

**Transfer Hydrogenation and Transfer Hydrogenolysis. 17.**  
**Hydrogenolysis of Triphenylphosphine Coordinated to Rhodium(I)**  
**by the Hydrogen Transfer from Organic Compounds**

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A considerable amount of benzene was formed in the reaction of  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{RhH}(\text{PPh}_3)_4$  with amines, alcohols, hydroaromatic compounds, and dioxane. For example, about eight or ten molecules of benzene were formed from a molecule of  $\text{RhCl}(\text{PPh}_3)_3$  or  $\text{RhH}(\text{PPh}_3)_4$ , respectively, when these complexes were heated at 100 °C for 6 h in pyrrolidine. In the reaction of  $\text{RhCl}(\text{PPh}_3)_3$  in pyrrolidine, diphenylphosphine and biphenyl also were detected; a bright yellow complex which was tentatively identified as  $\text{RhCl}(\text{PPh}_3)_2$  (pyrrolidine) was isolated as a reaction intermediate. The isolated complex gave benzene by heating in inert solvents. The hydrogen transfer from indoline, tetrahydroquinoline, and dioxane was confirmed by the quantitative analysis of reaction mixtures.

A number of tertiary phosphine complexes have been reported to exhibit interaction between the transition metals and carbon-hydrogen bonds of phosphine ligands.<sup>1</sup> However, relatively little is known about the cleavage of phosphorus-carbon bonds of tertiary phosphines coordinated to transition metals.<sup>2</sup> Recently Fahey and Mahan have reported that coordinatively unsaturated zerovalent nickel and palladium complexes can undergo a reversible oxidative addition reaction with triphenylphosphine.<sup>2a</sup>

During the course of investigations of catalytic hydrogen transfer between organic compounds, we found that a considerable amount of benzene was formed on heating triphenylphosphine complexes of transition metals with hydrogen donors in the absence of appropriate hydrogen acceptors. It seemed to be worthwhile to study such transfer hydrogenolysis, because a number of tertiary phosphine complexes of transition metals have been used in many homogeneously catalyzed reactions. A part of the results obtained have been reported in a preliminary communication.<sup>3</sup>

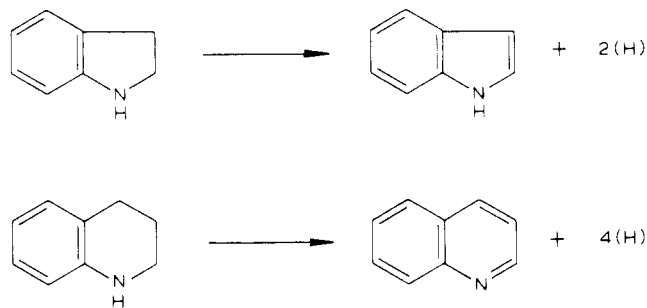
### Results and Discussion

The transition metal complex which has been investigated most extensively as a homogeneous hydrogen-transfer catalyst seemed to be  $\text{RhCl}(\text{PPh}_3)_3$ . Therefore, we studied the reaction of this complex first.

**Hydrogen-Giving Ability of Organic Compounds.** At first, the hydrogen-donating ability of organic compounds was investigated. As shown later, the dependence of the yield of products on the reaction time was complicated. Perhaps, for this reason, the hydrogen-giving power of organic compounds which is expressed by the yield of benzene was varied considerably by the alteration of reaction conditions, including reaction time. When  $\text{RhCl}(\text{PPh}_3)_3$  (0.05 M) was heated at 140 °C for 1 h in several organic compounds which served as a hydrogen source and solvent, the yield of benzene decreased in the following order: pyrrolidine > piperidine > piperazine > 2-propanol > *N*-methylpiperazine > *n*-propylamine > indoline > 1-phenylpropanol > di-*n*-propylamine > 1,2,3,4-tetrahydroquinoline > *N,N'*-dimethylpiperazine > dioxane > D-limonene > 1-propanol > tetralin, as shown in Table I. In the reactions in phenetole, pyrrole, and xylene under the same conditions no benzene was detected. When  $\text{RhCl}(\text{PPh}_3)_3$  (0.1 M) and a hydrogen donor (1.0 M) were heated at 140 °C for 3 h in phenetole, the amount of the benzene formed decreased in the following order: pyrrolidine > piperidine > 1,2,3,4-tetrahydroquinoline > indoline > 2-propanol > 1-phenylpropanol > dioxane. Both in the reactions without solvents and the ones in phenetole, secondary alkylamines of less steric hindrance, such as pyrrolidine and piperidine,

