[4] For example, the catalyst composed of $AlBr_3 + RhClP_3$ exhibited a rate for cyclohexene hydrogenation that was twice that of $RhClP_3$. This was attributed to a metathetical reaction producing $RhBrP_3$, known to be a more active catalyst than $RhClP_3$,[12] because $AlCl_3 + RhClP_3$ exhibited no significant rate enhancement over $RhClP_3$. In another instance rate inhibition by BCl_3 was attributed to the formation of $RhClP_3{\cdot}2BCl_3$ (this adduct is believed[15] to contain Rh–BCl_3 or Rh–Cl–BCl_3 bonds). The catalyst composed of $Al(i\text{-}Bu)_3 + RhClP_3$ exhibited a rate for ethylene hydrogenation that was an order of magnitude greater than $RhClP_3$ alone. A Cl/*i*-Bu metathesis followed by β elimination would produce $RhHP_3$, and it was proposed without proof that this hydride complex was formed and is a more active ethylene hydrogenation catalyst than $RhClP_3$.

In the present work we describe the chemistry of $AlR_3 + RhClP_3$ under hydrogenation conditions in more detail. We have confirmed that $RhHP_3$ is formed and we have investigated the influence of the $AlClR_2$ by-product. We also have studied $RhHP_3$ and a related hydride complex, $RhHP_4$, as ethylene hydrogenation catalysts with and without added Lewis acids in order to understand what factors favor phosphine abstraction.

Experimental Section

Materials. All of the complexes and the Lewis acids employed in this work are air sensitive and were handled under a nitrogen atmosphere using appropriate standard techniques.[16] Ethylene (Matheson C.P. grade) was degassed at −196 °C to remove traces of methane and any atmospheric gases. Hydrogen (Linde) was passed through a Baker Deoxo purifier. Aluminum chloride (Baker) and $Yb(\eta^5\text{-}C_5H_5)_3$ (a gift from Professor T. J. Marks) were sublimed prior to use. Trimethylaluminum, $AlEt_3$, and $Al(i\text{-}Bu)_3$ (Ethyl Corp.), $AlPh_3$ (Research Organics/Inorganics), and triphenylphosphine (Aldrich) were used as received. Solutions of $AlClEt_2$ were prepared by mixing the appropriate amounts of $AlCl_3$ and $AlEt_3$ in benzene at room temperature. Triisopropylaluminum diethyl etherate was prepared by a literature procedure.[17] Trimethylboron, BF_3, and BCl_3 had been previously purified by fractionation.[18] Their vapor pressures, measured immediately prior to use, agreed well with literature values. Benzene and diethyl ether were distilled under nitrogen from sodium ben-

0020-1669/78/1317-3069$01.00/0

Table I. Spectral Characteristics for $RhHP_3$

ν(Rh–H), cm^{-1}	δ(H), ppm	J(Rh–H), Hz	ref
1890	-7.9^a	13	*b*
2020	-8.9^c	13	19
1885	-7.8^d	14	20
1910			21

[a] In benzene-d_6 at 30 °C. [b] This work. [c] In THF at 40 °C. [d] In benzene or in THF. Temperature unspecified.

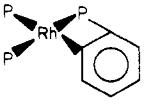
zophenone ketyl. Absolute ethanol was bubbled with nitrogen prior to use.

Commercial $RhClP_3$ (Strem Chemical Co.; P = triphenylphosphine) was purified by stirring the compound with triphenylphosphine in refluxing absolute ethanol for about 10 h. Filtration followed by several ethanol washes and vacuum drying yielded the burgundy colored solid compound. Relative purity was established by monitoring IR spectral bands due to triphenylphosphine oxide at 1122 and 725 cm^{-1}.

Treatment of a slurry of $RhClP_3$ in diethyl ether with an excess of trialkylaluminum yielded the orange compound $RhHP_3$ which was filtered, washed several times with ether, and dried under vacuum (yield 70%). This procedure was reported by Keim[19] using Al(i-Pr)$_3$, and we achieved comparable results with Al(i-Pr)$_3$ as well as with the commercially available $AlEt_3$ and Al(i-Bu)$_3$. Although our spectral characterization of this compound is different than Keim's, it is in close agreement with that reported for the same compound prepared by other routes (Table I). Further proof of the composition of this compound is provided by $^{31}P\{^1H\}$ NMR spectroscopy and an X-ray diffraction study which demonstrate a square-planar structure with two equivalent (in solution) mutually trans phosphines and one unique phosphine trans to the hydride ligand.[22] Moreover, an upper limit of 0.2% can be placed on the amount of triphenylphosphine oxide impurity present in the compound.[23]

A slurry of $RhHP_3$ (ca. 0.3 g) in diethyl ether (ca. 20 mL) was treated with an excess of triphenylphosphine and stirred at room temperature for 2 h. The bright yellow compound, $RhHP_4$, was filtered, washed several times with ether, and dried under vacuum. The IR spectrum showed ν(Rh–H) at 2140 cm^{-1} (lit.[24] 2140 cm^{-1}), and the ^1H NMR spectrum in toluene-d_8 showed a broad singlet at $\delta = -10.6$ (lit.[24] -10.6 ppm in THF).

Two methods were used to prepare the ortho-metalated complex Rh(P–C)P_2 (**1**).



1

Method 1. A benzene solution of $RhHP_3$ (5–10 mM) was treated with ca. 300 mm of ethylene and stirred at room temperature for 24 h. The solvent was stripped from the solution under vacuum leaving the yellow-brown compound Rh(P–C)P_2.

