Experimental Section

Materials. RhCl(PPh$_3$)$_3$[6] and dioxene[12] were prepared by the methods previously reported. *Olefins and ethers were purified by* distillation over metallic sodium. Alcohols were dried with molecular sieves after distillation. Amines, except for piperadine, were distilled. Piperadine was recrystallized from benzene. Tetralin and all solvents were purified by distillation and dried by usual methods. The compounds corresponding to the dehydrogenation products, excluding dioxene, were purchased and purified by distillation.

Transfer Hydrogenation in Excess Hydrogen Donor. Cycloheptene (48.1 mg, 0.50 mmol) or cyclopentene (34.1 mg, 0.50 mmol) and RhCl(PPh$_3$)$_3$ (18.5 mg, 0.02 mmol) were put into a Pyrex glass tube which had been sealed at one end. Into the mixture, an organic compound, which serves both as a hydrogen donor and a solvent, was added, and the total volume of the solution was made 1.0 ml. The tube was sealed under vacuum after two freeze–pump–thaw cycles at 10^{-2} Torr on a vacuum line with liquid nitrogen. The sealed tube was heated for 1 hr in the silicone-oil bath kept at 190 ± 1°. The reaction mixture was submitted to glc analysis which was performed at 90° for cycloheptene or at 50° for cyclopentene with Hitachi K 53 equipped with a flame-ionization detector, using 25 µl of cyclohexane as an internal standard. A 2 m × 6 mm stainless steel column packed with 25% of 1,2,3-tris(2'-cyanoethoxy)propane on Celite 545 was used. The detection and identification of dehydrogenation products were tried using various columns.

An Example of Stoichiometric Transfer Hydrogenation in a Solvent. Cycloheptene (48.1 mg, 0.50 mmol), indoline (59.5 mg, 0.50 mmol), and RhCl(PPh$_3$)$_3$ (9.3 mg, 0.01 mmol) were put into a Pyrex glass tube sealed at one end and the total volume of the solution was made 1.0 ml by the addition of toluene as a solvent. The tube, sealed by the method described above, was heated in a silicone-oil bath kept at 170 ± 1° for 1 hr. Though the catalyst dissolved slowly at room temperature, it dissolved at once at the elevated temperature. The reaction mixture was submitted to glc analysis. The amounts of cycloheptane and cycloheptene were measured using the column described above, and the amounts of

indole and indoline were measured using a 1 m × 6 mm stainless steel column packed with 25% of Silicone GE SE-30 on Celite 545. In the latter, *n*-tetradecane was used as an internal standard.

Other transfer hydrogenations were carried out in a similar way.

An Example of Kinetic Runs. Six reaction samples, prepared by the method described above, were heated in the silicone-oil bath kept at 150 ± 1° for 10, 20, 30, 40, 50, and 60 min. The reaction mixtures were submitted to glc analysis.

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Transfer Hydrogenation and Transfer Hydrogenolysis. VI. The Mechanism of Hydrogen Transfer from Indoline to Cycloheptene Catalyzed by Chlorotris(triphenylphosphine)rhodium(I)

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The mechanism of hydrogen transfer from indoline to cycloheptene in toluene catalyzed by RhCl(PPh$_3$)$_3$ has been studied. The rate data of the reaction can be accommodated by the rate expression of the form, rate = a[D][C]$_0$/(b + [L]) where [C]$_0$, [D], and [L] are the concentration of the catalyst, indoline, and triphenylphosphine, respectively. The rate-determining step of the reaction is inferred to be the dehydrogenation of indoline, that is, the hydrogen transfer from the amine to a Rh(I) complex to form a hydride complex by oxidative addition.

In the previous paper,[1] we have reported that in hydrogen transfer from organic compounds to olefins catalyzed by RhCl(PPh$_3$)$_3$, some cyclic amines, such as indoline, pyrrolidine, tetrahydroquinoline, and piperidine, have much higher hydrogen-donating ability than ethers, hydroaromatic compounds, and most alcohols. This study was undertaken to investigate the mechanism of the hydrogen transfer from amines to olefins catalyzed by RhCl(PPh$_3$)$_3$.