showed stronger hydrogen-giving power, although indoline reduced olefins, nitrobenzenes, and aryl halides more efficiently.<sup>4</sup> The amount of the benzene formed was surprisingly large. For example, in the reaction of pyrrolidine, about eight molecules of benzene were formed from one molecule of  $\text{RhCl}(\text{PPh}_3)_3$ , which has nine phenyl groups.

To discuss the sources of hydrogen, quantitative analysis of products and reagents in the reaction mixtures was carried out. When  $\text{RhCl}(\text{PPh}_3)_3$  (0.04 M) and indoline (0.4 M) were heated at 170 °C for 1 h in xylene, the formation of 0.14 M benzene and 0.15 M indole, in addition to the recovery of 0.26 M original amine, was shown by GC analysis. A similar reaction in which 1,2,3,4-tetrahydroquinoline was used instead of indoline gave 0.12 M benzene, 0.05 M quinoline, and 0.38 M tetrahydroquinoline. These results may be summarized as follows: (1) the yield of benzene was almost equal to that of indole in the former reaction; (2) the yield of benzene was roughly twice that of quinoline in the latter reaction, because the conversion of tetrahydroquinoline to quinoline releases 2 mol of hydrogen; (3) the total amounts of the recovered original amines and dehydrogenated amines were nearly equal to the amount of amines before reaction. This result shows

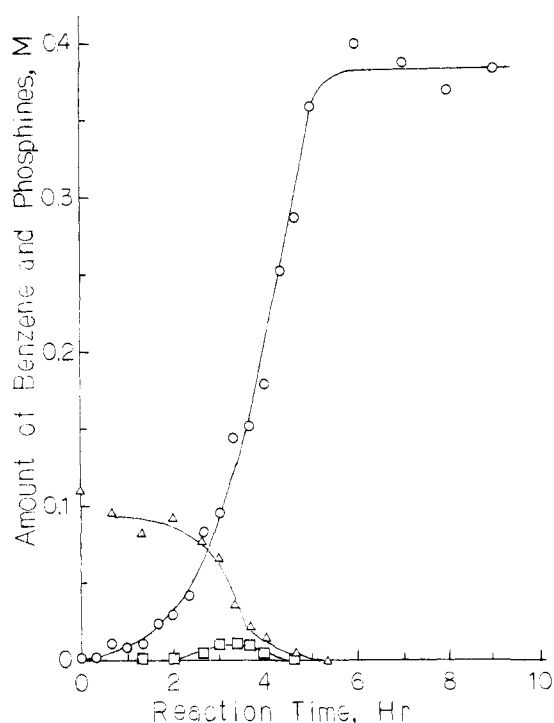


that these amines gave hydrogen to ligands of rhodium species to cause the hydrogenolysis and were dehydrogenated as follows. The amount of the piperidine consumed was roughly equal to that of the benzene formed, but no low boiling dehydrogenation products, such as pyridine, were detected. The amount of the surviving pyrrolidine could not be measured precisely and the dehydrogenation products of low boiling points, such as pyrrolines and pyrrole, were not detected. It has been reported that 1-piperidine and 1-pyrroline are unstable and undergo rapid trimerization<sup>5</sup> and addition reactions with amines.<sup>6</sup> Therefore, it is inferred that such unstable dehydrogenation intermediates yielded products of high boiling points which were not detected by GC analysis. The speculation that a pyrrolidine molecule gives only two hydrogen atoms may be supported by the observation that the complex which was isolated in the reaction between  $\text{RhCl}(\text{PPh}_3)_3$  and