Method 2. A slurry of $RhClP_3$ (ca. 0.5 g) in diethyl ether (ca. 25 mL) was treated with a twofold excess of $AlMe_3$ and stirred at room temperature for 24 h. Addition of heptane to the dark orange solution caused precipitation of the orange compound Rh(P–C)P_2 which was filtered, washed several times with heptane, and dried under vacuum. Benzene solutions (ca. 2 mM) of yields from both methods of preparation were the same amber color and exhibited λ_{max} at 382 nm (lit.[25] 384 nm in THF solution).

The complexes $[RhClP_2]_2$[26] and Rh(CH_3)P_3[19] were prepared by literature procedures.

Spectra. IR spectra were recorded as Nujol mulls on either a Beckman IR-12 or a Perkin-Elmer 283 spectrometer. NMR spectra were recorded on a Varian CFT-20 spectrometer operating at 79.54 MHz for ^1H spectra or at 32.199 MHz for $^{31}P\{^1H\}$ spectra. Internal Me_4Si and external 85% H_3PO_4 (at 30 °C) were the ^1H and ^{31}P standards, respectively. For all chemical shifts a negative sign denotes an upfield shift from the standard. UV–vis spectra were recorded on a Cary 17D spectrophotometer.

Kinetics. Ethylene hydrogenation was followed at 20.0 ± 0.2 °C in a simple manometer system which contained ethylene, hydrogen, and the stirred catalyst solution. The system volume was ca. 100 mL. The 2.1 ± 0.1 mM benzene solutions were typically 5 mL in volume. The hydrogen:ethylene pressure ratio was 1.1 ± 0.1, with $P(H_2)$ = ca. 240 mm, resulting in a catalyst:ethylene ratio of ca. 100. No reaction other than ethylene hydrogenation was observed. A solution of each catalyst was allowed to stir for ca. 12 h under 230 mm of ethylene with no perceptible change in pressure, thereby ruling out ethylene oligomerization or polymerization as possible side reactions. Furthermore, the theoretical and experimentally determined changes in the number of gas moles for the reaction $H_2 + C_2H_4 \rightarrow C_2H_6$ were within experimental error (±10%).

Table II. Hydrogenation of Ethylene

catalyst	$10^3 k_{obsd}$, s^{-1}
$RhClP_3$	0.025
$(RhClP_2)_2$	0.024
$RhHP_3$	0.98
$RhHP_3 + AlEt_3$	1.0
$RhHP_3 + 0.5BCl_3$	0.011
Rh(P–C)P_2	0.96
$RhHP_4$	0.43
$RhHP_4 + AlEt_3$	0.48
$RhHP_4 + 5AlEt_3$	0.40^a
$RhHP_4 + AlEt_3$ (0.73 M)	$\sim 0.005^b$
$RhHP_4 + AlPh_3$	0.23
$RhHP_4 + AlCl_3$	$0.056^{a,c}$
$RhHP_4 + BMe_3$	0.45
$RhHP_4 + 5BMe_3$	0.43
$RhHP_4 + BF_3$	$0.030^{a,c}$
$RhHP_4 + BCl_3$	0^a
$RhHP_4 + SnCl_4$	0^a
$RhHP_4 + Yb(\eta^5\text{-}C_5H_5)_3$	0.078^a
$RhHP_4 + AsF_5$	*d*

[a] One determination only. [b] Estimated from initial rate data. [c] Solids were present. [d] Rate not measured; very insoluble compound formed.

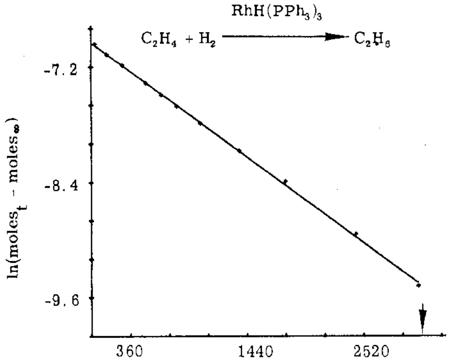


Figure 1. ln (gas moles) vs. time for ethylene hydrogenation catalyzed by $RhH(PPh_3)_3$. The line was fit to the data (crosses) by linear least squares. The arrow indicates the point on the abscissa that represents 4 half-lines.

A plot of ln (gas moles$_t$ − gas moles$_\infty$) vs. time yields a straight line for at least 4 half-lives. Thus, under the conditions of our experiments the reactions were first order with respect to gas moles. First-order rate constants, k_{obsd}, derived from these data are listed in Table II. In a typical experiment ethylene was added to a stirred, degassed, and thermostated solution of the catalyst. After a period of time to allow for equilibration (in our system ca. 10% of the ethylene was dissolved in the solution—see below), 10–15 min, the ethylene pressure was ca. 215 mm. Hydrogen (ca. 240 mm) was quickly added and the pressure drop was recorded at appropriate intervals. A typical set of data is shown in Figure 1. After 4 half-lives, ethane and any unreacted hydrogen and ethylene were removed from the system by three successive freeze (−112 °C)–pump–thaw cycles. The experiment was then repeated using the same catalyst solution with no significant (±10%) change in k_{obsd}.

In a separate experiment the rate of ethylene uptake in benzene was determined to ensure that this process was not a rate-limiting factor. At 20.0 °C and 200 mm partial pressure of ethylene the first-order rate constant for the reaction $C_2H_4(gas) \rightarrow C_2H_4(solution)$, derived from a plot of ln (moles of ethylene) vs. time, was 0.011 s^{-1}, fully an order of magnitude greater than the largest k_{obsd} in Table

Table III. Hydrogenation of Ethylene

expt	catalyst	run[a]	initial rate, 10^{-7} mol/s
1	$RhHP_3$	1	8.7
		2	8.4
2	$RhClP_3$	1	0.30
		2	0.29
3	$RhClP_3 + AlEt_3$	1	5.3
		2	0.78
		3	0.63
		4	0.33
		5	0.33
4	$RhHP_3 + AlClEt_2$	1	5.8
		2	3.2
		3	0.63
5[b]	$RhHP_3 + AlClEt + H_2$	1	1.3

[a] See Experimental Section. [b] See text for a description of this experiment.