Results and Discussion

Indoline was used as a hydrogen donor because the amine had the highest hydrogen-donating ability and gave the dehydrogenation product, indole, stoichiometrically.

Cycloheptene and toluene were used as a hydrogen acceptor and a solvent, respectively.

Dependence on the Catalyst Concentration. It has been reported that RhCl(PPh$_3$)$_3$ dimerizes to the inactive species, [RhCl(PPh$_3$)$_2$]$_2$, during the reduction by molecular hydrogen in benzene and that the rate is expressed in the form: $R = \alpha'[\text{RhCl(PPh}_3)_3] - \beta'[\text{RhCl(PPh}_3)_3]_2$ in which α' and β' are constants and the second term is due to the deactivation of the catalyst by dimerization.[2] However, in the region where the catalyst concentration was higher than 1.0 × 10^{-3} *M*, the initial rate of the transfer hydrogenation had first-order dependence on the catalyst concentration and was expressed in the form: $R =$
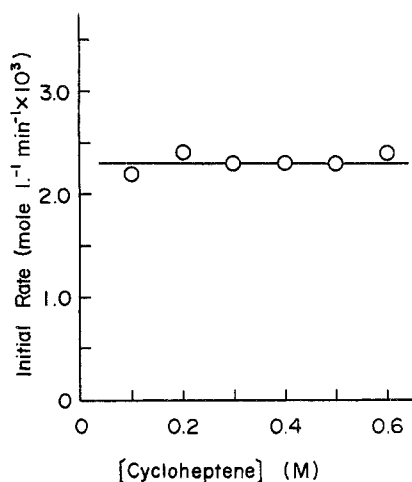
Figure 1. Dependence of the initial rate on the concentration of cycloheptene. Cycloheptene, indoline (0.25 M), and RhCl(PPh$_3$)$_3$ (0.01 M) in toluene were heated at 160°.
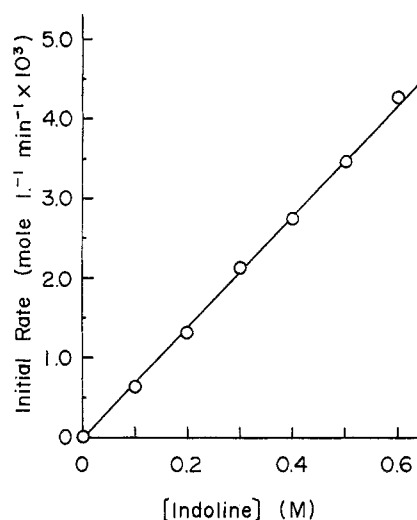

Figure 2. Dependence of the initial rate upon the concentration of indoline. Cycloheptene (0.30 M), indoline, and RhCl(PPh$_3$)$_3$ (0.006 M) in toluene were heated at 160°.

Table I
Dependence of the Initial Rate on the Concentration of Catalysts[a]

[Rh],[b] 1. mol^{-1} x 10^3	Rate, 1. mol^{-1} min x 10^3	
	RhCl(PPh$_3$)$_3$	[RhCl(PPh$_3$)$_2$]$_2$
1.0	0.3	
1.5	0.7	
2.0	1.0	1.3
4.0	1.9	2.8
6.0	2.9	3.9
8.0	3.7	5.0

[a] Cycloheptene (0.30 M), indoline (0.25 M), and a catalyst in toluene were heated at 160°. [b] In the case of [RhCl(PPh$_3$)$_2$]$_2$, [Rh] is twice the concentration of [RhCl(PPh$_3$)$_2$]$_2$.

