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TRANSFER HYDROGENATION AND TRANSFER HYDROGENOLYSIS

XXII *. HYDROGENOLYSIS OF TRIPHENYLPHOSPHINE COORDINATED TO TRANSITION METALS BY HYDROGEN TRANSFER FROM ORGANIC COMPOUNDS

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Summary

When heated with some organic compounds, the triphenylphosphine ligand of $RuH_2(PPh_3)_4$, $RhH(PPh_3)_4$, $RuCl_2(PPh_3)_3$, and $RhCl(PPh_3)_3$ were hydrogenolyzed almost completely to benzene and those of $PtCl_2(PPh_3)_2$, $Pt(PPh_3)_4$, and $PdCl_2(PPh_3)_2$ underwent this conversion to a considerable extent. In the reaction of $RuH_2(PPh_3)_4$ in pyrrolidine the amount of the benzene formed was about three times as much as that of the triphenylphosphine consumed. Biphenyl was detected in the reaction of the Ru^{II}-species. In the hydrogen transfer from 2-propanol and 2-propanol-d_8 no primary kinetic isotope effect was observed, and the cleavage and oxidative addition of P—C bonds of phosphine ligands was inferred to be the rate-determining step of the reaction.

Introduction

During investigations of hydrogen transfer between organic compounds, we found that a considerable amount of benzene was formed when triphenylphosphine complexes of transition metals were heated with hydrogen donors in the absence of appropriate hydrogen acceptors. It seemed worthwhile to study such transfer hydrogenolysis because several tertiary phosphine complexes of transition metals have been used in many homogeneously catalyzed reactions and the inference is that this hydrogenolysis is related to catalyst decay.

The hydrogenolysis of triphenylphosphine coordinated to rhodium(I) has been reported previously [1]. We now report further studies of such hydrogen transfer reactions. Some of these results have been reported in a preliminary communication [2].

Results and discussion

Reactivity of complexes

Initially, the reactivity of the triphenylphosphine coordinated to transition metals was investigated by using pyrrolidine, 2-propanol, and tetralin as hydrogen donors. When a complex (0.05 *M*) was heated at 140°C for 11 h in pyrrolidine, which had shown the highest hydrogen-donating ability in the reaction of $RhCl(PPh_3)_3$ [1], the amount of the benzene formed decreased in the order: $RhH(PPh_3)_4 > RuH_2(PPh_3)_4 > RhCl(PPh_3)_3 > RuCl_2(PPh_3)_3 > PtCl_2(PPh_3)_2 > RhCl(CO)(PPh_3)_2 > PdCl_2(PPh_3)_2 > Pt(PPh_3)_4 > Pd(CN)_2(PPh_3)_2$, as shown in Table 1. In the reaction at 150°C for 20 h, $NiCl_2(PPh_3)_2$ and $FeCl_2(PPh_3)_2$ gave little benzene, and $CoCl_2(PPh_3)_2$ gave none. One mole of $RhH(PPh_3)_4$, $RuH_2(PPh_3)_4$, $RhCl(PPh_3)_3$, and $RuCl_2(PPh_3)_3$ gave 10.4, 9.6, 8.0, and 7.8 moles of benzene, respectively. This result suggests that the triphenylphosphine molecules coordinated to Ru^{II} and Rh^{I} underwent hydrogenolysis almost completely and that the following reactions proceeded successively: $PPh_3 + 2\,(H) \xrightarrow{-PhH} PHPh_2 \xrightarrow[-PhH]{2\,(H)} PH_2Ph \xrightarrow{2\,(H)} PH_3 + PhH$. In the hydrogenolysis at

TABLE 1

SUSCEPTIBILITY OF TRIPHENYLPHOSPHINE COMPLEXES TO TRANSFER HYDROGENOLYSIS [a]