Table IV. $RhHP_3$-Catalyzed C_2H_4 Hydrogenation[a]

C_2H_4 pressure, mm	H_2 pressure, mm	initial rate, 10^{-7} mol/s
50	240	5.9
140	240	12
210	240	16
210	165	8.9
210	70	3.4

[a] See Experimental Section.

II. In this experiment the solubility of ethylene in benzene was also measured and was found to agree to within 15% of the value extrapolated from data in the literature.[27]

For several catalysts first-order behavior was not observed. In these cases the experiments were set up as described above and initial rates were determined from the slopes of gas moles vs. time plots at the point gas moles = 0.0022 mol. After ca. 95% completion of reaction, ethane, hydrogen, and ethylene were removed as described above. Repeating the experiment several times with the same catalyst solution gave progressively lower initial rates. These data are listed in Table III.

For a series of experiments with $RhHP_3$ as the catalyst the gas pressures were varied to determine rate dependences on ethylene or hydrogen pressure. In these cases too the experiments were set up as described above, except that the H_2:C_2H_4 ratio was varied, and initial rates were determined. These data are listed in Table IV.

Results and Discussion

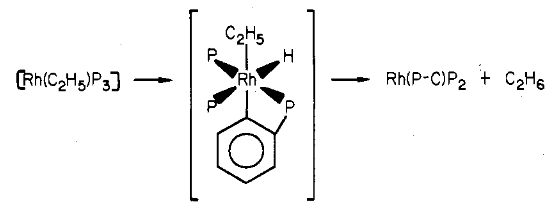
Preparation and Stoichiometric Reactions of $RhHP_3$. The reaction of $RhClP_3$ with AlR_3 (R = Et, *i*-Pr, *i*-Bu) in ethyl ether or in benzene produces $RhHP_3$ in high yields (reactions 7 and 8). The best yields and the purest product were obtained when the $RhClP_3$ used had been purified as outlined in the Experimental Section. For R = *i*-Pr, propene, identified by its ^1H NMR spectrum, was isolated from the reaction mixture.

$$RhClP_3 + AlR_3 \rightarrow RhRP_3 + AlClR_2 \qquad (7)$$

$$RhRP_3 \rightarrow RhHP_3 + \text{olefin} \qquad (8)$$

In diethyl ether the reaction mixture was not homogeneous. The color of a saturated ether solution of $RhClP_3$ is light yellow and that of $RhHP_3$ is amber, yet after the solid $RhHP_3$ was filtered off following the completion of the reaction, the filtrate was a very dark orange. This indicated that there is some interaction between $AlClR_2$ and either $RhHP_3$ or unreacted $RhClP_3$, producing a species that is either highly colored or much more soluble than either $RhHP_3$ or $RhClP_3$.

The reaction in benzene using $AlEt_3$ produced both ethylene and small amounts of ethane, the latter arising by ortho metalation (reaction 9). The first step in the ortho-metalation sequence, oxidative addition of the ortho C–H bond to the metal, is apparently inhibited by coordinating solvents such as ethers, resulting in little or no ortho-metalated product, $Rh(P–C)P_2$. Keim found that $Rh(CH_3)P_3$ and $RhPhP_3$, isolated from ether solutions of $RhClP_3$ plus the appropriate Grignard reagent, decompose in aromatic solvents to give $Rh(P–C)P_2$ plus methane and benzene, respectively.[25] It has also been observed that the thermal stability (with respect to $Ir(P–C)P_2$ formation) of diethyl ether solutions of $Ir(CH_3)P_3$ is enhanced by the addition of THF or 1,4-dioxane.[29]



(9)

The IR spectrum of $Rh(P–C)P_2$ contains a medium-intensity band at 720 cm^{-1} in addition to bands normally attributable to coordinated triphenylphosphine. (A band in this region has frequently been attributed to the ortho metalation of a coordinated triphenylphosphine ligand, the original assignment having been made by Bennett[30] based on the analogy to IR spectra of ortho-disubstituted benzenes.[33] However, $O{=}PPh_3$, a common impurity in these very air-sensitive compounds, also displays a band in this region,[32] and care should be taken when making this assignment to ensure that the other bands due to $O{=}PPh_3$ are absent.)

The rate of formation of $Rh(P–C)P_2$ from $RhRP_3$ (R = CH_3, C_2H_5) was followed spectrophotometrically in benzene at 20 °C by monitoring the increase in absorbance of λ_{max} for the unique band at 382 nm in the visible spectrum of $Rh(P–C)P_2$. Solutions of $Rh(C_2H_5)P_3$ were prepared by treating solutions of $RhHP_3$ with two different partial pressures of ethylene, 230 and 840 mm (reaction 10). The reactions

$$RhHP_3 + C_2H_4 \rightleftharpoons Rh(C_2H_5)P_3 \qquad (10)$$

were found to be first order with respect to absorbance, and rate constants of 5.0×10^{-5} and 5.2×10^{-5} s^{-1} were obtained for experiments performed at 230 and 840 mm, respectively. The first-order rate constant determined from the experiment with $Rh(CH_3)P_3$ is 28×10^{-5} s^{-1}. The absence of an ethylene pressure dependence for the rate constant may be due to either (1) complete conversion of $RhHP_3$ to $Rh(C_2H_5)P_3$ under 230 mm of ethylene or (2) an inhibition due to excessive amounts of ethylene at 840 mm, similar to the inhibition of ortho metalation by ethereal solvents (reaction 11). The almost