α[RhCl(PPh$_3$)$_3$], in which α is a constant, as shown in Table I. This suggests the absence of the deactivation of the catalyst by the dimerization and may be rationalized by the assumption that in the presence of indoline, the chloro bridges of the binuclear complex are cleaved by the amine. This assumption is supported by the fact that in this transfer hydrogenation, the catalytic activity of [RhCl(PPh$_3$)$_2$]$_2$ is higher than that of RhCl(PPh$_3$)$_3$ even at the same concentration of rhodium atom in the solution, as shown in Table I.

Dependence of the Olefin Concentration. It has been reported that the influence of the olefin concentration on the rate is rather complicated in the reduction by molecular hydrogen in which the rate-limiting step is the coordination of an olefin to the dihydride complex, RhH$_2$Cl-(PPh$_3$)$_2$ (solvent), by replacing a solvent molecule.[2,3] However, as seen from Figure 1, the initial rate of the transfer hydrogenation was independent on the olefin concentration, as in the transfer hydrogenation in dioxane.[4] This may correspond to the fact that the rate of this reaction system is hardly influenced by the kind of cyclic monoenes whose coordinating power differs a little.[1] The zero-order dependence may be interpreted either by the assumption that the olefin coordinates to the metal of the catalyst after the rate-determining step or by the assumption that the olefin coordinates so completely as to show a leveling effect as it does before the rate-limiting step. The former assumption seems to be more plausible, because the complexing power of internal monoenes on the phosphine catalyst is weak,[2,3] no olefin complex was detected in this system, and
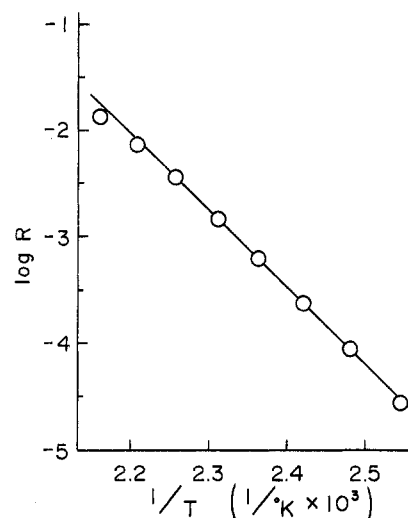

Figure 3. Arrhenius plot of the transfer hydrogenation at 120, 130, 140, 150, 160, 170, 180, and 190°. Cycloheptene (0.30 M), indoline (0.25 M), and RhCl(PPh$_3$)$_3$ (0.006 M) were heated in toluene.

the results in the transfer hydrogenation in dioxane accorded with the former assumption.[4]

Dependence on the Donor Concentration. As shown in Figure 2, the initial rate of the reduction has first-order dependence upon the concentration of indoline. Upon this result, it may be guessed that the coordination of indoline occurs before the rate-determining step and the coordinating power is not so strong as to show a leveling effect. The supposition is supported by the fact that no indoline complexes were isolated even from indoline solution.

Dependence on Temperature. Initial rates were measured at the temperatures ranging from 120 to 190° and a plot of log R against $1/T$ is shown in Figure 3. A good linear plot is obtained, indicating that the kinetics of the system are not so complicated. From Figure 3, a value for the activation energy, E_a, of 33.2 kcal mol^{-1} is obtained; ΔH^* is 32.0 kcal mol^{-1} and ΔS^* is 10.2 eu.

Effect of Added Phosphine. The reduction rate was decreased by the addition of excess triphenylphosphine to the reaction system, as in the case of the reduction by molecular hydrogen,[2,3] although such addition effect of the phosphine was not observed in the transfer hydrogenation in dioxane.[4] The plot of the reciprocal of the rate against the
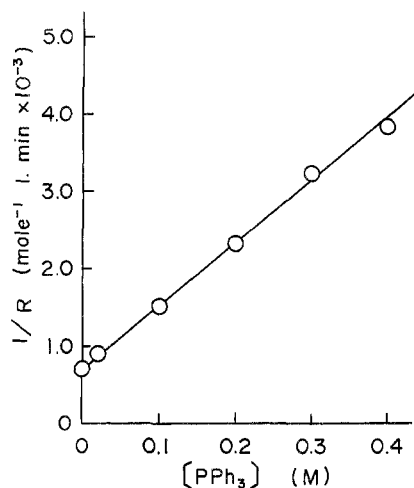
Figure 4. Dependence of the initial rate on the added triphenylphosphine. Cycloheptene (0.30 *M*), indoline (0.25 *M*), RhCl(PPh₃)₃ (0.005 *M*), and triphenylphosphine were heated in toluene at 160°.