**Table I. Hydrogen-Donating Ability of Hydrogen Donors in Transfer Hydrogenolysis of Triphenylphosphines of  $\text{RhCl}(\text{PPh}_3)_3^c$** 

hydrogen donor	registry no.	benzene <sup>a</sup>		benzene <sup>b</sup>	
		M	mol/ $\text{RhCl}(\text{PPh}_3)_3$	M	mol/ $\text{RhCl}(\text{PPh}_3)_3$
pyrrolidine	123-75-1	0.40	8.0	0.42	8.4
piperidine	110-89-4	0.35	6.9	0.31	6.3
piperazine	110-85-0	0.31	6.2		
2-propanol	67-63-0	0.29	5.8	0.19	3.8
<i>N</i> -methylpiperazine	109-01-3	0.24	4.7		
<i>n</i> -propylamine	107-10-8	0.20	3.9		
indoline	496-15-1	0.18	3.6	0.20	4.1
1-phenylpropanol	93-54-9	0.17	3.4	0.13	2.6
di- <i>n</i> -propylamine	142-84-7	0.11	2.3		
1,2,3,4-tetrahydroquinoline	635-46-1	0.10	2.1	0.23	4.6
<i>N,N'</i> -dimethylpiperazine	106-58-1	0.10	2.1		
dioxane	123-91-1	0.06	1.2	0.03	0.6
D-limonene	5989-27-5	0.05	0.9		
1-propanol	71-23-8	0.04	0.8		
tetralin	119-64-2	0.03	0.5		

<sup>a</sup>  $\text{RhCl}(\text{PPh}_3)_3$  (0.05 M) was heated in the designated hydrogen donor at 140 °C for 1 h. <sup>b</sup> The designated hydrogen donor (1.0 M) and  $\text{RhCl}(\text{PPh}_3)_3$  (0.1 M) were heated at 140 °C for 3 h in phenetole. <sup>c</sup> Registry no.: 14694-95-2.



**Figure 1.** The dependence of the amount of benzene (O), triphenylphosphine (Δ), and diphenylphosphine (□) on reaction time;  $\text{RhCl}(\text{PPh}_3)_3$  (0.05 M) was heated at 100 °C in pyrrolidine.

pyrrolidine and identified tentatively as  $\text{RhCl}(\text{PPh}_3)_2$  (pyrrolidine) gave 1 mol of benzene, as described later. In the reaction in dioxane, dioxene was detected and the amount of the dehydrogenation product was nearly equal to that of benzene.

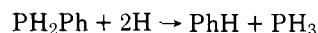
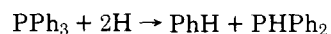
**Effect of Reaction Solvents.** The influence of solvents on the yield of benzene was investigated by heating  $\text{RhCl}(\text{PPh}_3)_3$  (0.05 M) and pyrrolidine or indoline (0.45 M) at 140 °C for 3 h in some solvents which dissolve the complex fairly well and are inert to hydrogen-transfer reactions under these conditions. The effect of the solvents examined hardly depended on the hydrogen donors and the yield of benzene decreased in the order: phenetole > xylene > cumene > benzonitrile, as shown in Table II.

**Table II. Effect of Reaction Solvents<sup>a</sup>**

hydrogen donor	solvent	benzene, M
indoline	phenetole	0.24
	xylene	0.20
	cumene	0.16
	benzonitrile	0.13
pyrrolidine	phenetole	0.26
	xylene	0.15
	cumene	0.15
	benzonitrile	0.05

<sup>a</sup>  $\text{RhCl}(\text{PPh}_3)_3$  (0.05 M) and a hydrogen donor (0.45 M) were heated in the designated solvent at 140 °C for 3 h.

**Dependence of the Amount of Benzene and Phosphines on Reaction Time.** The dependence of the yield of benzene upon reaction time was investigated by heating  $\text{RhCl}(\text{PPh}_3)_3$  (0.05 M) in pyrrolidine at 100 °C, and the result is shown in Figure 1. Benzene formed slowly until 1.5 h and then more rapidly. The reason why such an induction period appeared is not clear as yet. After 5 h, the amount of benzene reached about 0.4 M and the formation of it stopped suddenly. The fact that eight molecules of benzene were formed from a molecule of  $\text{RhCl}(\text{PPh}_3)_3$  shows that all of the three triphenylphosphine molecules coordinated on rhodium underwent hydrogenolysis almost completely and the following reactions occurred successively:



To confirm the occurrence of these successive reactions, the detection and the quantitative analysis of phosphines were undertaken. After the hydrogen-transfer reactions were carried out, the reaction mixtures were shaken with potassium cyanide-potassium hydroxide aqueous solution for several hours to generate free phosphines<sup>7</sup> and then the organic layer that separated was submitted to GC analysis. It seems to be rather difficult to measure exactly the amount of phosphines in the reaction mixtures, partly because the complete decomposition of the rhodium complexes having phosphines as ligands was not realized easily in solvents, and partly because

Table III. Effect of Additives<sup>a</sup>

additive	hydrogen donor	yield of benzene, M	
none	pyrrolidine	0.42	
triphenylphosphine		0.38	
tri- <i>n</i> -propylamine		0.40	
<i>N,N</i> -diethylaniline hydrochloride		0.32	
<i>N,N</i> -diethylaniline hydrochloride <sup>b</sup>		0.26	
<i>N,N</i> -diethylaniline <sup>b</sup>		0.27	
pyrocatechol		0.55	
hydroquinone		0.39	
$\alpha,\alpha'$ -azodiisobutyronitrile <sup>c</sup>		0.41	
none		indoline	0.20
triphenylphosphine			0.12
tri- <i>n</i> -propylamine	0.18		
<i>N,N</i> -diethylaniline hydrochloride	0.14		
<i>N,N</i> -diethylaniline hydrochloride <sup>b</sup>	0.10		
<i>N,N</i> -diethylaniline <sup>b</sup>	0.13		
pyrocatechol	0.28		
hydroquinone	0.23		
$\alpha,\alpha'$ -azodiisobutyronitrile <sup>c</sup>	0.19		

<sup>a</sup> A hydrogen donor (1.0 M), RhCl(PPh<sub>3</sub>)<sub>3</sub> (0.1 M), and an additive (0.5 M) were heated at 140 °C for 3 h in phenetole. <sup>b</sup> The amount of this additive was 0.5 M. <sup>c</sup> The amount of this additive was 0.02 M.

phosphines in solvents were oxidized rapidly in air in the presence of rhodium species.<sup>8</sup> In fact, even when RhCl(PPh<sub>3</sub>)<sub>3</sub> in pyrrolidine which had not been heated was analyzed, the amount of the triphenylphosphine detected was much smaller than the theoretical value, as seen in Figure 1. Moreover, if phosphines existed in anionic forms in the reaction mixtures, the hydrolysis of rhodium-phosphorous bonds, such as Rh-PPh<sub>2</sub> + H<sub>2</sub>O → Rh(OH) + PPh<sub>2</sub>, would be required for the anionic phosphines to be detected by GC analysis.

The high reactivity of phosphines with oxygen was observed even without transition-metal ions and solvents. The authentic phenylphosphine which had been prepared according to literature<sup>9</sup> was oxidized very rapidly in air with the evolution of heat. The authentic diphenylphosphine<sup>10</sup> also reacted with oxygen in air quickly though slower than phenylphosphine. Further, it has been reported that tertiary phosphines coordinated on rhodium are oxidized easily.<sup>8</sup>

The amount of the triphenylphosphine detected decreased rapidly after the induction period in the formation of benzene, and became negligible after about 5 h, as shown in Figure 1. Diphenylphosphine was also detected after the induction period and disappeared after about 5 h. The amount of the diphenylphosphine detected was small and about 0.015 M at the maximum point. These observations suggest that the rate of the hydrogenolysis of diphenylphosphine is faster, but is not so widely faster than that of triphenylphosphine. The yield of benzene increased with time smoothly without showing steps, and the formation of benzene ceased rapidly at the end of the reaction. The cessation of the formation of benzene was not much later than that of the disappearance of triphenylphosphine and diphenylphosphine. These facts also suggest that the hydrogenolysis of diphenylphosphine and phenylphosphine is faster than that of triphenylphosphine and that of phenylphosphine is not much slower than that of diphenylphosphine. The detection of phenylphosphine was obscured because the peak of phenylphosphine in GC analysis, which had been determined by the authentic sample, was covered by broad and strong peaks of pyrrolidine and impurity. Further, the phosphine was not detected even when RhCl(PPh<sub>3</sub>)<sub>3</sub> and indoline were heated in phenylcyclohexane at 100 °C for 5 h. In the latter reaction system the peak of the phosphine would not be covered by others. However, it cannot be denied

a priori that phenylphosphine was not detectable because of the difficulty of the departure of it from rhodium or of the oxidation during the pretreatment described earlier, though it was formed in detectable amount.