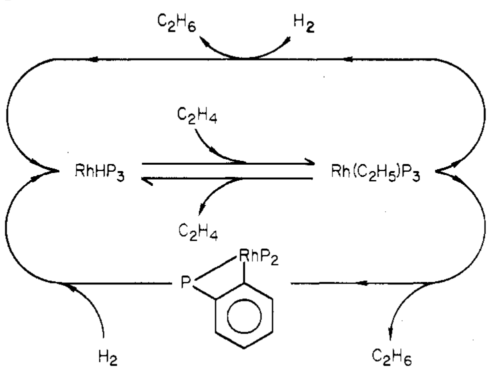
$$Rh(C_2H_5)P_3 \underset{}{\overset{C_2H_4}{\rightleftharpoons}} [Rh(C_2H_5)(C_2H_4)P_3] \qquad (11)$$

sixfold difference in the rate constants for the CH_3 and C_2H_5 complexes also may be due to one of two factors: (1) incomplete conversion to $Rh(C_2H_5)P_3$ or (2) a steric inhibition ($C_2H_2 > CH_3$) of the oxidative addition step. The present data do not permit choices to be made among these alternative explanations.

Ethylene Hydrogenation Catalysis by $RhHP_3$. Ethylene is convenient for this study of Lewis acid influenced hydrogenation because (1) the gaseous reactants and products allow the reaction to be followed in a simple manometer system, (2) the hydrogenation cannot be accompanied by isomerization, (3) olefin oligomerization can readily be detected manometrically (see Experimental Section), and (4) ethane can be readily removed after the reaction, allowing multiple trials with the same solution without a buildup of product.

It is now known[12,34] that ethylene hydrogenation catalyzed by $RhClP_3$ is very slow relative to other olefins because (1) the equilibrium constant for the formation of $RhCl(C_2H_4)P_2$ from $RhClP_3$ and ethylene is very large[12,35] and (2) $RhCl(C_2H_4)P_2$ reacts with hydrogen only very slowly.[12,14] In agreement with our previous hypothesis,[4] $RhHP_3$ is a much

Scheme I



more active catalyst than $RhClP_3$ for ethylene hydrogenation. This difference, a factor of 39 under our conditions, probably stems from the fact that ethylene does not form an unreactive complex with $RhHP_3$ (i.e., whatever the position of the equilibrium in reaction 10, it is obtained very rapidly). Apparently $RhH(C_2H_4)P_3$ undergoes rapid rearrangement, by insertion of the coordinated ethylene into the rhodium–hydrogen bond, to produce $Rh(C_2H_5)P_3$. It also is possible that the difference in rates between $RhHP_3$ and $RhClP_3$ is a function of the rapid intramolecular rearrangement of the phosphine ligands observed for $RhHP_3$ and postulated for $Rh(C_2H_5)P_3$.[22] The rhodium–ethyl complex can then add a molecule of hydrogen, forming ethane and regenerating $RhHP_3$ (reaction 12). It previously has been observed that

$$\mathrm{Rh(C_2H_5)P_3 + H_2 \rightarrow [RhH_2(C_2H_5)P_3] \rightarrow RhHP_3 + C_2H_6} \qquad (12)$$

hydrogen reacts with $Rh(CH_3)P_3$ and $RhPhP_3$ to form $RhHP_3$ plus methane or benzene, respectively, but in that study more severe conditions (650 psig hydrogen) were used.[25] Our data demonstrate that reaction 12 is rapid at subatmospheric pressures of hydrogen.

Since $Rh(P{-}C)P_2$ is formed from $RhHP_3$ and ethylene, it should also be formed in the hydrogenation experiments. If this complex could not reenter the catalytic cycle, the activity of the $RhHP_3$ solution would decrease with time. This is in fact not observed. When preformed $Rh(P{-}C)P_2$ is used as the catalyst, no induction period is observed and k_{obsd} is the same as for $RhHP_3$ (Table II). Thus, on the basis of the kinetic data, reaction 13 must be very rapid and must lie far to the right.

$$\mathrm{Rh(P{-}C)P_2 + H_2 \rightleftharpoons RhHP_3} \qquad (13)$$

Although $RhHP_3$ will exchange ortho hydrogens with deuterium,[36] implying that some amount of $Rh(P{-}C)P_2$ must be present in solutions of $RhHP_3$, ^{31}P NMR data also require that reaction 13 lies very far to the right.[37] Moreover, the visible spectrum of a solution of $Rh(P{-}C)P_2$ taken immediately after exposure to 230 mm of hydrogen was identical with the spectrum of $RhHP_3$, with no trace of a band at 382 nm. It is of interest to note that the available data suggest that the Rh–H bond enthalpy is at least 10 kcal/mol greater than the Rh–C bond enthalpy in $Rh(CH_3)P_3$.[38]

The data in Table IV indicate that the rate law for $RhHP_3$-catalyzed ethylene hydrogenation includes an ethylene dependence and a hydrogen dependence. We did not investigate these dependences, or any catalyst concentration dependence, in more detail.