**Table II
Dependence of Initial Rates on Ratio of
Phosphine to Rhodium[a]**

PPh₃/Rh	Initial rate, mol l.$^{-1}$ min^{-1} x 10^4
0	180[b]
1	22
2	37
3	31
4	22
5	21

[a] Cyclopentene (0.50 *M*), indoline (0.50 *M*),[RhCl(cyclooctene)₂]₂ (0.0025 *M*), and triphenylphosphine were heated at 160° in toluene. [b] A metallic mirror was formed.

added phosphine concentration is linear with a positive intercept on the *y* axis, as shown in Figure 4. The relation is expressed in the form $1/R = a[\text{PPh}_3] + b$, in which *a* and *b* are constants. From Figure 4, 8×10^3 mol^{-2} l.^{2} min and 7×10^2 mol^{-1} l. min were obtained as the values of *a* and *b*, respectively. From these values the dissociation constant of the catalyst was derived as described later.

Further, we examined the catalytic activity of [RhCl(cyclooctene)₂]₂ to which various amounts of triphenylphosphine were added, and the result summarized in Table II shows that the maximum rate appeared when the ratio of the phosphine to rhodium was equal to two. It is inferred from the appearance of the maximum rate and the depressing effect of the added phosphine that the coordinating power of indoline which is a sterically hindered aromatic amine is not so strong and the amine competes with triphenylphosphine for a vacant coordination site of an intermediate which is formed by the release of a triphenylphosphine from RhCl(PPh₃)₃ and has two triphenylphosphines. The inference is supported by the fact that no indoline complex was isolated even by heating the catalyst in indoline.

Effect of Added Indole. As seen from Figure 5 the addition of the dehydrogenation product, indole, made the rate increase. It may be explained either by the assumption that indole has the ability to donate hydrogen or by the one that indole shows such solvent effect as increases the reaction rate by the appropriate coordinating ability as the halogenated benzenes. The former assumption is denied by the fact
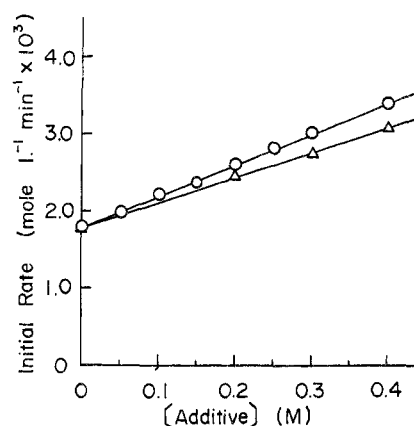
Figure 5. Effect of the added indole and chlorobenzene. Cycloheptene (0.30 *M*), indoline (0.25 *M*), and RhCl(PPh₃)₃ (0.005 *M*) in toluene were heated at 160° along with indole (O) or chlorobenzene (△).
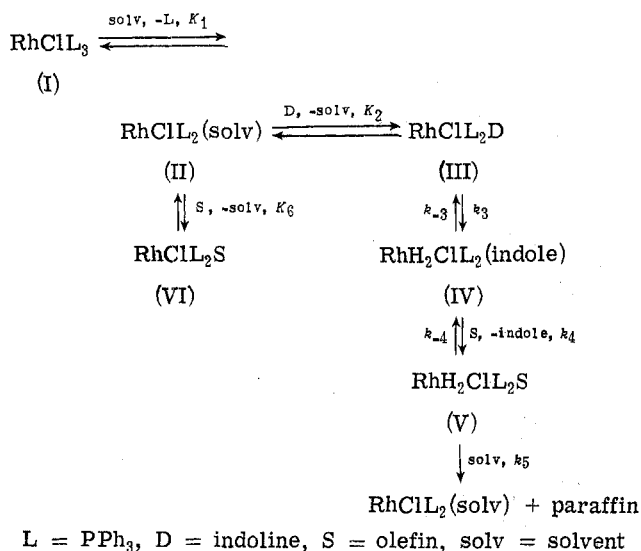
that the transfer hydrogenation never proceeded when indole was used as a hydrogen source. The latter one seems to be supported by the result that the effect of the added chlorobenzene was similar to that of indole, as shown in Figure 5. The promoting effect of indole seems to show also that the aromatized amine is no longer hydrogenated to indoline, so it does not compete with the olefin.