Complex	Hydrogen donor	Benzene	
		Concentration (*M*)	Moles/complex
$RhH(PPh_3)_4$	Pyrrolidine	0.52	10.4
	2-Propanol	0.56	11.2
	Tetralin	0.07	1.4
$RuH_2(PPh_3)_4$	Pyrrolidine	0.48	9.6
	2-Propanol	0.52	10.4
	Tetralin	0.11	2.2
$RhCl(PPh_3)_3$	Pyrrolidine	0.40	8.0
	2-Propanol [b]	0.14	2.8
	Tetralin	0.07	1.4
$RuCl_2(PPh_3)_3$	Pyrrolidine	0.39	7.8
	2-Propanol [b]	0.03	0.6
	Tetralin [b]	Trace	Trace
$PtCl_2(PPh_3)_2$	Pyrrolidine	0.15	3.0
	2-Propanol [b]	Trace	Trace
	Tetralin [b]	Trace	Trace
$RhCl(CO)(PPh_3)_2$	Pyrrolidine	0.14	2.8
$PdCl_2(PPh_3)_2$	Pyrrolidine	0.13	2.6
	2-Propnaol [b]	Trace	Trace
$Pt(PPh_3)_4$	Pyrrolidine	0.09	1.8
	2-Propanol [b]	0.07	1.4
	Tetralin	0.07	1.4
$Pd(CN)_2(PPh_3)_2$	Pyrrolidine [c]	0.05	1.0
$NiCl_2(PPh_3)_2$	Pyrrolidine [c,d]	0.01	0.2
$FeCl_2(PPh_3)_2$	Pyrrolidine [c,d]	Trace	Trace

[a] The designated complex (0.05 *M*) was heated in the designated hydrogen donor at 140°C for 11 h.
[b] This complex did not dissolve completely. [c] Metallic precipitates were formed. [d] This reaction was carried out at 150°C for 20 h.

150° C for 20 h in 2-propanol, which is a representative hydrogen donor, the amount of benzene decreased in the following order: $RhH(PPh_3)_4 > RuH_2(PPh_3)_4 > RhCl(PPh_3)_3 > Pt(PPh_3)_4$. The complexes $PtCl_2(PPh_3)_2$ and $PdCl_2(PPh_3)_2$ gave only traces of benzene, and $RhCl(CO)(PPh_3)_2$ and $Pd(CN)_2(PPh_3)_2$ gave none. The benzene yield of the hydride complexes was very high but the reactivity of the chloro complexes, including $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$, was much lower than that of hydride complexes. In the reactions in tetralin the benzene yields were lower than in those in the other two hydrogen donors and decreased in the order: $RuH_2(PPh_3)_4 > RhH(PPh_3)_4 > RhCl(PPh_3)_3 > Pt(PPh_3)_4$. The complexes $RuCl_2(PPh_3)_3$ and $PtCl_2(PPh_3)_2$ gave very little benzene and $RhCl(CO)(PPh_3)_2$, $PdCl_2(PPh_3)_2$, and $Pd(CN)_2(PPh_3)_2$ gave none at all. It is noteworthy that in 2-propanol and tetralin, $Pt(PPh_3)_4$ gave considerably more benzene than did $PtCl_2(PPh_3)_2$, although in pyrrolidine the latter complex was more reactive than the former.

Hydrogen-donating ability of organic compounds

The hydrogen-donating power of organic compounds was investigated in the reactions of $RuCl_2(PPh_3)_3$ and $RuH_2(PPh_3)_4$ at 140° C and the results are summarized in Tables 2 and 3. As shown later, the dependence of the yield of products on reaction time was complicated. Perhaps for this reason, the hydrogen-giving ability of organic compounds which is expressed in terms of the yield of benzene was varied considerably by the alteration of reaction conditions, including reaction time. When $RuCl_2(PPh_3)_3$ (0.05 *M*) was heated in organic compounds which served as both hydrogen donor and solvent, alicyclic secondary amines, such as piperidine, pyrrolidine, and *N*-methylpiperazine, showed the highest ability to donate hydrogen. *N*,*N*′-Dimethylpiperazine, which is an alicyclic tertiary diamine, showed considerable ability. Indoline, which showed the highest hydrogen-giving ability in most transfer hydrogenations [3] and