A summary of the mechanism is shown in Scheme I. Under the conditions used here ethane production by the upper loop is ca. 4×10^3 times faster than by the lower loop for the first half-life. The small amount of $Rh(P{-}C)P_2$ that is formed reacts rapidly with hydrogen to reenter the catalytic cycle as $RhHP_3$. Note that phosphine dissociation, while certainly possible, is not required. An upper limit of 0.4% can be placed on the amount of $RhHP_2$ present, based on ^{31}P NMR data.[22] Evidence that phosphine dissociation may not be important for $RhHP_3$-catalyzed ethylene hydrogenation is that RhHL (L = a chelating triphosphine) is a good olefin hydrogenation catalyst while RhClL reacts irreversibly with hydrogen and exhibits no catalytic activity.[41] In contrast to our proposed mechanism for ethylene hydrogenation by $RhHP_3$, it is now widely accepted that $RhClP_3$-catalyzed olefin hydrogenation involves dissociation to produce $RhClP_2$ as the most active species in solution,[13,14] although $RhClP_2$ cannot be detected by colligative properties[42] or by spectroscopy.[14]

Ethylene Hydrogenation Catalysis by $RhClP_3$ + $AlEt_3$. Although $RhHP_3$ is formed from $RhClP_3$ and $AlEt_3$ (reactions 7 and 8), the mixture exhibits a lower initial rate for ethylene hydrogenation than when preformed $RhHP_3$ is used (experiment 3, Table III). The activity of this catalyst mixture also decreases as successive trials are performed, as outlined in the Experimental Section. Similar behavior is observed if the mixture $RhHP_3$ + $AlClEt_2$ is used as the catalyst. Furthermore, the limiting rate in experiment 3 is close to the value for $RhClP_3$.

Close inspection of the catalyst solution after experiment 3 showed that a small amount of precipitate had formed. The $^{31}P\{^1H\}$ NMR spectrum of the solution at 30 °C showed that $RhCl(C_2H_4)P_2$ was the major phosphine-containing species present (observed $\delta = 35.1$ (doublet), $J(\mathrm{Rh{-}P}) = 129$ Hz; lit.[14] $\delta = 35.7$ (doublet), $J(\mathrm{Rh{-}P}) = 128$ Hz in CH_2Cl_2). In experiment 5 the catalyst mixture $RhHP_3$ + $AlClEt_2$ was stirred under 600 mm of hydrogen for 39 h. The solution was then degassed by three successive freeze (−196 °C)–pump–thaw cycles. This catalyst solution showed a lower initial rate than the same solution without hydrogen pretreatment. The same behavior was observed when the hydrogen was passed through a column of molecular sieves (Linde 4A) at −78 °C to ensure the removal of adventitious water. If the $RhHP_3$ + $AlClEt_2$ solution is pretreated with ethylene, the initial rate is the same as that observed without the ethylene pretreatment. When $RhClP_3$ and $AlEt_3$ react in benzene on a preparative scale (0.14 g of $RhClP_3$ in ca. 50 mL of benzene) under a hydrogen atmosphere (i.e., hydrogen was bubbled through the solution overnight), a pale orange solid is isolated. The IR spectrum of this product is different from that of $RhHP_3$ but is identical with the IR spectrum of $[RhClP_2]_2$.

The above observations taken together provide convincing evidence that while reactions 7 and 8 represent the initial interaction between $RhClP_3$ and $AlEt_3$, under hydrogenation conditions there is a slow conversion back to Rh–Cl containing species. Because of the complexity and sensitivity of this system (we were unable to obtain reproducible results for experiments 3–5 in Table III) we did not attempt to study the mechanism of this unusual reaction sequence. We speculate that reactions 14–16 might account for the behavior observed

$$\mathrm{AlClEt_2 \xrightarrow{RhHP_3,\ H_2} AlClH_2 + 2C_2H_6} \qquad (14)$$

$$\mathrm{3AlClH_2 \rightleftharpoons 2AlH_3\downarrow + AlCl_3} \qquad (15)$$

$$\mathrm{AlCl_3 + RhHP_3 \rightarrow AlCl_2H + RhClP_3} \qquad (16)$$

in our system. It has been reported that certain Ziegler-type catalysts will catalyze the hydrogenation of $AlEt_3$ to $AlHEt_2$, although much more severe conditions (60 °C, 10 atm of H_2) were used.[43]

Ethylene Hydrogenation Catalysis by $RhHP_4$. Under our conditions $RhHP_4$ is only half as active as $RhHP_3$ as an ethylene hydrogenation catalyst (Table II). One interpretation of these data is that $RhHP_4$ has lost a phosphine ligand to give a 50:50 mixture of $RhHP_4$ and $RhHP_3$ (reaction 17). The

$$\mathrm{RhHP_4 \xrightleftharpoons{K_{17}} RhHP_3 + P} \qquad (17)$$

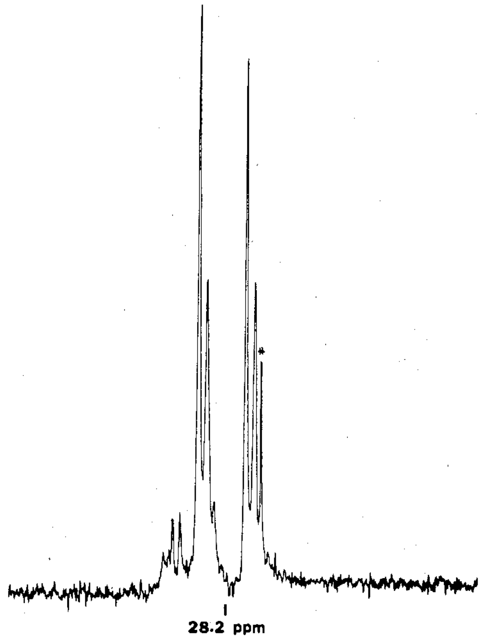
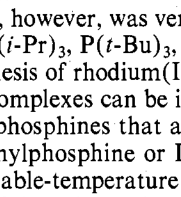