Catalytic Activity of [RhCl(PPh₃)₂]₂. Though the dimerization of RhCl(PPh₃)₃ inhibits the reduction by molecular hydrogen,[2] in this transfer hydrogenation using indoline the catalytic activity of [RhCl(PPh₃)₂]₂ was greater than that of RhCl(PPh₃)₃ even in the same rhodium concentration, as shown in Table I. This may be compatible with the observation that the transfer hydrogenation was faster at the phosphine–rhodium ratio of 2 than at the ratio of 3, as seen in Table II.[5] The results suggest that in the presence of indoline, the dimer decomposes at the reaction temperature to give RhCl(PPh₃)₂L′, in which L′ represents a solvent, a hydrogen donor, or an olefin molecule.

Attempt to Isolate Reaction Intermediates. Complexes coordinated by indoline were obtained neither from the reaction mixtures nor from the indoline solution which was heated at 80° and cooled. The complex obtained in both cases contained no nitrogen and showed the elemental analysis and the ir and the nmr spectrum which may be due to the mixture of RhCl(PPh₃)₃ and [RhCl(PPh₃)₂]₂. In the reactions in which [RhCl(PPh₃)₂]₂ was used, the original binuclear complex was recovered and no indoline complex was obtained. These results may be interpreted by the assumption that the coordinating ability of indoline is not so great because the aromatic amine does not have as strong basicity as alkyl amines and has rather large steric hindrance. However, yellow needles were obtained from RhCl(PPh₃)₃ or [RhCl(PPh₃)₂]₂ in pyrrolidine, which has greater basicity and lesser steric hindrance, and gave the elemental analysis and the ir and the nmr spectrum explainable by RhCl(PPh₃)₂(pyrrolidine). Perhaps this complex may be a reaction intermediate in the transfer hydrogenation by pyrrolidine.

Kinetic Discussion

The reduction,[2,3,6] the isomerization,[7] and the hydrogen–deuterium exchange[8] of olefins under hydrogen atmosphere catalyzed by RhCl(PPh₃)₃ have been studied in detail by many researchers. Based on the studies of these reactions, the transfer hydrogenation in dioxane,[4] and the results described earlier, we should like to propose the following reaction scheme for the transfer hydrogenation.

$$RhClL_3 \xrightleftharpoons[]{\text{solv, -L, } K_1}$$

(I)

$$RhClL_2(\text{solv}) \xrightleftharpoons[]{D, \text{ -solv, } K_2} RhClL_2D$$

(II)   (III)

$$\updownarrow \text{ S, -solv, } K_6 \qquad k_{-3} \updownarrow k_3$$

$$RhClL_2S \qquad\qquad RhH_2ClL_2(\text{indole})$$

(VI)   (IV)

$$k_{-4} \updownarrow \text{ S, -indole, } k_4$$

$$RhH_2ClL_2S$$

(V)