Biphenyl also was detected in the reaction in pyrrolidine. For example, 0.6 M biphenyl was obtained when RhCl(PPh<sub>3</sub>)<sub>3</sub> (0.05 M) was heated in the amine at 100 °C for 4 h. As Fahey and Mahan have described, the formation of biphenyl suggests that the oxidative addition of phosphines to central metals occurred to form phenyl complexes.<sup>2a</sup>

**Isolation of a Reaction Intermediate.** When red crystals of RhCl(PPh<sub>3</sub>)<sub>3</sub> (0.05 M) in pyrrolidine were heated at 100 °C for 2 h or left for a week at room temperature, bright yellow crystals which were stable under vacuum were obtained in about 30% yield. The structure of the crystals obtained was inferred tentatively as RhCl(PPh<sub>3</sub>)<sub>2</sub> (pyrrolidine), formed by replacing a triphenylphosphine molecule of RhCl(PPh<sub>3</sub>)<sub>3</sub> with a pyrrolidine molecule, based on elemental, IR, and <sup>1</sup>H NMR analysis (see Experimental Section). The yellow crystals were formed by heating salmon-pink crystals of [RhCl(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in pyrrolidine, too. This complex is inferred as a reaction intermediate because it gave benzene when it was heated in inert solvents. For example, when 0.05 M complex was heated in phenetole at 140 °C for 3 h, 0.043 M benzene was formed. In addition, this result suggests that pyrrolidine, which would release four hydrogen atoms to form pyrrole, gave only two hydrogen atoms, as indicated before.

When RhCl(PPh<sub>3</sub>)<sub>3</sub> was heated in pyrrolidine at 100 °C for more than 3 h, no crystals were precipitated by cooling. Moreover, the reaction mixtures of prolonged heating gave no solid substances, but only oil materials with the addition of ether or with the evaporation of compounds of low boiling points under reduced pressure.

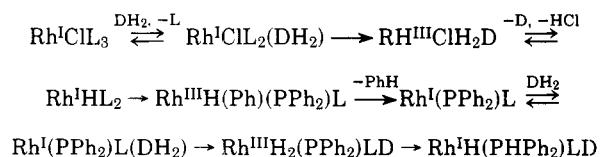
**Effect of Additives.** The effect of additives was studied by the hydrogen transfer from pyrrolidine and indoline in phenetole, and the results are summarized in Table III. The yield of benzene was decreased by the addition of triphenylphosphine, especially in the reaction of indoline. As in the hydrogen transfer from indoline to olefins catalyzed by RhCl(PPh<sub>3</sub>)<sub>3</sub>,<sup>4a</sup> this fact may be explained by the presumption 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 molecule from RhCl(PPh<sub>3</sub>)<sub>3</sub>.

The addition of tri-*n*-propylamine did not promote the hydrogenolysis, although we had forecasted that the additive would raise the yield of benzene by the removal of the hydrogen chloride which is assumed to be formed during the reaction, as described later. *N,N*-Diethylaniline hydrochloride, which is considered as a potential generator of hydrogen chloride, decreased the yield of benzene considerably, but *N,N*-diethylaniline also decreased it, though to a slightly lesser extent. Consequently, the effect of hydrogen chloride did not become so clear.

Pyrocatechol and hydroquinone, which are the inhibitors of radical reactions, did not retard this hydrogenolysis reaction, and  $\alpha,\alpha'$ -azodiisobutyronitrile, which is an initiator of radical processes, did not raise the yield of benzene. These results may indicate that the hydrogenolysis does not proceed via radical process.<sup>11</sup>

**Reaction of Hydridotetrakis(triphenylphosphine)-rhodium(I).** We speculated at first that the formation of hydrogen chloride brought about the induction period in the formation of benzene in the reaction of RhCl(PPh<sub>3</sub>)<sub>3</sub> in pyrrolidine, so the dependence of the yield of benzene on reaction time was investigated in the reaction of RhH(PPh<sub>3</sub>)<sub>4</sub> in the amine (Figure 2). However, the similarity of the yield of benzene vs. reaction time curve in the reaction of RhH(PPh<sub>3</sub>)<sub>4</sub>