TABLE 2

HYDROGEN-DONATING ABILITY IN THE REACTION OF $RuCl_2(PPh_3)_3$

Hydrogen donor	Yield of benzene (*M*) [a]	Yield of benzene (*M*) [b]
Piperidine	0.42	0.29
Pyrrolidine	0.40	0.24
N-Methylpiperazine	0.25	
N,*N*′-Dimethylpiperazine	0.16	
Indoline	0.12	0.08
Dipropylamine	0.09	
1-Phenyl-1-propanol	0.08	0.01
1,2,3,4-Tetrahydroquinoline	0.07	0.01
2-Propanol	0.05	0.01
d-Limonene	0.04	
1-Propanol	0.03	
Propylamine	0.02	
Dioxane	0.02	
1,2-Dihydronapthalene	Trace	

[a] $RuCl_2(PPh_3)_3$ (0.05 *M*) was heated in the designated hydrogen donor at 140° C for 12 h. [b] The hydrogen donor (1.0 *M*) and the complex (0.05 *M*) were heated at 140° C for 11 h in phenetole.

TABLE 3

HYDROGEN-DONATING ABILITY IN THE REACTION OF $RuH_2(PPh_3)_4$

Hydrogen donor	Yield of benzene (M)[a]	Yield of benzene (M)[b]
Piperidine	0.54	0.21
N-methylpiperazine	0.53	0.23
Pyrrolidine	0.47	0.20
2-Propanol	0.46	0.17
Indoline	0.38	0.14
Propylamine	0.27	0.16
3-Pentanol	0.26	0.14
1-Phenyl-1-propanol	0.23	0.13
d-Limonene	0.21	0.13
N,N'-Dimethylpiperazine	0.19	0.17
Benzyl alcohol	0.15	0.12
Dipropylamine	0.13	0.13
1,2-Dihydronapthalene	0.12	0.12
Dioxane	0.11	0.11
Tripropylamine	0.11	0.11
1-Propanol	0.11	0.10
None		0.11

[a] $RuH_2(PPh_3)_4$ (0.05 M) was heated in the designated hydrogen donor at 140°C for 10 h. [b] The designated hydrogen donor (1.0 M) and the complex (0.05 M) were heated at 140°C for 3 h in phenetole.

transfer hydrogenolyses [4], did not give so much benzene. In the reaction of acyclic aliphatic amines, the ability of dipropylamine was higher than that of propylamine and tripropylamine gave no benzene. In the reaction of alcohols, the yield of benzene decreased in the order: 1-phenyl-1-propanol > 2-propanol > 1-propanol. *d*-Limonen and dioxane gave a little benzene, but 1,2-dihydronaphthalene and tetralin gave hardly any.

In the reaction of $RuH_2(PPh_3)_4$, the alicyclic secondary amines showed the highest hydrogen-donating ability, as in the reaction of $RuCl_2(PPh_3)_3$, but the ability of 2-propanol was also comparable to that of the cyclic amines. In the reaction of alcohols, the benzene yield decreased in the order: 2-propanol > 3-pentanol > 1-phenyl-1-propanol > benzyl alcohol > 1-propanol. The fact that 2-propanol gave more benzene than 3-pentanol shows that steric hindrance of hydrogen donors retards the hydrogen transfer reaction. In the reaction of acyclic aliphatic amines the benzene yield decreased in the order: propylamine > dipropylamine > tripropylamine. In the reaction of hydrocarbons, *d*-limonene gave benzene most efficiently.

The order of the hydrogen-donating ability of organic compounds in the reactions in phenetole did not change much from that in the reactions without solvents, although the relative activity of the amines was a little higher in the solvent system than in the absence of solvents.

One mole of $RuH_2(PPh_3)_4$ gave 2.1 moles of benzene when the complex was heated in phenetole in the absence of hydrogen donors. This results suggests that the reaction, $RuH_2(PPh_3)_2L_n \rightarrow Ru(PPh_2)_2L_n + 2\ PhH$, in which L_n represents ligands, occurred. However, the possibility that hydrogen atoms attached to the *o*-position of benzene rings of triphenylphosphine were used to some extent as a hydrogen source cannot be discounted, for *ortho*-metallation of triphenylphosphine ligands in ruthenium complexes is well known [5].