$$\downarrow \text{solv, } k_5$$

$$RhClL_2(\text{solv}) + \text{paraffin}$$

L = PPh$_3$, D = indoline, S = olefin, solv = solvent

In spite of the report that RhCl(PPh$_3$)$_3$ scarcely releases a triphenylphosphine at room temperature in rigorously oxygen-free benzene although even a trace of oxygen intensely promotes the dissociation,[9] we introduced the species, RhClL$_2$(solvent), based on the following grounds: (1) the kinetic expressions derived from the schemes which do not involve the intermediate cannot explain the experimental results obtained;[10] (2) the fact that RhCl-(PPh$_3$)$_2$(solvent) is isolated from dioxane,[4] acetonitrile,[2] or pyridine[2] solution suggests that RhCl(PPh$_3$)$_2$(toluene) also exists in toluene solution; (3) the dissociation of RhCl(PPh$_3$)$_3$ may be considered to be easier at the elevated temperatures at which the transfer hydrogenation was carried out than at room temperature.

Based on the proposed reaction scheme and the assumptions described later, the rate, R, is expressed as follows

$$R = \frac{k_3 K_1 K_2 [D][C]_0}{[L] + K_1 + K_1 K_2 [D] + K_1 K_6 [S]} \quad (1)$$

where k_3 is a rate constant, K_1, K_2, and K_6 are equilibrium constants, $[C]_0$ is the total concentration of rhodium species, and $[D]$, $[L]$, and $[S]$ are the concentration of the hydrogen donor, triphenylphosphine, and the olefin, respectively. The assumptions used are (1) the intermediates, IV and V, are so unstable and exist in so small a concentration that the steady state treatment is applicable to them, and (2) indole is not hydrogenated, that is, k_{-3} is zero. The former assumption is supported by the fact that hydride olefin complexes are intermediates in the hydrogenation by molecular hydrogen which occurs under milder conditions; so the hydrogen transfer to olefins in the intermediates is considered to be fast. The latter assumption also seems to be not so unreasonable by the fact that indole is an aromatized product and the addition of indole to the reaction system did not show the decrement of the reaction rate which suggests the competition of indole with the olefin for the reduction.

We rearranged eq 1 as follows

$$1/R = \frac{K_6}{k_3 K_2 [D][C]_0}[S] + \frac{K_1 + [L] + K_1 K_2 [D]}{K_1 K_2 [D][C]_0} \quad (2)$$

As the rate was independent on the olefin concentration, $K_6 / k_3 K_2 [D][C]_0$ must be so small as to be negligible. Perhaps this means K_6 is negligibly small, that is, the concentration of VI is small.[11] This reasoning may be partly supported by the fact that no olefin complex was detected in this system and by the reports that the coordinating power

of internal olefins to the catalyst is weak[2] and the concentration of the Rh(I)–olefin complex is small in the transfer hydrogenation in dioxane.[4] Then the rate expression is reduced to

$$R = \frac{k_3 K_1 K_2 [D][C]_0}{K_1 + [L] + K_1 K_2 [D]} \quad (3)$$

As described earlier, the rate had the first-order dependence on the concentration of indoline. This fact may require $K_1 + [L] \gg K_1 K_2 [D]$, that is, [I] + [II] ≫ [III]. This supposition seems to be reasonable because no indoline complex was isolated even from indoline solution of the catalyst. Then the rate expression becomes

$$R = k_3 K_1 K_2 [D][C]_0 / (K_1 + [L]) \quad (4)$$

This expression is found to accommodate reasonably all the experimental observations described earlier. (1) The dependence of the rate on the catalyst concentration should be linear. This agrees with the result that the initial rate of the transfer hydrogenation was proportional to the charged catalyst concentration. (2) When triphenylphosphine is added to the reaction system catalyzed by RhCl(PPh$_3$)$_3$, the concentration of the added phosphine may approximately be regarded as the phosphine concentration. The dependence of the rate on the phosphine concentration is