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of $RhH(PPh_3)_4$ in toluene-d_8 at −78 °C. H_0 increases to the right. The resonance marked with an asterisk is due to a ca. 3% triphenylphosphine oxide impurity. A resonance due to free triphenylphosphine (ca. 1.5%) is off the scale of the figure to the right at −8.6 ppm.

active catalytic species is still $RhHP_3$, and hydrogenation would proceed as outlined in Scheme I. In an earlier study of $RhHP_4$-catalyzed 1-hexene hydrogenation the kinetic data were interpreted in terms of $RhHP_2$ being the major rhodium-containing species in solution (reaction 18).[44] The ex-

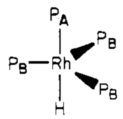
$$RhHP_3 \overset{K_{18}}{\rightleftharpoons} RhHP_2 + P \tag{18}$$

tensive phosphine dissociation was supported by molecular weight measurements at 38 °C. However, molecular weight measurements of high molecular weight phosphine complexes are known to be extremely sensitive to small amounts of oxygen,[45] and in a recent ^{31}P NMR study it was found that at most 0.4% of $RhHP_2$ is present in solutions of $RhHP_3$ at 30 °C.[22] This places an upper limit on K_{18} of ca. 10^{-4} M at 30 °C. The kinetics of $RhH(DBP)_4$ (DBP = 5-phenyl-5*H*-dibenzophosphole, **2**) catalyzed 1-hexene hydrogenation also were interpreted in terms of $RhH(DBP)_3$ being present in substantial amounts.[46] Dissociation to the bis(phosphine) complex $RhH(DBP)_2$, however, was very slight. When bulky phosphines such as $P(i\text{-}Pr)_3$, $P(t\text{-}Bu)_3$, or $P(cyclohexyl)_3$ are employed in the synthesis of rhodium(I) hydrides, $RhHL_2$ (L = bulky phosphine) complexes can be isolated.[47] Apparently K_{18} can be large for phosphines that are more sterically demanding than triphenylphosphine or DBP.



2

We studied the variable-temperature $^{31}P\{^1H\}$ NMR spectra of $RhHP_4$ in toluene-d_8 in order to determine the rate and the extent of reaction 17. The spectrum at −78 °C (Figure 2) is an AB_3X pattern of a double doublet and a less intense double multiplet, which is consistent with the known C_{3v} (distorted trigonal bipyramid) solid-state structure,[48] **3** ($\delta(P_A)$ = 31.7 (double multiplet), $J(Rh\text{–}P_A)$ = 113 Hz, $J(P_A\text{–}P_B)$ = 27 Hz; $\delta(P_B)$ = 28.2 (double doublet), $J(Rh\text{–}P_B)$ = 162 Hz). Triphenylphosphine oxide (ca. 3%) and triphenylphosphine (ca. 1.5%) are present in small amounts. As the temperature is raised, the spectrum broadens appreciably with the concomitant loss of all coupling. At 0 °C the spectrum is featureless (i.e., no spectrum is observed) and shows no change up to 80 °C, the highest temperature used in this study. This behavior is indicative of an intermolecular process that exchanges the triphenylphosphine ligands with free dissociated phosphine. Proof that the trace of free phosphine is not catalyzing this exchange is provided by the variable-temperature spectra of a 50:50 mixture of $RhHP_3$ and $RhHP_4$. At −78 °C the spectrum shows distinct peaks for $RhHP_3$[22] and for $RhHP_4$ (with no trace of free phosphine). At 30 °C no spectrum is observed, whereas the spectrum of $RhHP_3$ at 30 °C is normally a doublet.[22] Thus, in this experiment $RhHP_3$ must be exchanging with free phosphine that has dissociated from $RhHP_4$.



3

Although we cannot estimate K_{17} from the NMR data, we can estimate the rate of this phosphine dissociation. Assuming that at 20 °C the spectrum is at or near the coalescence point, the rate of phosphine exchange can be calculated from standard equations[49] to be ca. 4×10^3 s^{-1}. Under our conditions the initial turnover rate for $RhHP_4$-catalyzed ethylene hydrogenation is 4.4×10^{-2} turnover s^{-1}. Thus, phosphine dissociation is fully 5 orders of magnitude faster than ethylene hydrogenation and cannot be the rate-determining step for the $RhHP_4$-catalyzed reaction.

Despite the NMR evidence for phosphine dissociation from $RhHP_4$, none of the Lewis acids we employed enhanced the k_{obsd} for $RhHP_4$ (Table II). The relatively weak acids $AlEt_3$ and BMe_3 had no significant effect on k_{obsd} even when a 1:5 rhodium:acid ratio was used. Ethylene hydrogenation catalyzed by $RhHP_4$ in a 0.73 M benzene solution of $AlEt_3$ was extremely slow. Stronger Lewis acids only caused rate inhibition, possibly due to metal center adduct formation (reaction 1) or hydride-bridged adduct formation (reaction 2). The former, common for rhodium(I) complexes,[15] would block potential coordination sites and would withdraw electron density from the rhodium center, making the oxidative addition of hydrogen less likely. The latter would inhibit the insertion of ethylene into the rhodium–hydrogen bond. This has been observed for a niobium–hydride–$AlEt_3$ adduct.[50]