Dependence of the amount of benzene and triphenylphosphine on reaction time

When $RuCl_2(PPh_3)_3$ (0.05 *M*) was heated in pyrrolidine at 140°C, benzene was formed slowly for ca. 3 h and then more rapidly, as shown in Fig. 1. The reason for such an induction period is not yet clear. After ca. 7 h, the amount of benzene reached about 0.4 *M* and became constant. A small amount of benzene was detected at zero reaction time, probably because the complex reacted slightly with pyrrolidine in the process of the GLC analysis of benzene. Such a phenomenon was observed also in the reactions of $RuH_2(PPh_3)_4$ and $PdCl_2(PPh_3)_2$, as shown in Figs. 2 and 3.

The detection and the quantitative analysis of phosphines were tried as well. After the analysis of benzene, the reaction mixtures were treated with aqueous potassium cyanide-potassium hydroxide solution to generate free phosphines and then submitted to GLC analysis. The amount of the triphenylphosphine detected was 0.1 *M* in the reaction mixture which had not been heated as yet and was considerably lower than the theoretical amount, 0.15 *M*. This may be attributable at least partly to the difficulty of decomposing the complexes completely. The amount of triphenylphosphine decreased rapidly after the induction period in the formation of benzene and became 0.01—0.02 *M* after about 7 h. Diphenylphosphine and phenylphosphine were not detected. This result suggests that diphenylphosphine and phenylphosphine underwent the hydrogenolysis more rapidly than triphenylphosphine.

Biphenyl was detected in some cases. For example, 0.2 m*M* biphenyl was obtained along with 0.05 *M* benzene when $RuCl_2(PPh_3)_3$ (0.05 *M*) and indoline (0.05 *M*) were heated in xylene at 170°C for 1 h. As Fahey and Maham have reported [6], the formation of biphenyl in the reactions of triphenylphosphine complexes of transition metals suggests that oxidative addition of the phos-

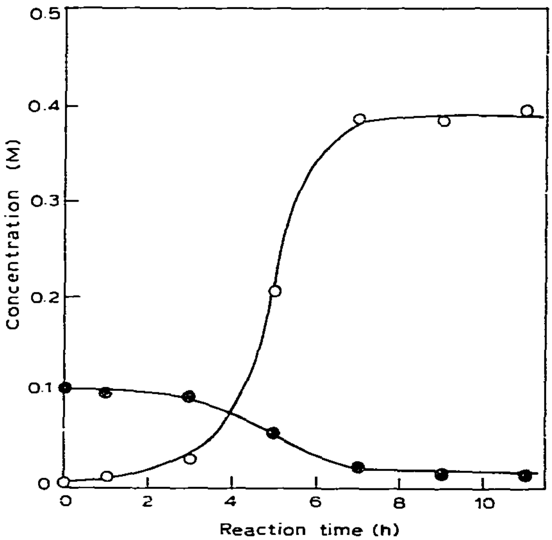

Fig. 1. The dependence of yield of benzene (○———○) and recovery of triphenylphosphine (●———●) on reaction time; $RuCl_2(PPh_3)_3$ (0.05 *M*) was heated at 140°C in pyrrolidine.

phine to central metals to give phenyl complexes, such as $RuHCl(PPh_3)L_n \rightarrow RuHCl(Ph)(PPh_2)L_n$, occurs.

As shown in Fig. 2, the reaction of $RuH_2(PPh_3)_4$ was very similar to that of $RuCl_2(PPh_3)_3$. This reaction also had an induction period of ca. 2 h and the formation of benzene ceased suddenly after ca. 9 h. The concentration of the triphenylphosphine detected in the reaction mixtures in which the hydrogenolysis had hardly proceeded was about 0.1 *M* and lower than the theoretical value, 0.15 *M*. The amount of the benzene formed seems to be about three times as much as that of the triphenylphosphine consumed, that is, in the reactions for 3 and 5 h, 0.09 and 0.28 *M* benzene was formed and 0.02 and 0.08 *M* triphenylphosphine was consumed, respectively. This result suggests that a triphenylphosphine molecule was hydrogenolyzed completely to give three molecules of benzene and then the next triphenylphosphine molecule underwent the complete hydrogenolysis. Diphenylphosphine and phenylphosphine were not detected. Biphenyl was also detected in most cases. For example, 0.08 mM biphenyl was obtained when the hydride complex (0.05 *M*) was heated in pyrrolidine at 140°C for 6 h.

The reaction mixtures obtained by heating $RuCl_2(PPh_3)_3$ or $RuH_2(PPh_3)_4$ in pyrrolidine at 140°C for 5 h, gave no crystals by cooling, by adding hexane or ether, by evaporating volatile compounds under reduced pressure, or by treating the residues by ether.

The benzene yield vs. reaction time curves in the reactions of $RuCl_2(PPh_3)_3$, $RuH_2(PPh_3)_4$, $RhCl(PPh_3)_3$ [1a], and $RhH(PPh_3)_4$ [1a] in pyrrolidine are similar. This may imply that similar reaction mechanisms are involved.

Further, the dependence of the amount of benzene on time in the reaction of $PdCl_2(PPh_3)_2$ in pyrrolidine was investigated at temperature ranging from 60 to 180°C, and the results are shown in Fig. 3. They differed considerably from

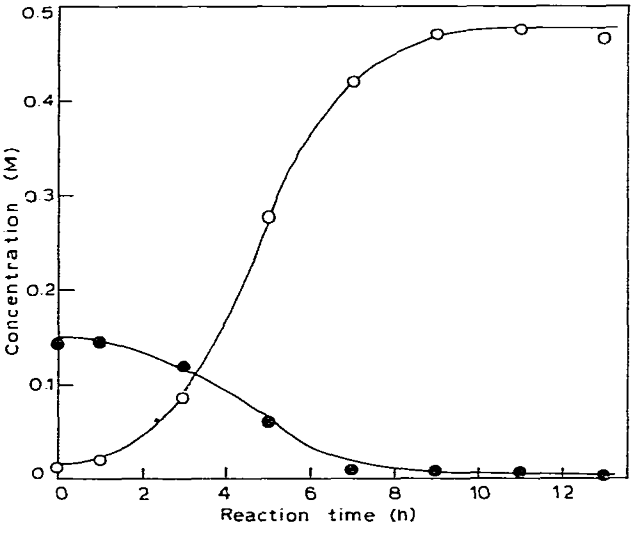

Fig. 2. The dependence of yield of benzene (○———○) and recovery of triphenylphosphine (●———●) on reaction time; $RuH_2(PPh_3)_4$ (0.05 *M*) was heated at 140°C in pyrrolidine.

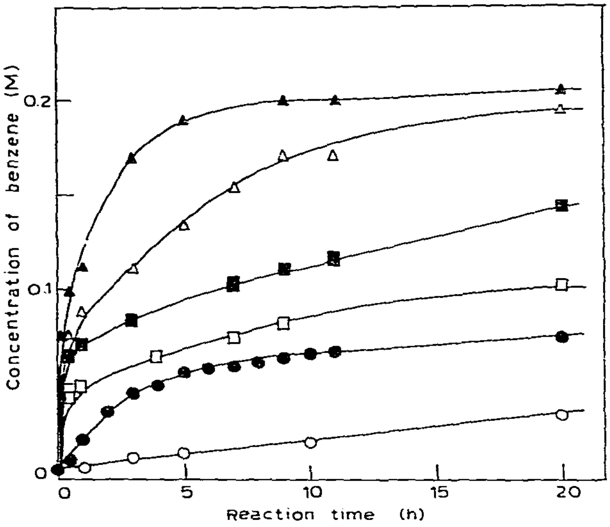

Fig. 3. The dependence of yield of benzene on reaction time; $PdCl_2(PPh_3)_2$ (0.05 *M*) was heated in pyrrolidine at 60 (○——○), 100 (●——●), 120 (□——□), 140 (■——■), 160 (△——△), and 180°C (▲——▲).

the results of the Ru^{II}-species shown in Figs. 1 and 2, and indicate the following characteristics: (1) no induction period was observed in the formation of benzene; (2) at first benzene formed in proportion to time, but its formation slowed down rather rapidly when its concentration reached certain values which were determined by reaction temperatures; and (3) the hydrogenolysis seems to have stopped before it was complete.

Reaction solvents

When $RuCl_2(PPh_3)_3$ (0.05 *M*) and pyrrolidine (0.45 *M*) were heated at 160°C for 5 h in some solvents which dissolve the complex fairly well and are inert to hydrogen transfer reactions under these conditions, the benzene yield decreased in the following order: phenetole (0.17 *M*), xylene (0.14 *M*), cumene (0.14 *M*), and benzonitrile (0.01 *M*): the figures shown in the parentheses represent the concentration of the benzene formed. When indoline was used instead of pyrrolidine, the concentration became 0.07, 0.05, 0.05, and 0.01 *M*, respectively. This result indicates that the effect of the solvent examined was scarcely influenced by the hydrogen donors. In the subsequent experiments phenetole was used as a solvent.

The effect of additives

In the reaction in phenetole, the effect of additives was studied and the results are summarized in Table 4. The results suggest the removal of hydrogen chloride from chloro complexes by amines occurs, such as $RuCl_2L_n \xrightarrow{2\,(H)} RuH_2Cl_2L_n \xrightarrow[-\text{amine}\cdot\text{HCl}]{\text{amine}} RuHClL_n$, because (1) in $RuCl_2(PPh_3)_3$-2-propanol and -tetralin systems the addition of tripropylamine which showed no hydrogen-donating power promoted the formation of benzene, while it did not in the systems

TABLE 4

EFFECT OF ADDITIVE [a]

Complex	Hydrogen donor	Additive	Yield of benzene (M)
$RuCl_2(PPh_3)_3$	Indoline	None	0.08
		Tripropylamine	0.08
		Triphenylphosphine	0.03
		AIBN [b]	0.09
		Hydroquinone	0.08
	Pyrrolidine	None	0.24
		Tripropylamine	0.21
		Triphenylphosphine	0.28
	2-Propanol	None	0.01
		Tripropylamine	0.06
	Tetralin	None	Trace
		Tripropylamine	0.11
$RuH_2(PPh_3)_4$	Indoline	None	0.14
		Tripropylamine	0.14
		AIBN [b]	0.11
	Pyrrolidine	None	0.20
		Tripropylamine	0.18
	2-Propanol	None	0.17
		Tripropylamine	0.15
	Tetralin	None	0.11
		Tripropylamine	0.11

[a] A complex (0.05 M), a hydrogen donor (1.0 M), and an additive (0.5 M) were heated at 140°C for 11 h in phenetole. [b] The concentration of this additive was 0.05 M.

including indoline and pyrrolidine which are bases, and (2) in any reaction of $RuH_2(PPh_3)_4$ the addition of the tertiary amine did not raise the yield of benzene, and finally (3) $RuH_2(PPh_3)_4$ gave much more benzene than did $RuCl_2(PPh_3)_3$ in the reaction of 2-propanol without additives.

In the $RuCl_2(PPh_3)_3$-pyrrolidine system the addition of triphenylphosphine, which is a ligand and hydrogen acceptor, raised the benzene yield, but in the $RuCl_2(PPh_3)_3$-indoline system it lowered the yield. This phenomenon may be explained by assuming that the excess of triphenylphosphine, which has strong coordinating power, retarded the coordination of the hydrogen donors and that the coordinating ability of indoline is lower than that of pyrrolidine. This assumption is supported by the fact that the addition of the phosphine hindered catalytic hydrogen transfer reaction in some cases [1,3,7] and by the inference that pyrrolidine, which is a five-membered alicyclic amine, shows higher basicity and smaller steric hindrance than indoline which is a cyclic aromatic amine.

Hydroquinone, which is an inhibitor of radical reactions, did not retard the hydrogenolysis and α,α'-azobisisobutyronitrile (AIBN), which is a radical source, did not promote the reaction. This makes it unlikely that the hydrogen transfer reaction proceeds via a radical process, although the result does not necessarily deny the existence of radical intermediates.

Isotope effect

In the hydrogen transfer from 2-propanol and 2-propanol-d_8 to olefins catalyzed by $RuCl_2(PPh_3)_3$ [8], $RuH_2(PPh_3)_4$ [7c,8], $RhCl(PPh_3)_3$ [8], and

TABLE 5

ISOTOPE EFFECT [a]

Complex	Hydrogen donor	Temp. (°C)	Time	Yield of benzene (M)
$RuH_2(PPh_3)_4$	2-Propanol	130	3 h	0.20
	2-Propanol-d_8	130	3 h	0.21
$RhH(PPh_3)_4$	2-Propanol	130	70 min	0.34
	2-Propanol-d_8	130	70 min	0.35
$RhCl(PPh_3)_3$	2-Propanol	150	20 h	0.21
	2-Propanol-d_8	150	20 h	0.20

[a] The designated complex (0.05 M) and the designated hydrogen donor (3.0 M) were heated in phenetole.

$RhH(PPh_3)_4$ [7a,8], a primary kinetic isotope effect was observed and the hydrogen transfer from the alcohols to the central metals of the catalyst was inferred to be rate-determining. In the reduction of aldehydes with these alcohols catalyzed by $RuH_2(PPh_3)_4$, no primary kinetic isotope effect was observed and the coordination of the hydrogen donors to the catalyst was assumed to be rate-limiting [8].

As shown in Table 1, $RuH_2(PPh_3)_4$, $RhH(PPh_3)_4$, and $RhCl(PPh_3)_3$ gave consierable amounts of benzene in the reaction with 2-propanol. So the isotope effect in the hydrogenolysis of triphenylphosphine was investigated by heating each complex (0.05 M) and 2-propanol (3.0 M) or 2-propanol-d_8 in phenetole. The results, summarized in Table 5, show that the both hydrogen donors yielded comparable amounts of benzene in the reactions of any complex. The absence of a primary kinetic isotope effect indicates that hydrogen transfer steps in the hydrogenolysis are not rate-determining. The coordination of the hydrogen donors also cannot be rate-limiting because the hydrogen transfer from alcohols to olefins proceeds more rapidly under milder conditions than the hydrogenolysis [7]. Therefore, the cleavage and the oxidative addition of the P—C bonds of the phosphine ligands is assumed to be the rate-determining step. The formation of phenyl complexes by oxidative addition was suggested by the detection of biphenyl, as described before.

Experimental

The transition metal complexes were prepared by the methods reported in the literature [9]. 2-Propanol-d_8 was purchased and used without purification. The preparation and purification of the other reagents were reported in a previous paper [1a].

An example of the hydrogenolysis in a hydrogen donor

$RuCl_2(PPh_3)_3$ (24 mg, 0.025 mmol) was placed in a Pyrex glass tube sealed at one end. Pyrrolidine was added to the vessel and the total volume of the solution was made 0.5 ml. The tube was sealed in vacuo after two freeze-thaw (liquid N_2) cycles on a vacuum line. The sealed tube was heated for 6 h in a polyethylene glycol bath kept at 140 ± 1°C. After cooling, the tube was opened and sealed with a cap made of silicone rubber. The reaction mixture, to which 15 μl of dibutyl ether was added with a syringe as an internal standard, was submitted to GLC analysis (15% 1,2,3-tris(2-cyanoethoxy)propane on Diasolid L). After the analysis of benzene, 15 μl of trioctylamine (internal standard), 0.2 ml of phenetole, and 0.5 ml of an aqueous solution saturated with potassium cyanide and potassium hydroxide (1 : 1) were added to the mixture. The mixture was shaken for 3 h on a shaker and the organic layer separated was submitted to GLC analysis for phosphines in which a 1 m column packed with 15% Apiezon grease L was used.

Other experiments of the transfer hydrogenolysis were carried out in a similar way, although in the reactions using 2-propanol benzene analysis was performed with a column packed with 15% Carbowax 20 M and undecane was an internal standard.

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