$$1/R = \frac{1}{k_3 K_1 K_2 [D][C]_0}[L] + \frac{1}{k_3 K_2 [D][C]_0}$$

which is identical in form with that obtained previously with

$$a = 1/k_3 K_1 K_2 [D][C]_0$$

$$b = 1/k_3 K_2 [D][C]_0$$

From Figure 5, the value for the gradient, a, and the one for the intercept, b, 8 × 10^3 l.^{2} min mol^{-2} and 7 × 10^2 l. min mol^{-1} were obtained, respectively. By using these values, $K_1 = b/a = 9 \times 10^{-2}$ mol l.$^{-1}$ and $k_3 K_2 = 1$ l. mol^{-1} min^{-1} were obtained, as the values at 160°. As the reaction was carried out at the much higher temperature, the K_1 value, which suggests about 25% of RhCl(PPh$_3$)$_3$ replaced a molecule of the phosphine by a molecule of the solvent, seems to be not so unreasonable, in spite of the report that only 1.2% of the complex dissociates in oxygen-free benzene at 25°.[12] Then the overall rate expression at 160° may be formulated as $R = 9 \times 10^{-2}[D][C]_0 / (9 \times 10^{-2} + [L])$ (3) As the reduction,[2,3,6] the isomerization,[7] and the hydrogen-deuterium exchange[8] of olefins under hydrogen gas occur under milder conditions than the transfer hydrogenation, the steps which can correspond to the steps in the former reactions may not be rate determining in the latter. In eq 4, k_3 is the only rate constant; so the dehydrogenation step, III → IV, may be the rate limiting in the transfer hydrogenation. This is supported by the fact that the reactions under hydrogen involve no dehydrogenation step.

Experimental Section

All the transfer hydrogenations and kinetic measurements were carried out by the method reported previously.[1]

Materials. RhCl(PPh$_3$)$_3$,[2] [RhCl(PPh$_3$)$_2$]$_2$,[2] and [RhCl(cyclooctene)$_2$]$_2$[13] were prepared according to the literature. Other reagents were treated as reported previously.[1]

An Attempt to Isolate Reaction Intermediates. To a mixture of RhCl(PPh$_3$)$_3$ (93 mg, 0.1 mmol), indoline (238 mg, 2.0 mmol), and cyclopentene (68 mg, 1.0 mmol), toluene was added, and the total volume of the solution was made up to 1.0 ml. Three samples prepared by the method described above were heated at 80° for 2 hr, at 110° for 1 hr, and at 140° for 30 min, respectively, and

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cooled. The precipitated crystals were separated by filtration, washed with ether, and dried *in vacuo*. The ir and nmr spectra of all the complexes obtained were identical with one another, similar to the mixture of RhCl(PPh₃)₃ and [RhCl(PPh₃)₂]₂, and showed no peaks assignable to indoline. The elemental analysis of the complex isolated in the reaction at 140° was also explainable by the mixture.

Anal. Calcd for the mixture of $C_{54}H_{45}ClP_3Rh$ and $C_{72}H_{60}Cl_2P_4Rh_2$ (1:3): C, 66.44; H, 4.65; N, 0.0. Found: C, 66.46; H, 4.82; N, 0.0.

A similar mixture was obtained also when RhCl(PPh₃)₃ (0.03 mmol) was heated in indoline (2.0 mmol) at 80° for 5 hr.

Anal. Found: C, 67.99; H, 4.84; N, 0.0.

When [RhCl(PPh₃)₂]₂ (0.03 mmol) was heated in indoline (2.0 mmol) at 80° for 5 hr, the dimer was recovered.

Isolation of RhCl(PPh₃)₂(pyrrolidine). RhCl(PPh₃)₃ (27.8 mg, 0.03 mmol) and pyrrolidine (142 mg, 2.0 mmol) were sealed in a Pyrex glass tube *in vacuo* and heated at 80° for 30 min. The yellow crystals isolated melted at 105–106°. The nmr spectrum of them showed three multiplets centered at τ 8.2, 6.8, and 2.7, with 1:1:8 area (in CDCl₃ with TMS as the internal standard). The ir spectrum showed bands at 2930, 2860, and 886 cm⁻¹ which are assignable to pyrrolidine.