Aluminum compounds are known to undergo metathesis reactions (reaction 5) with rhodium compounds.[51] The rate inhibition due to $AlCl_3$ might possibly arise by reaction 19 (see

$$RhHP_4 + AlCl_3 \rightarrow RhClP_3 + AlCl_2H + P \tag{19}$$

also reactions 14–16). Boron trichloride completely inhibits the catalytic activity of $RhHP_4$. However, 0.5 equiv of BCl_3 interacts with more than 0.5 equiv of $RhHP_3$ in the $RhHP_3 + 0.5BCl_3$ experiment because k_{obsd} for that experiment is much less than $0.5k_{obsd}$ for $RhHP_3$. The reaction of BCl_3 with group 8 metal hydrides leads to the formation of $M\text{–}BCl_2$ bonds with the liberation of HCl (reaction 20).[52] The 0.5

$$M\text{–}H + BCl_3 \rightarrow M\text{–}BCl_2 + HCl \tag{20}$$

equiv of HCl liberated would add to the remaining 0.5 equiv of $RhHP_3$ (reaction 21). Note that k_{obsd} for $RhHP_3 + 0.5BCl_3$

$$RhHP_3 + HCl \rightarrow RhH_2ClP_3 \rightleftharpoons RhClP_3 + H_2 \tag{21}$$

is roughly half that of $RhClP_3$. A similar sequence of reactions is predicted for $SnCl_4$.

The foregoing work demonstrates that there are sites on rhodium(I) hydrides that are more basic than triphenylphosphine toward common Lewis acids. The difficulty in promoting phosphine dissociation underscores the earlier observation[4] that a myriad of reactions may occur when catalyst complexes and Lewis acids are mixed together. A very careful choice of each component will be necessary to achieve a desired effect.

Acknowledgment. This work was supported by a grant from the National Science Foundation. The authors wish to thank Professor R. G. Pearson and Dr. F. N. Tebbe for enlightening discussions, Professor T. J. Marks for the loan of Yb(η^5-C_5H_5)$_3$, and Professor D. R. Greig for assistance in computer programming.

Registry No. C_2H_4, 74-85-1; $RhClP_3$, 14694-95-2; $(RhClP_2)_2$, 14653-50-0; $RhHP_3$, 16973-49-2; Rh(P-C)P_2, 20692-58-4; $RhHP_4$, 18284-36-1; $AlEt_3$, 97-93-8; BCl_3, 10294-34-5; $AlPh_3$, 841-76-9; $AlCl_3$, 7446-70-0; BMe_3, 593-90-8; BF_3, 7637-07-2; Yb(η^5-C_5H_5)$_3$, 1295-20-1; $AlClEt_2$, 96-10-6.

References and Notes

(1) (a) C. A. Eaborn, N. Farrell, and A. Pidcock, *J. Chem. Soc., Chem. Commun.*, 766 (1973); (b) R. G. Miller et al., *J. Am. Chem. Soc.*, **96**, 4211, 4221, 4235 (1973).

(2) (a) M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Am. Chem. Soc.*, **85**, 4014 (1963); (b) M. Hidai, T. Kuse, T. Hikita, Y. Uchida, and A. Misono, *Tetrahedron Lett.*, 1715 (1970).

(3) (a) W. B. Hughes, U.S. Patent No. 3 697 615 (1972); (b) W. B. Hughes, personal communication.

(4) R. A. Porter and D. F. Shriver, *J. Organomet. Chem.*, **90**, 41 (1975).

(5) (a) R. G. Miller, T. J. Kealy, and A. L. Barney, *J. Am. Chem. Soc.*, **89**, 3756 (1967); (b) M. Iwamoto and S. Yuguchi, *Chem. Commun.*, 28 (1968); (c) J. R. Jones, *J. Chem. Soc. C*, 1117 (1971); (d) J. R. Jones and T. J. Symes, *ibid.*, 1124 (1971); (e) K. Maruga, T. Mizoroki, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, **43**, 3630 (1971); (f) K. Maruyama, T. Kuroki, T. Mizoruki, and A. Ozaki, *ibid.*, **44**, 2002 (1972); (g) K. Fischer, K. Jones, P. Misbach, R. Stabba, and G. Wilke, *Angew. Chem., Int. Ed. Engl.*, **12**, 943 (1973); (h) G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **14**, 104 (1975).

(6) For recent reviews see J. C. Mol and J. A. Moulijn, *Adv. Catal.*, **24**, 131 (1975), and N. Calderon, E. A. Ofstead, and W. A. Judy, *Angew. Chem., Int. Ed. Engl.*, **15**, 401 (1976).

(7) W. C. Drinkard, Jr., U.S. Patent No. 3 655 723 (1972).

(8) B. W. Taylor and H. E. Swift, *J. Catal.*, **26**, 254 (1972).

(9) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Am. Chem. Soc.*, **88**, 4890 (1966).

(10) M. Ennis and A. R. Manning, *J. Organomet. Chem.*, **116**, C31 (1976).

(11) (a) D. F. Shriver, *Acc. Chem. Res.*, **3**, 231 (1970); (b) *J. Organomet. Chem.*, **94**, 259 (1975).

(12) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(13) J. Halpern and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 629 (1973).

(14) C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).

(15) D. D. Lehman and D. F. Shriver, *Inorg. Chem.*, **13**, 2203 (1974).

(16) D. F. Shriver, "The Manipulation of Air-sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.

(17) H. Lehmkuhl, *Justus Liebigs Ann. Chem.*, **719**, 40 (1968).

(18) (a) R. N. Scott, D. F. Shriver, and D. D. Lehman, *Inorg. Chim. Acta*, **4**, 73 (1969); (b) J. S. Kristoff and D. F. Shriver, *Inorg. Chem.*, **13**, 499 (1974).

(19) W. Keim, *J. Organomet. Chem.*, **8**, P25 (1967).