## Scheme I



to that of the one of  $\text{RhCl}(\text{PPh}_3)_3$  denied the speculation. In the reaction of  $\text{RhH}(\text{PPh}_3)_4$  also, the induction period of about 1 h was observed and the reaction was complete after 5 h with the formation of from nine to ten molecules of benzene from one molecule of  $\text{RhH}(\text{PPh}_3)_4$ , which has 12 benzene rings. The recovery of triphenylphosphine in the reaction of this complex was more difficult than in that of  $\text{RhCl}(\text{PPh}_3)_3$ , and the amount of the phosphine detected by GC analysis was smaller than half of the theoretical amount. However, it was presumed that most of triphenylphosphine was consumed after 4 h, because the amount of the phosphine detected was 0.02 M in the reaction of 3.5 h, a trace in the one of 4 h, and zero in the one of 5 h.

In the reaction of this complex also, biphenyl was detectable but diphenylphosphine and phenylphosphine were not detected.

When 0.01 M  $\text{RhH}(\text{PPh}_3)_4$  was heated at 110 °C for 30 min in xylene without hydrogen donors, 0.004 M benzene was formed.

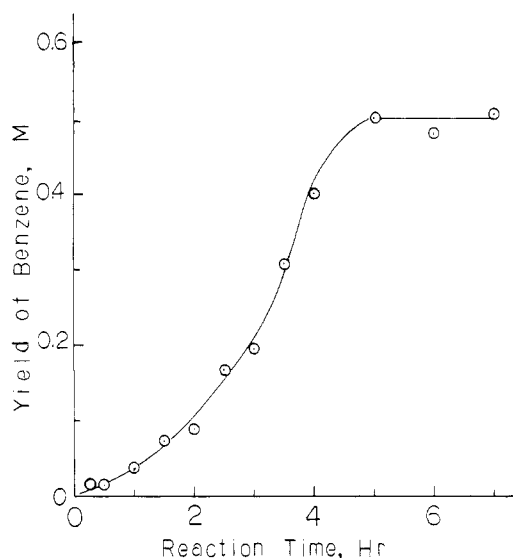
## Discussion

It seems unlikely that a Rh(III) species forms a Rh(V) species by oxidative addition of a reactant.<sup>12</sup> Therefore, the schemes which contain the conversion of Rh(III) species to Rh(V) species seem to be unreasonable and the formation of monohydride Rh(I) species may be essential. Based on this assumption and the results described previously, we should like to propose the following reaction scheme (Scheme I) for the hydrogenolysis of the triphenylphosphines of  $\text{RhCl}(\text{PPh}_3)_3$  in the early stage. In the scheme, L,  $\text{DH}_2$ , and D represent triphenylphosphine, a hydrogen donor, and a dehydrogenation product, and some of the species may be coordinated by solvents or some other ligands. The departure of a triphenylphosphine molecule from  $\text{RhCl}(\text{PPh}_3)_3$  is inferred from the retarding effect of the phosphine added. The formation of  $\text{Rh}^{\text{I}}\text{ClL}_2(\text{DH}_2)$  was shown by the isolation of the complex which is considered as  $\text{RhClL}_2$  (pyrrolidine) in the reaction in pyrrolidine. The removal of the hydrogen chloride formed from reaction intermediates was not shown clearly, but it is essential for the formation of monohydride Rh(I) species. Perhaps the departure of hydrogen chloride from Rh(III) species coordinated by both hydrides and chlorides may be easy and fast in the reaction systems of basic atmosphere. The formation of phenyl complexes is supported by the detection of biphenyl,<sup>2a</sup> although the species to give biphenyl might not only be  $\text{RhH}(\text{Ph})(\text{PPh}_2)\text{L}$  but also others containing no hydride ligand, such as  $\text{RhCl}(\text{Ph})(\text{PPh}_2)\text{L}_2$  and  $\text{Rh}(\text{Ph})(\text{PPh}_2)_2$ . The inference that hydride complexes such as  $\text{RhHL}_2$  (solvent) can give benzene may be supported by the formation of benzene from  $\text{RhH}(\text{PPh}_3)_4$  by heating in inert solvents.