Anal. Calcd for $C_{40}H_{39}ClNP_2Rh$: C, 65.45; H, 5.37; N, 1.91. Found: C, 65.11; H, 5.48; N, 1.83.

The same complex which was identified by elemental analysis, ir spectrum, and melting point was obtained in the similar reaction between (RhCl(PPh₃)₂)₂ and pyrrolidine.

Registry No.—RhCl(PPh₃)₃, 14694-95-2; [RhCl(PPh₃)₂]₂, 25966-16-9; [RhCl(cyclooctene)₂]₂, 12279-09-3; RhCl(PPh₃)₂(pyrrolidine), 53166-29-3; indoline, 496-15-1; cycloheptene, 628-92-2; pyrrolidine, 123-75-1.

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(5) When [RhCl(cyclooctene)₂]₂ was added to the toluene solution of triphenylphosphine at the phosphine–rhodium ratio of 2, [RhCl(PPh₃)₂]₂ was isolated.
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(10) For example, the kinetic expression derived from the fact shown in Figure 1, and the scheme which is formed by removing RhCl(PPh₃)₂(solvent) from the scheme in the text, is the type $R = a'[D][C]_0/(b'[L] + c'[D])$. This cannot explain the facts shown in Figures 2 and 4 without contradiction.
(11) Because $[VI] = K_6 [II][S]$.
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# Catalytic Hydrogenolysis–Reduction of Aryl Phosphate Esters[1]

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The platinum-catalyzed hydrogenolysis–reduction of aryl phosphate esters has been investigated with a view toward the determination of the sequence of reaction steps. The aromatic hydrocarbons related to the ester functions have been isolated and identified as intermediates; these arenes, when subjected to facilitated reaction conditions, yield reduction products in the same proportions as observed in the hydrogenolysis reaction systems. The course of intermediate formation and decay has been followed and the stereoregularity of the reduction process has also been investigated.

The hydrogenolysis–reduction of aryl esters of phosphorus-containing acids over platinum catalysts (eq 1) is a
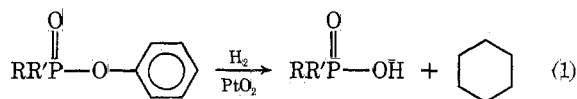
reaction which has been of significant utility in the synthesis of numerous organophosphorus compounds; the phenyl ester linkage is cleaved yielding the free acid while the original aromatic ring is reduced to cyclohexane. Its utility arises as it allows the protection of a phosphorus acid function with an ester linkage at an early stage in a synthetic sequence and at a later stage allows the generation of the free acid without resorting to hydrolytic conditions.

One example of this utility is shown in the synthesis of dihydroxyacetone phosphate.[2] At an early stage of the synthetic route the critical phosphate linkage is introduced by the reaction of diphenyl phosphorochloridate with an aliphatic alcohol. The alkyl position is then properly functionalized and at a latter stage the phenyl groups are removed by hydrogenolysis generating the free acid (eq 2).
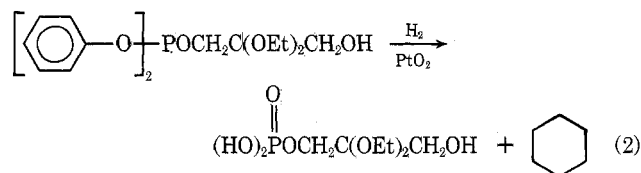
The hydrolytic removal of either aryl or alkyl protecting ester linkages is not feasible as the critical phosphate linkage in the desired product would also be cleaved.

A most interesting aspect of this reaction is the overall reduction of the phenyl ring to cyclohexane under the relatively mild reaction conditions. Thereby it is rather surprising that so little attention has been given to this point. No efforts have been reported to elucidate the course of this overall reaction, and it appears that, aside from phenyl esters themselves, only *p*-nitrophenyl esters have been used in this reaction;[3] in this latter work it was presumed that hydrogenolysis–reduction yielded cyclohexylamine although this was not shown definitively.

As it is known that aromatic hydrocarbons undergo com-