(20) B. Ilmaier and R. S. Nyholm, *Naturwissenschaften*, **56**, 415, 636 (1969).

(21) (a) S. E. Diamond, Abstracts, 174th National Meeting of the American Chemical Society, Chicago, Ill., 1977, No. INOR 77; (b) S. E. Diamond and F. Mares, *J. Organomet. Chem.*, **142**, C55 (1977).

(22) S. H. Strauss, S. E. Diamond, F. Mares, and D. F. Shriver, *Inorg. Chem.*, preceding paper in this issue.

(23) Triphenylphosphine oxide (O=PPh_3) was not detected in the $^{31}P\{^1H\}$ NMR spectrum of $RhHP_3$ in toluene-d_8 at −78 °C.[22] Under these conditions δ(O=PPh_3) = 24.5 (downfield from 85% H_3PO_4 at 30 °C). From the signal-to-noise ratio an upper limit of 0.2% can be placed on the percent total phosphorus that is present as O=PPh_3.

(24) K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, **7**, 546 (1968).

(25) W. Keim, *J. Organomet. Chem.*, **14**, 179 (1968).

(26) J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, **10**, 67 (1967).

(27) The solubility of ethylene in benzene at 20 °C is reported to be 3.6 mL of ethylene (at 20 °C and 760 mm)/mL of benzene at 760 mm partial pressure ethylene (ref 28). Assuming that Henry's law is valid under these conditions the solubility can be extrapolated to 0.94 mL of ethylene (20 °C, 760 mm)/mL of benzene at 200 mm of ethylene. The measured solubility at 200 mm of ethylene was 0.78 mL of ethylene (20 °C, 760 mm)/mL of benzene.

(28) A. Seidell, "Solubilities of Organic Compounds", Vol. 2, 3rd ed, Van Nostrand, New York, N.Y., 1941.

(29) J. Schwartz and J. B. Cannon, *J. Am. Chem. Soc.*, **94**, 6228 (1972).

(30) M. A. Bennett and D. L. Milner, *Chem. Commun.*, 581 (1967).

(31) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 3rd ed, Chapman and Hall, London, 1975, p 87.

(32) The four strongest bands in the IR spectrum of O=PPh_3 are 1193, 1122, 721, and 542 cm^{-1}.[33]

(33) G. B. Deacon and J. H. S. Green, *Spectrochim. Acta, Part A*, **24**, 845 (1968).

(34) J. P. Candlin and A. R. Oldham, *Discuss. Faraday Soc.*, **46**, 60 (1968).

(35) The fact that $RhClP_3$ and $[RhClP_2]_2$ exhibit the same k_{obsd} under our conditions supports Tolman's observations[14] that both complexes are nearly completely converted to $RhCl(C_2H_4)P_2$ under 0.3 atm of ethylene, although in that work it was found that the rate was higher when the Rh was originally present as the dimer.

(36) W. Keim, *J. Organomet. Chem.*, **19**, 161 (1969).

(37) No trace of any complex other than $RhHP_3$ is observed in the $^{31}P\{^1H\}$ NMR spectrum of $RhHP_3$, even when the NMR tubes are sealed under vacuum.[22]

(38) The experimental data demonstrate that for R = H the equilibrium

$$RhRP_3 \overset{K}{\rightleftharpoons} Rh(P\text{–}C)P_2 + RH$$

lies far to the left but that for R = CH_3 or Ph it lies far to the right.[39] If one assumes the conservative values $K = 10^{-2}$ (R = H) and $K = 10^2$ (R = CH_3), then $\Delta G(R = H) - \Delta G(R = CH_3) \approx -5$ kcal/mol. The H–H bond enthalpy is also ca. 5 kcal/mol greater than an average C–H bond enthalpy.[40] If ΔS for the equilibrium is assumed to be the same for R = H and R = CH_3 and if any steric contributions to the ΔG values are assumed to be small, than a lower limit of ca. 10 kcal/mol can be placed on the difference between the Rh–H and Rh–C bond enthalpies.

(39) (a) See ref 25. (b) This work.

(40) F. T. Wall, "Chemical Thermodynamics", 3rd ed, Freeman, San Francisco, Calif., 1974, p 63.

(41) D. L. Dubois and D. W. Meek, *Inorg. Chim. Acta*, **19**, L29 (1976).

(42) D. D. Lehman, D. F. Shriver, and I. Wharf, *Chem. Commun.*, 1486 (1970).

(43) K. S. Minsker, V. I. Biryukov, A. I. Graevskii, and G. A. Razuraev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 572 (1963).

(44) (a) J. Hjortkjaer, Abstracts, 166th National Meeting of the American Chemical Society, Chicago, Ill., 1973, No. INDE 10; (b) J. Hjortkjaer, *Adv. Chem. Ser.*, **No. 132**, 133 (1974).

(45) See ref 42 and references therein.

(46) (a) D. E. Budd, D. G. Holah, A. N. Hughes, and B. C. Hui, *Can. J. Chem.*, **52**, 775 (1974); (b) D. G. Holah, I. M. Hoodless, A. N. Hughes, B. C. Hui, and D. Martin, *ibid.*, **52**, 3758 (1974).

(47) S. Otsuka, personal communication.

(48) R. W. Baker and P. Pauling, *Chem. Commun.*, 1495 (1969).

(49) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, Chapter 10.

(50) F. N. Tebbe, *J. Am. Chem. Soc.*, **95**, 5412 (1973).

(51) See ref 4 and reaction 7.

(52) G. Schmid, *Angew. Chem., Int. Ed. Engl.*, **9**, 819 (1970).