The transfer hydrogenolysis of the tertiary phosphines coordinated on transition metals occurred in some other complexes, as reported in a preliminary communication,<sup>3</sup> and the detailed study of them is now going on.

## Experimental Section

**Materials.** Chlorotris(triphenylphosphine)rhodium(I),<sup>8a</sup> hydridotetrakis(triphenylphosphine)rhodium(I),<sup>13</sup> diphenylphosphine,<sup>10</sup> phenylphosphine,<sup>9</sup> and dioxene<sup>14</sup> were prepared by the method re-



**Figure 2.** The dependence of the yield of benzene on reaction time;  $\text{RhH}(\text{PPh}_3)_4$  (0.05 M) was heated at 100 °C in pyrrolidine.

ported in the literature. All the solvents and the hydrogen donors except for piperazine were purified by distillation. Piperazine, triphenylphosphine, hydroquinone, and pyrocatechol were recrystallized from toluene.

**An Example of Transfer Hydrogenolysis in Hydrogen Donors.**

$\text{RhCl}(\text{PPh}_3)_3$  (23.1 mg, 0.025 mmol) was put into a Pyrex glass tube which had been sealed at one end. Into the vessel pyrrolidine was added and the total volume of the solution was made 0.5 mL. The tube was sealed under vacuum after two freeze-pump-thaw cycles in a vacuum line with liquid nitrogen. The sealed tube was heated for 1 h in the polyethylene glycol bath kept at  $140 \pm 1$  °C. After cooling the sealed tube was opened and sealed rapidly with a cap made of silicone rubber. The reaction mixture was submitted to GC analysis in which 15  $\mu\text{L}$  of di-*n*-butyl ether was used as an internal standard. A 2 m  $\times$  6 mm column packed with 15% 1,2,3-tris(2-cyanoethoxy)propane on Diasolid L was used. After the analysis of benzene, 0.5 mL of aqueous solution saturated with potassium cyanide and potassium hydroxide (1:1) was added to the reaction mixture. The mixture was shaken for several hours (usually 3 h) using a shaker, and at the end of the shaking a dioxane solution of carbazole was added as an internal standard. After the shaking, the organic layer separated was submitted to GC analysis for triphenyl- and diphenylphosphine. A 1 m  $\times$  6 mm column packed with 10% Apiezone grease L on Diasolid L was used.

Other reactions of  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{RhH}(\text{PPh}_3)_4$  in hydrogen donors which serve as solvents also were carried out in a similar way.

**An Example of Transfer Hydrogenolysis in a Solvent.**

Indoline (47.7 mg, 0.40 mmol) and  $\text{RhCl}(\text{PPh}_3)_3$  (37.0 mg, 0.04 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 xylene as a solvent. The tube, sealed by the method described above, was heated for 1 h in a silicone-oil bath kept at  $170 \pm 2$  °C. The amount of benzene was measured by the method described above. The amount of indoline and indole was measured by the use of a 2 m  $\times$  6 mm column packed with 10% diethylene glycol succinate on Diasolid L and of dibenzyl ether (35  $\mu\text{L}$ ) as an internal standard.

Other transfer hydrogenolyses in solvents were carried out in a similar way.

**Isolation of a Reaction Intermediate.**  $\text{RhCl}(\text{PPh}_3)_3$  (93 mg, 0.1 mmol) was put into a Pyrex glass tube which had been sealed at one end. Pyrrolidine was added, and the total volume of the solution was made 2 mL. The solution was left for a week at room temperature. Bright yellow crystals which precipitated were isolated by filtration, washed with ether, and dried in vacuo. The crystals obtained weighed about 20 mg (the yield of 30%). Nearly the same result was obtained when the solution was heated at 100 °C for from 1 to 3 h and left overnight. The crystals isolated melted at 105–106 °C. The <sup>1</sup>H NMR spectrum of them showed three multiplets centered at  $\tau$  8.2, 6.8, and 2.7, with 1:1:8 area (in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as the internal standard). The IR spectrum showed bands at 2930, 2860, and 886  $\text{cm}^{-1}$  which are assignable to pyrrolidine.

Anal. Calcd for  $\text{C}_{40}\text{H}_{39}\text{ClNP}_2\text{Rh}$ : C, 65.45; H, 5.37; N, 1.91. Found:

