od B does not seem valid, since equilibrium control implies reversibility of alkylation, and the lack of rearrangement of phenylhexanes present in the chloropentane alkylations at −20° appears to refute this possibility. Of course one must remember that the reaction mixtures produced by both methods A and B are heterogeneous, and the isomeric chloroalkanes, catalyst, arene, and solvent (hexane) may be distributed quite differently in the reaction medium when the order of addition is changed. It is conceivable that in the reactions carried out by method B either (1) equilibration of the product phenylalkanes *does* occur even at −20°, or (2) there is not the same difference in rates of alkylation by 2- and 3-chloroalkanes in the reaction medium of method B as in the reaction medium of method A.

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Transfer Hydrogenation and Transfer Hydrogenolysis. IX. Hydrogen Transfer from Organic Compounds to Aldehydes and Ketones Catalyzed by Dihydridotetrakis(triphenylphosphine)ruthenium(II)

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In the hydrogen transfer from organic compounds to aldehydes and ketones, $RuH_2(PPh_3)_4$ was found to have an excellent catalytic activity under mild conditions. Ethers, hydroaromatic compounds, tertiary amines, and alcohols showed hydrogen donating ability, and the ability decreased in the order 2,5-dihydrofuran > tri-*n*-propylamine > benzyl alcohol > cyclohexanol > ethyl alcohol > tetralin ≈ 1,2-dihydronaphthalene > dioxane. The mechanism of hydrogen transfer from alcohols to the aldehydes was investigated. The data of the reaction can be accommodated by the rate expression of the form rate = k[D][Cat]$_0$/(1 + K[RCHO]), where [D], [Cat]$_0$, and [RCHO] are alcohol, catalyst, and aldehyde concentration, respectively. The kinetic isotope effect, R_H/R_D = 0.9, and other data suggests that the rate-determining step of the reaction is the coordination of the alcohols to the complex. The process of the hydrogen transfer from alcohols to aldehydes on the metal is also proposed.

In catalytic hydrogenation using transition metal complexes as catalysts, olefins have been mainly used as hydrogen acceptors and the reduction of other functional groups has received little attention. As for the reduction of aldehydes and ketones by molecular hydrogen, it has been reported that several cobalt,[1] iridium,[2] and rhodium[3] complexes have activities as homogeneous catalysts. In the catalytic transfer hydrogenation of aldehydes and ketones to alcohols, only primary and secondary alcohols seem to have been used as hydrogen donors, and transition metal salts,[4] $CoH_3(PPh_3)_3$,[5] $RhCl(PPh_3)_3$,[6] $RuCl_2(PPh_3)_3$,[7] and $IrCl_3[P(OMe)_3]_3$,[8] have been reported to have activity as homogeneous transition metal catalysts. However, no detailed studies of the mechanism of the reaction, including that of heterogeneous systems, have yet been carried out.

This study was undertaken to examine the transfer hydrogenation of aldehydes and ketones in detail.

Results and Discussion

Catalytic Activity of Some Phosphine Complexes. The catalytic activity of some representative phosphine complexes for the reduction of *n*-hexaldehyde was investigated. When a catalyst (0.02 M), benzyl alcohol (2.0 M), and *n*-hexaldehyde (1.0 M) were heated in bromobenzene at 120° for 150 min, the yield of *n*-hexyl alcohol was given as follows: $RuH_2(PPh_3)_4$, 0.90 M; $RuH_2(CO)(PPh_3)_3$, 0.78 M; $RuCl_2(PPh_3)_3$, 0.43 M; $RhH(PPh_3)_4$, 0.02 M; and $RhCl(CO)(PPh_3)_2$, $CoH[P(OPh)_3]_3$, and $MCl_2(PPh_3)_2$ (M = Fe, Ni, Co, Pd, and Pt) had no catalytic activity under this condition. $RhCl(PPh_3)_3$ showed no catalytic activity, because the complex was transformed to $RhCl(CO)(PPh_3)_2$ by the reaction with aldehyde[9] which has no catalytic activity. $RuH_2(PPh_3)_4$ was found to have the highest activity among complexes tried in this transfer hydrogenation, and the complex catalyzed the hydrogen transfer even at room temperature. In this study, $RuH_2(PPh_3)_4$ was used as a catalyst.

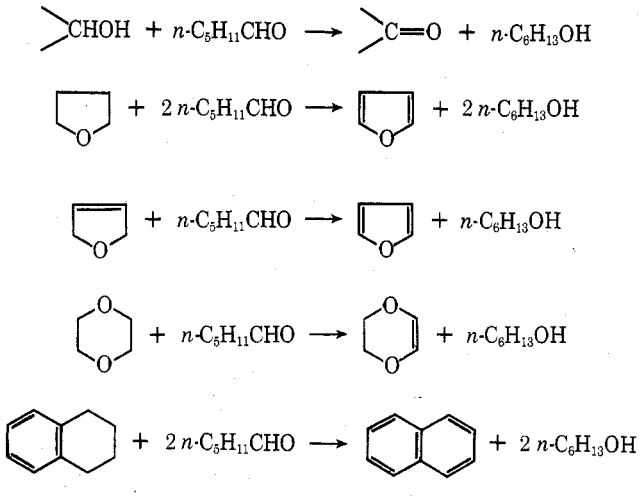
Hydrogen-Donating Ability of Some Organic Compounds. We have previously reported that cyclic ethers,[10] amines,[11] and alcohols[12] donate hydrogen to olefins in the presence of $RhCl(PPh_3)_3$, $RhH(PPh_3)_4$, or $RuH_2(PPh_3)_4$. The hydrogen-donating ability of some organic compounds to *n*-hexaldehyde was evaluated (Table I). 2,5-Dihydrofuran, benzyl alcohol, and cyclohexanol showed especially excellent hydrogen-donating abilities. Perhaps these compounds donate hydrogen rapidly and the resulted dehydrogenation products are relatively resistant to reduction. Other alcohols, hydroaromatic compounds, and ethers had almost the same hydrogen-donating abilities under the reaction condition. It is noteworthy that noncyclic ethers gave hydrogen in homogeneous catalysis, because such a phenomena seems not to be reported. When primary and secondary amines were used, *n*-hexyl alcohol was not detected and *n*-hexaldehyde disappeared. In the case of tertiary amines, the alcohol was obtained in good yield, but the amount of the surviving aldehyde was smaller than the theoretical one. These results show the existence of side reactions between the aldehyde and amines.

Analyses of the dehydrogenation products summarized in Table II clearly shows that the following reactions proceeded almost stoichiometrically without remarkable side reactions.

Table I
Transfer Hydrogenation of *n*-Hexaldehyde[a]

Registry no.	Hydrogen donor	Yield of *n*-hexyl alcohol, %	Dehydrogenation product
1708-29-8	2,5-Dihydrofuran	30	Furan
123-91-1	Dioxane	10	Dioxene
109-99-9	Tetrahydrofuran	9	Furan
111-43-3	Di-*n*-propyl ether	9	*b*
108-20-3	Diisopropyl ether	9	*b*
142-68-7	Tetrahydropyran	8	2,3-Dihydropyran
142-96-1	Di-*n*-butyl ether	7	*b*
628-81-9	Butyl ethyl ether	6	*b*
102-69-2	Tri-*n*-propylamine	25	*b*
1116-76-3	Tri-*n*-octylamine	11	*b*
100-51-6	Benzyl alcohol	23	Benzaldehyde
108-93-0	Cyclohexanol	19	Cyclohexanone
64-17-5	Ethyl alcohol	13	Acetaldehyde
67-63-0	Isopropyl alcohol	10	Acetone
119-64-2	Tetralin	11	1,2-Dihydronaphthalene Naphthalene
447-53-0	1,2-Dihydronaphthalene	11	Naphthalene
110-83-8	Cyclohexene	9	Benzene

[a] $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and the hydrogen donor (2.0 M) were heated in bromobenzene at 36.5 ± 0.5° for 72 h. [b] Dehydrogenation product was not identified.



When the reaction was carried out in alcohols, the produced alcohol was scarcely dehydrogenated to *n*-hexaldehyde and *n*-hexyl alcohol was obtained in good yield. In the case of 2,5-dihydrofuran, *n*-hexyl alcohol was obtained in the yield of 100%, partly because the dehydrogenation product, furan, is an aromatic compound and resists hydrogenation. Even when excess triphenylphosphine was added to 2-propanol solution, the yield of *n*-hexyl alcohol was about 100%. This fact suggests that the aldehyde has large coordinating ability to the complex.

Hydrogen Acceptor. Several aldehydes and ketones were examined as hydrogen acceptors (Table III). Aliphatic aldehydes were efficiently reduced. A more steric aldehyde was hydrogenated more easily than a less steric one. As a less steric aldehyde has strong coordinating ability, it may act as a poison of the catalyst and make the coordination of the hydrogen donor difficult. These results and reasoning are compatible with the dependence of the reaction rate on aldehyde concentration, as described later. Crotonaldehyde, which has two unsaturated bonds, C=C and C=O, was hydrogenated to *n*-butyraldehyde and *n*-butyl alcohol. As it has been reported that in the case of α,β-unsaturated carbonyl compounds only the C=C bond was hydrogenated,[13] this catalyst action seems to be a unique one. The low conversion of crotonaldehyde may be due to the stabilization by resonance between C=C and C=O bonds and/or to the coordination to the complex as bidentate ligand blocking the coordination of the hydrogen donor. Compared with aldehydes, ketones were relatively resistant to reduc-

Table II
Stoichiometric Relation of Transfer Hydrogenation[a]

Hydrogen donor	Yield of *n*-hexyl alcohol, M	Survived *n*-hexaldehyde, M	Dehydrogenation product, M
2,5-Dihydrofuran	1.00	0.00	Furan, 1.00
Isopropyl alcohol	1.00	0.00	Acetone, 1.00
Isopropyl alcohol[b]	0.99	Trace	Acetone, 1.00
Benzyl alcohol	0.97	0.03	Benzaldehyde, 0.97
Cyclohexanol	0.93	0.06	Cyclohexanone, 0.93
n-Propyl alcohol	0.88	0.11	Propionaldehyde, 0.86
Tetralin	0.29	0.70	1,2-Dihydronaphthalene, 0.10 Naphthalene, 0.09
Dioxane	0.29	0.70	Dioxene, 0.30
Tetrahydrofuran	0.10	0.88	Furan, 0.05

[a] $RuH_2(PPh_3)_4$ (0.02 M) and *n*-hexaldehyde (1.0 M) were heated at 140° for 2 h in the designated hydrogen donor. [b] 0.2 M of PPh_3 was added.

Table III
Transfer Hydrogenation of Aldehydes and Ketones[a]

Registry no.	Hydrogen acceptor	Yield of product, M
123-38-6	Propionaldehyde	*n*-Propyl alcohol, 0.22
123-72-8	*n*-Butyraldehyde	*n*-Butyl alcohol, 0.34
78-84-2	Isobutylaldehyde	Isobutyl alcohol, 0.50
110-62-3	*n*-Pentaldehyde	*n*-Pentyl alcohol, 0.40
66-25-1	*n*-Hexaldehyde	*n*-Hexyl alcohol, 0.42
111-71-7	*n*-Heptaldehyde	*n*-Heptyl alcohol, 0.44
124-13-0	*n*-Octaldehyde	*n*-Octyl alcohol, 0.48
123-05-7	2-Ethyl-1-hexaldehyde	2-Ethyl-1-hexyl alcohol, 0.49
4170-30-3	Crotonaldehyde	*n*-Butyl alcohol, 0.05 *n*-Butyraldehyde, 0.08
67-64-1	Acetone	Isopropyl alcohol, 0.18
96-22-0	Diethyl ketone	3-Pentanol, 0.09

[a] $RuH_2(PPh_3)_4$ (0.02 M), benzyl alcohol (2.0 M), and the hydrogen acceptor (1.0 M) were heated in bromobenzene at 100° for 1 hr.

Table IV
Solvent Effect in Transfer Hydrogenation[a]

Registry no.	Solvent	Rate, M min^{-1}	Registry no.	Solvent	Rate, M min^{-1}
67-68-5	Dimethyl sulfoxide	7.0×10^{-3}	110-54-3	*n*-Hexane	3.8×10^{-3}
98-95-3	Nitrobenzene	4.6×10^{-3}	108-90-7	Chlorobenzene	3.7×10^{-3}
140-11-4	Benzyl acetate	4.0×10^{-3}	1330-20-7	Xylene	3.5×10^{-3}
110-82-7	Cyclohexane	4.0×10^{-3}	150-76-5	Anisole	3.1×10^{-3}
108-86-1	Bromobenzene	3.8×10^{-3}	60-29-7	Diethyl ether	2.5×10^{-3}
71-43-2	Benzene	3.8×10^{-3}			

[a] $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and benzyl alcohol (2.0 M) were heated in the designated solvent at 80°.

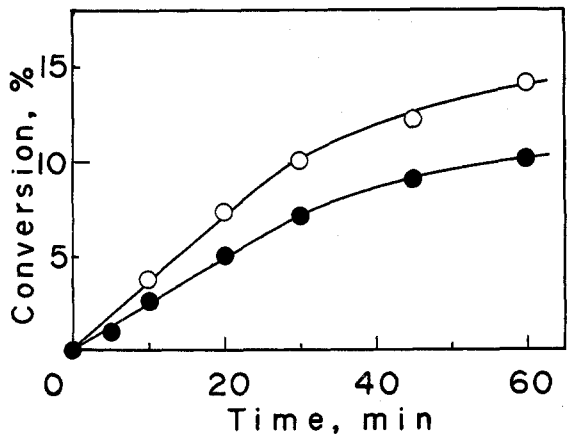


Figure 1. Plot of conversion vs. reaction time: $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and the hydrogen donor (2.0 M) were heated in bromobenzene at 80°. ○, benzyl alcohol; ●, isopropyl alcohol.

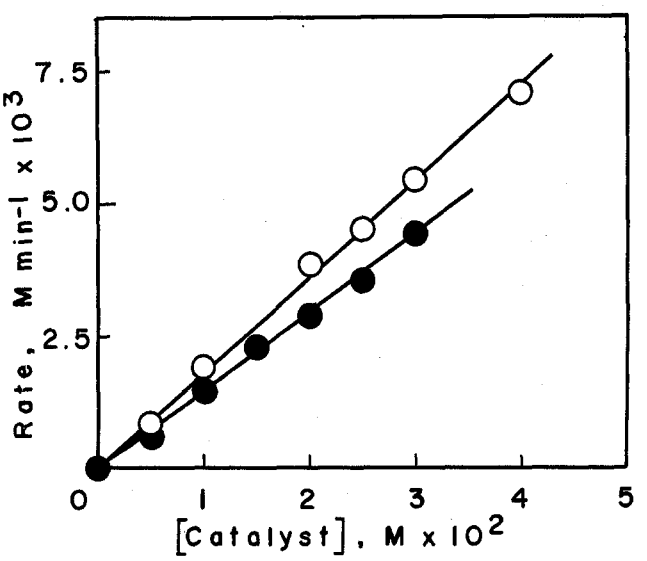


Figure 2. Dependence of rate of reduction of *n*-hexaldehyde on catalyst concentration: the catalyst, *n*-hexaldehyde (1.0 M), and the hydrogen donor (2.0 M) were heated in bromobenzene at 80°. ○, benzyl alcohol; ●, isopropyl alcohol.

tion. This may be explained by the fact that the formed secondary alcohols donate hydrogen more easily than primary alcohols, as shown in Table II. Nitrobenzene, benzonitrile, and acetonitrile were not reduced under the same condition. In this study, *n*-hexaldehyde was used as an acceptor because of the ease in GLC analysis.

Reaction Solvent. Initial rates of the transfer hydrogenation in several solvents were measured (Table IV). The catalyst dissolved well in these solvents at reaction temperature. The rate was not so varied by the kinds of solvents except for dimethyl sulfoxide and nitrobenzene. The fact

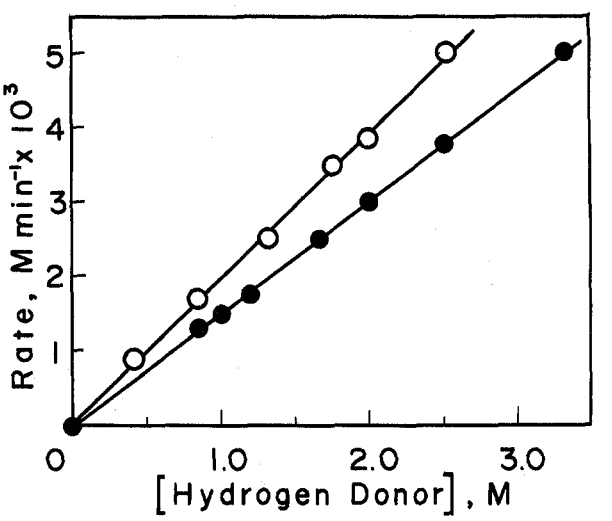


Figure 3. Dependence of rate of reduction of *n*-hexaldehyde on the hydrogen donor concentration: $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and the hydrogen donor were heated in bromobenzene at 80°. ○, benzyl alcohol; ●, isopropyl alcohol.

that the reduction of the aldehyde proceeded effectively in highly polar and coordinative solvents such as dimethyl sulfoxide and nitrobenzene suggests that the coordinating powers of alcohols and aldehydes are not so weak and strongly polar solvents promote the displacement of the dehydrogenation products by reactants. In this study, bromobenzene was used as a solvent because of convenience.

Measurement of Initial Rate. Figure 1 shows an example of the conversion of *n*-hexaldehyde to *n*-hexyl alcohol against reaction time. At the initial stage of the reaction, the conversion was proportional to the time. However, the linearity did not hold in the conversion more than 10% (benzyl alcohol) and 7% (isopropyl alcohol), perhaps because the produced *n*-hexyl alcohol itself was dehydrogenated to *n*-hexaldehyde and the dehydrogenated products, such as benzaldehyde and acetone, were hydrogenated to the original alcohols. The initial rate of the reaction (R) was derived from the linear part.

The initial rate of the reduction was found to be proportional to the concentration of the catalyst and hydrogen donors (Figures 2 and 3). This result indicates that either the coordination of the hydrogen donor takes place before the rate-determining step or this step is rate limiting.

The initial rate of the reduction decreased with the increase of aldehyde concentration, and the reciprocal of the rate against aldehyde concentration was linear with a positive intercept on the y axis (Figure 4). It is thought that the aldehyde has strong coordinating power and that a considerable amount of aldehyde complexes exists in the reaction system.

Dependence on Added Phosphine. In transfer hydrogenation of olefins,[11,12] except for the $RhCl(PPh_3)_3$–dioxane system,[10] the addition of triphenylphosphine decreased

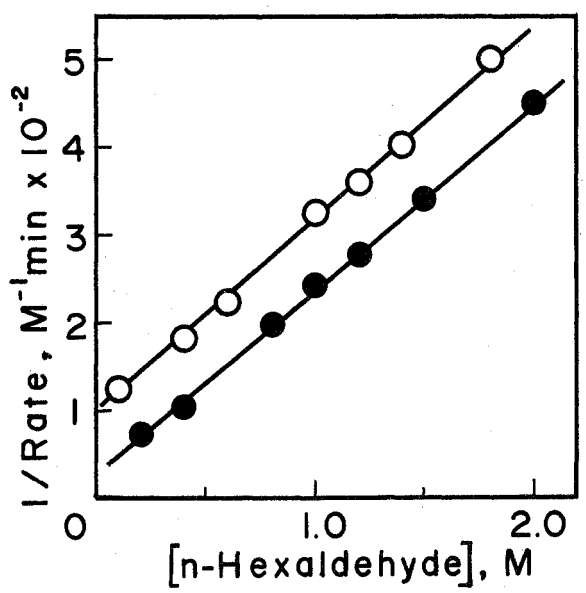


Figure 4. Dependence of rate of reduction of *n*-hexaldehyde on the aldehyde concentration: $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde, and the hydrogen donor (2.0 M) were heated in bromobenzene at 80°. ○, benzyl alcohol; ●, isopropyl alcohol.

the reaction rate. In contrast, the rate of the reduction of aldehyde was not decreased at all by the addition of the phosphine over the range of 0.02–0.2 M.

Dependence on Reaction Temperature. Initial rates were measured at 60, 70, 80, 90, 100, and 110°. Good linear plots of log R against $1/T$ were obtained in the case of benzyl alcohol and isopropyl alcohol, indicating that the kinetics of the reaction system are not so complicated. From the plots, activation energy, E_a, and activation enthalpy, $\Delta H^{\ddagger}$ are obtained (Table V), and activation entropy, $\Delta S^{\ddagger}$, is calculated with the observed rate constant (k'). The values of the corresponding parameters are almost equal in the reduction in bromobenzene, and this seems to show the similarity in the reaction mechanism. It is inferred that active intermediates are not ionized or strongly polarized and the coordination of bromobenzene occurs, because the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the reaction in bromobenzene are considerably lower than those in *n*-hexane. Further, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the reduction of *n*-hexaldehyde are much lower than those in the case of cyclohexene. Perhaps this suggests that the nature of the rate-determining step is different in the two reactions and that active intermediates in the reduction of the aldehyde are more crowded or more ordered than in the reduction of cyclohexene.[14]

Isotopic Study. When isopropyl alcohol-d_8 (1.0 M) was used instead of isopropyl alcohol at 80°, the initial rate was 1.9×10^{-3} M min^{-1}, while in the case of isopropyl alcohol it was 1.7×10^{-3} M min^{-1}. The value of the kinetic isotope effect, $R_H/R_D = 0.9$, shows that a hydrogen transfer step is not rate limiting. In the transfer hydrogenation of olefins catalyzed by representative Rh(I) and Ru(II) complexes, the kinetic isotope effect of large values was observed, and the dehydrogenation of the hydrogen donor was considered to be rate limiting. The difference of the kinetic isotope effect in $RuH_2(PPh_3)_4$ catalysis indicates that the nature of reaction intermediates and the rate-determining step are different from one another. Other complexes shown in Table VI had no catalytic activity for the reduction of the aldehyde.

Dependence of the Rate on Hydrogen Donor. The initial rate of the hydrogenation of *n*-hexaldehyde was measured in the presence of several hydrogen donors (Table VII). The fact that aliphatic secondary alcohols, having a bulky branched chain, had less effective hydrogen-donating abilities suggests that the coordination of alcohols to the catalyst is an important reaction step. Benzyl alcohol and 2-phenylethyl alcohol showed more excellent hydrogen-donating abilities than aliphatic alcohols. Perhaps this fact may be rationalized by the stability of the formed carbonyl groups conjugated with benzene ring and/or by the promoting effect of benzene ring on the coordination of the hydrogen donors to the catalyst complex. The effective hydrogen-donating abilities of 2,5-dihydrofuran and tetralin may be due to aromatization.

Table V
Kinetic Parameters

Hydrogen donor	Solvent	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$ (80°), kcal mol^{-1}	$\Delta S^{\ddagger}$ (80°), eu
Benzyl alcohol[a]	Bromobenzene	10.3	9.6	−41.8
Benzyl alcohol[a]	*n*-Hexane	17.2	16.6	−17.0
Isopropyl alcohol[a]	Bromobenzene	11.0	10.3	−42.5
Isopropyl alcohol[b]	Toluene	31.4	30.7	20

[a] $RuH_2(PPh_3)_4$ (0.02 M) and *n*-hexaldehyde (1.0 M) were used. [b] $RuH_2(PPh_3)_4$ (0.01 M) and cyclohexene (0.5 M) were used.

Table VI
Kinetic Isotope Effect

Registry no.	Complex	Olefin[a] R_H/R_D	*n*-Hexaldehyde[b] R_H/R_D
14694-95-2	$RhCl(PPh_3)_3$	2.6 (180°)	Decarbonylation occurred
18284-36-1	$RhH(PPh_3)_4$	1.33 (80°)	[c]
15529-49-4	$RuCl_2(PPh_3)_3$	2.8 (180°)	[c]
19529-00-1	$RuH_2(PPh_3)_4$	2.7 (80°)	0.9

[a] The catalyst (0.01 M), isopropyl alcohol or isopropyl alcohol-d_8 (1.0 M), and cyclohexene (0.5 M) were heated in toluene. [b] The catalyst (0.02 M), isopropyl alcohol or isopropyl alcohol-d_8 (1.0 M), and *n*-hexaldehyde (1.0 M) were heated in bromobenzene. [c] The reduction of the aldehyde was very slow.

Spectrophotometric Study. The visible spectrum of $RuH_2(PPh_3)_4$ in chloroform showed an absorption peak at 650 nm (ϵ 10^3). The strength of the peak decreased gradually with time by addition of aldehydes. The initial rates of the decrease of the absorption peak were measured for several aldehydes (Table VIII). The rates of the decrease of branched aldehydes were smaller than those of straight-chain aldehydes, and this shows the existence of steric hindrance in the coordination of aldehyde to the complex. The appearance of the maximum value at *n*-hexaldehyde may be due to the optimum balance between the coordination of the aldehyde and the release of the resulting alcohol, which can reduce the Ru(0) complex to Ru(II) dihydrido complex. Besides, the decreasing order of rates is not parallel to that of the conversion of aldehydes to alcohols, and it may suggest that the hydrogen transfer from the complex to aldehydes is not the rate-determining step of the catalytic cycle. Accompanied with the decrease of the strength of the peak at 650 nm, the new absorption peak at 560 nm appeared. The peak was assignable to Ru(0) species on the following observations: (1) when *n*-hexaldehyde (0.1 M) and $RuH_2(PPh_3)_4$ (0.1 M) were heated in chloroform at 36.5° for 72 hr, 0.1 M of *n*-hexyl alcohol was obtained. In the reaction mixture, the absorption peak appeared at 560 nm and the one at 650 nm disappeared. (2) The ir spectrum of the chloroform solution showed no peaks assignable to the hydride ligands. Moreover, when the volatile compounds were evaporated from the solution in vacuo, the ir

Table VII
Rate of Transfer Hydrogenation of *n*-Hexaldehyde[a]

Hydrogen donor	Rate, M min^{-1}	Hydrogen donor	Rate, M min^{-1}
2,5-Dihydrofuran	15.5×10^{-3}	Ethyl alcohol	2.5×10^{-3}
Tetralin	4.2×10^{-3}	*sec*-Butyl alcohol	1.8×10^{-3}
Benzyl alcohol	3.8×10^{-3}	3-Pentyl alcohol	1.6×10^{-3}
Isopropyl alcohol	2.8×10^{-3}	4-Methyl-2-pentyl alcohol	1.5×10^{-3}
2-Phenylethyl alcohol	2.7×10^{-3}		

[a] $RuH_2(PPh_3)_4$ (0.02 M), *n*-hexaldehyde (1.0 M), and the hydrogen donor (2.0 M) were heated in bromobenzene at 80°.

Table VIII
The Rate of Spectral Change of the Catalyst[a]

Additive	Rate, M min^{-1}	Additive	Rate, M min^{-1}
Propionaldehyde	2.80×10^{-6}	*n*-Heptaldehyde	3.74×10^{-6}
n-Butyraldehyde	4.76×10^{-6}	*n*-Octaldehyde	3.10×10^{-6}
Isobutyraldehyde	2.00×10^{-6}	2-Ethyl-1-hexaldehyde	2.20×10^{-6}
n-Pentaldehyde	4.82×10^{-6}	Acetone	8.00×10^{-7}
n-Hexaldehyde	5.62×10^{-6}		

[a] $RuH_2(PPh_3)_4$, 5×10^{-4} mol l.$^{-1}$, additive; 5×10^{-2} mol l.$^{-1}$, temperature 20°, solvent chloroform.

spectrum of the residual solid was almost the same as that of the original complex, $RuH_2(PPh_3)_4$, except that the peak due to the hydride ligands had disappeared. (3) When $RuH_2(PPh_3)_4$ (0.10 M) and propionaldehyde (0.30 M) were heated in *n*-hexane at 60° for 5 hr, a yellow solid was obtained by evaporation of the volatile compounds from the solution. It was washed with *n*-hexane twice and dried in vacuo. The ir spectrum of the residual solid showed a peak at 1520 cm^{-1} which may be attributable to the coordinated carbonyl group of the aldehyde.[15] The NMR spectrum of the residual solid showed peaks at τ 8.9, 7.7, and 2.7 with 3:2:136 area in $CDCl_3$ with Me_4Si as an internal standard. The peak assignable to the aldehyde proton was not detected. The peak at τ 8.9 and 7.7 are assignable to the methyl and methylene group of the aldehyde, and the one at τ 2.7 is assignable to phenyl protons, respectively. From the ratio of the peak at τ 2.7 to the one at τ 8.9 or 7.7, the ratio of triphenylphosphine to propionaldehyde was found to be about 3. However, the elemental analysis did not agree with the reasonably presumed complex, $Ru(PPh_3)_3(CH_3CH_2CHO)$. (Calcd for an example: C, 72.37; H, 5.43. Found: C, 70.70; H, 5.62.) Moreover, the reproducibility of the elemental analysis was bad and the ratio of carbon gradually decreased by the storage of the sample. This suggests that the aldehyde complex is labile and the aldehyde is lost little by little.

From these results, it is inferred that the first step of the catalytic transfer hydrogenation is the transfer of hydride ligands of the complex to aldehydes, as shown in Scheme I.

Scheme I

$$RuH_2(PPh_3)_4 + RCHO \longrightarrow RuH_2(PPh_3)_3(RCHO) + PPh_3$$

$$RuH_2(PPh_3)_3(RCHO) \xrightarrow{S} Ru(PPh_3)_3S + RCH_2OH$$

S = solvent

Kinetic Discussion

The first step of this transfer hydrogenation was as shown in Scheme I. Based on the results described earlier and the comparison with the mechanism of transfer hydrogenation of olefins,[10-12] Scheme II is reasonably proposed as the catalytic cycle of transfer hydrogenation of the aldehyde.

From Scheme II, the rate is expressed as eq 1

$$R = \frac{(k_4K_1 + k_5K_2)[\text{RCHO}][\text{Cat}]_0[\text{D}]}{1 + K_1[\text{RCHO}] + K_2[\text{D}] + K_1K_3[\text{RCHO}]^2} \quad (1)$$

Scheme II

$$\begin{array}{ccccc} RuP_3 & \overset{K_1,\ RCHO}{\rightleftharpoons} & RuP_3(RCHO) & \overset{K_3,\ RCHO}{\rightleftharpoons} & RuP_3(RCHO)_2 \\ \text{I} & & \text{II} & & \text{IV} \\ K_2,D \updownarrow & & D \downarrow k_4 & & \\ RuP_3D & \xrightarrow[RCHO]{k_5} & RuP_3D(RCHO) & \xrightarrow{k_6} & RuP_3 + De + RCH_2OH \\ \text{III} & & \text{V} & & \end{array}$$

P = PPh_3, D = hydrogen donor,

De = dehydrogenation product of donor

where K_1, K_2, and K_3 are equilibrium constants and k_4, k_5, and k_6 are rate constants, and [D], [RCHO], and $[\text{Cat}]_0$ are the concentration of the hydrogen donor, the aldehyde, and added catalyst, respectively. In eq 1, the hydrogen transfer step in which V decomposes to the products may be reasonably assumed to proceed fast, because the kinetic isotope effect was negligible as described earlier.

As the reciprocal of the rate against aldehyde concentration gave the linear relationship, the following relation should be satisfied in the numerator of eq 1: $1 + K_2[\text{D}] \ll K_1[\text{RCHO}](1 + K_3[\text{RCHO}])$, that is, [I] + [III] $\ll$ [II] + [IV]. This relation requires that the coordination power of aldehydes is strong, and this is supported by the observations that the reduction rate was not decreased by the addition of acetone, triphenylphosphine, or olefins. Then, the rate expression is reduced to

$$R = \frac{k'[\text{D}][\text{Cat}]_0}{1 + K_3[\text{RCHO}]} \quad (2)$$

where k' is the observed rate constant, $(k_5K_2 + k_4K_1)/K_1$. This expression is found to accommodate all of the other experimental observations fairly well. When isopropyl alcohol was used as the hydrogen donor, the values of the constants in eq 2 are analyzed, that is, (a) the rate should be proportional to the catalyst concentration, and this agrees with the experimental result, as shown in Figure 2. From this figure, 7.5×10^{-2} min^{-1} was obtained as the value of $k'/(1 + K_3)$. (b) The rate should be in proportion to the donor concentration, and this agrees with the result in Figure 3. From this figure, the same value, 7.5×10^{-2} min^{-1}, was obtained as the value of $k'/(1 + K_3)$. (c) Equation 2 is rearranged as follows.

$$1/R = \frac{1}{k'[\text{D}][\text{Cat}]_0} + \frac{K_3}{k'[\text{D}][\text{Cat}]_0}[\text{RCHO}] \quad (3)$$

From Figure 4, the value for gradient, 2.2×10^2 mol^{-2} l.^{2} min, and the value for intercept, 10^2 mol^{-1} l. min, were obtained, respectively. By using these values, $k' = 0.25$ mol l.$^{-1}$ min^{-1} and $K_3 = 2.2$ mol^{-1} l. were obtained as the values at 80°. When these values are put to $k'/(1 + K_3)$, the value of 7.8×10^{-2} min^{-1} is given and fairly agrees with the one obtained from Figures 2 and 3. Therefore, when the reaction was carried out in bromobenzene at 80° with isopropyl alcohol as a hydrogen donor, the overall rate expression is formulated as follows.

$$R = \frac{0.25[D][Cat]_0}{1 + 2.2[RCHO]} \quad (4)$$

Using a similar analytical method, the value for k', 1.0 mol l.$^{-1}$ min^{-1}, and the value for K_3, 9.0 mol^{-1} l., and rate expression, $R = [D][Cat]_0/(1 + 9[RCHO])$, are obtained in the case of benzyl alcohol. From these results, the rate-determining step of the reduction seems to be the coordination of the hydrogen donor.

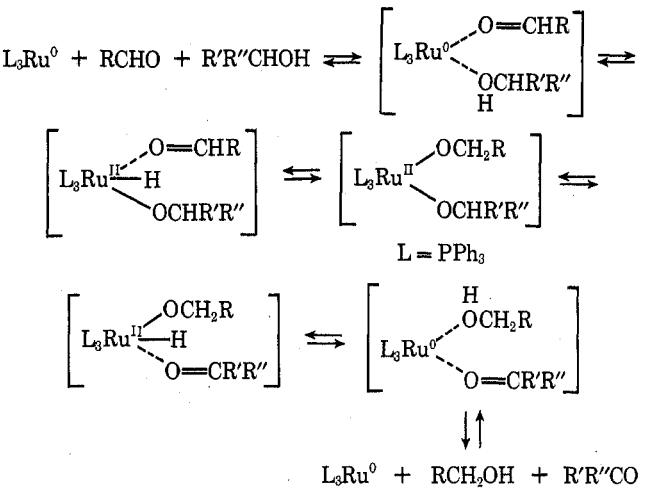
The hydrogen transfer from alcohol to aldehyde on the complex is thought to involve several steps. In the transfer hydrogenation of olefins, large R_H/R_D values were obtained as described earlier and the following reaction scheme has generally been shown

$$M + D \xrightarrow{-De} MH_2 \xrightarrow{olefin} M + \text{paraffin}$$

where M represents an active catalytic species. However, olefins were not reduced under the condition that aldehydes were effectively reduced, and the kinetic isotope effect in the reduction of aldehydes is negligible. In the hydrogen transfer from secondary alcohols to ketones catalyzed by $RuCl_2(PPh_3)_3$, a rather large kinetic isotope effect, $R_H/R_D = 1.68$, has been reported,[7] and Sasson et al. have proposed that $RuCl_2(PPh_3)_2$ is an active species and an alcohol coordinates to the complex in alkoxide form after a ketone has coordinated. Further, it has been reported that the dehydrogenation of alcohols via alkoxide complexes is generally promoted by the addition of basic compounds.[16] In the case of $RuH_2(PPh_3)_4$ catalysis, the hydride ligands rapidly transfer to aldehyde, and $Ru(PPh_3)_3S$ (S = solvent) is suitably considered as the main reaction intermediate. The rate of the reduction is not changed by the addition of triethylamine. These results suggest that in the transfer hydrogenation of aldehydes the mechanism of catalysis of $RuH_2(PPh_3)_4$ is greatly different from that of $RuCl_2(PPh_3)_3$ and that of any complex in the transfer hydrogenation of olefins. So we should like to propose that the hydrogen transfer from alcohols to aldehydes on the Ru(0) species may involve the following steps: (1) the oxidative addition of the Ru metal to the O–H bond of an alcohol to generate a monohydrido alkoxide complex and (2) the addition of the hydride ligand to the carbonyl group to give a dialkoxide complex, as shown in Scheme III.

According to Scheme III, the hydroxylic hydrogen transfers to the carbon atom of the carbonyl of aldehyde and the hydrogen atom attaching to the α carbon of the alcohol transfers to the oxygen atom of the aldehyde. This is supported by the following observations. In the presence of $RuH_2(PPh_3)_4$ (0.02 M), ethyl alcohol-d_1 (1.0 M) and propionaldehyde (1.0 M) were heated in benzene at 60° for 5 hr, and the NMR spectrum of the reaction mixture showed several peaks assignable to propionaldehyde, *n*-propyl alcohol, ethyl alcohol-d_1, and paraldehyde formed by trimerization of acetaldehyde. The peak attributable to a hydroxylic proton was found. The ir spectrum of the reaction mixture also showed peaks attributable to –OH and –CD bonds. The complex recovered after the reaction between $RuH_2(PPh_3)_4$ and isopropyl alcohol-d_8 in the absence of aldehydes had no peaks attributable to Ru–D and OH in the ir spectrum. This result indicates that no H–D exchange occurred between the alcohol and the hydride complex.

Scheme III



Experimental Section

Materials. Dihydridotetrakis(triphenylphosphine)rutheniumm(II),[17] dihydridocarbonyltris(triphenylphosphine)ruthenium(II),[18] dichlorotris(triphenylphosphine)ruthenium(II),[19] hydridotetrakis(triphenylphosphine)rhodium(I),[17] chlorocarbonylbis(triphenylphosphine)rhodium(I),[20] chlorotris(triphenylphosphine)rhodium(I),[20] hydridotris(triphenyl phosphite)cobalt(I),[21] dichlorobis(triphenylphosphine)iron(II),[22] dichlorobis(triphenylphosphine)nickel(II),[23] dichlorobis(triphenylphosphine)cobalt(II),[24] dichlorobis(triphenylphosphine)palladium(II),[25] and dichlorobis(triphenylphosphine)platinum(II)[26] were prepared by methods reported in the literature. Alcohols and aldehydes were purified by distillation followed by dehydration with molecular sieves. Solvents were purified by distillation and degassed on a vacuum line with a liquid nitrogen bath before use.

An Example of Kinetic Runs. Reactions were carried out in a Pyrex glass tube. The sealed tube was prepared by the following procedure. Catalysts, hydrogen donors, and aldehydes were put into Pyrex glass tubes which had been sealed on one end. Into the mixture, solvent 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 at 10^{-3} Torr on a vacuum line and liquid nitrogen bath. Five samples, prepared by the method described above, were heated in a polyethylene glycol bath kept at 80 ± 1° for 5, 10, 20, 30, and 45 min. The reaction mixture was submitted to GLC analysis which was performed at 120° using a 2 m × 6 mm stainless steel column packed with 20% of Carbowax (PEG) 20M on Celite 454 and 20 μl of benzene as an internal standard.

The other transfer hydrogenations were carried out in a similar way.

Spectrophotometric Measurement. The reactions of $RuH_2(PPh_3)_4$ and aldehydes have been studied using spectrophotometric techniques in the visible range. Oxygen was excluded from chloroform solvent by degassing on a vacuum line with a liquid nitrogen bath before use. However, the decreasing rate of the absorption peak was hardly affected by the existence of a small amount of oxygen. The reaction rates could be investigated by following the disappearance of the absorption peak with time: $RuH_2(PPh_3)_4$, λ_{max} 650 nm (ϵ 10^3). The measurement was made on a Shimazu double beam spectrophotometer.

Registry No.—*n*-Propyl alcohol, 71-23-8; toluene, 108-88-3; 4-methyl-2-pentyl alcohol, 108-11-2; 2-phenylethyl alcohol, 60-12-8; *sec*-butyl alcohol, 78-92-2; 3-pentyl alcohol, 584-02-1.

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Free-Radical and Hydrogen Bromide Inhibition in the Dark Reaction of Bromine with the 1,2-Dimethylcyclopropanes

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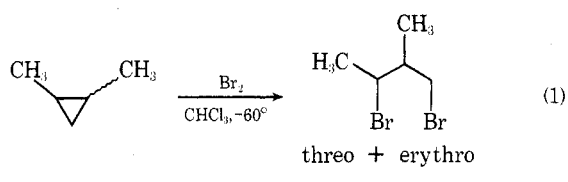
All detectable dibromide products and most of the tribromide products have been identified in the reaction of *cis*- and *trans*-1,2-dimethylcyclopropane with bromine in chloroform. The uncatalyzed reaction is close to 50% complete after 3 h at 0°. The addition of ferric bromide accelerates the reaction slightly but perturbs the product distribution to only a small extent, the main result being an increase in the proportion of the homovicinal dibromides (6) at the expense of some of the vicinal dibromides. Free-radical inhibition by either molecular oxygen or isoamyl nitrite has a similar effect on the product distribution. Suppression of the HBr in solution by the addition of NBS also enhances the proportion of the homovicinal dibromides. Some of the vicinal dibromides must therefore come from an addition–elimination–addition pathway, and the homovicinal dibromides 6 are indicated to be the primary electrophilic products. Nonstereospecific production of the homovicinal dibromides 6 in the identical ratio of 4:1 from both isomers is consistent with open carbonium ion intermediates.

Skell and co-workers[2] have recently found that a significant part of the products from the dark reaction of bromine with alkyl-substituted cyclopropanes results from attack by HBr rather than Br_2 on the ring. Opening of the ring by protonation, followed by loss of a proton, gives an alkene, which yields a vicinal dibromide on addition of Br_2. These authors found that this pathway may be suppressed by carrying out the reaction in the presence of *N*-bromosuccinimide.[2] We had previously reported that the major products from the uncatalyzed bromination of *cis*- and *trans*-1,2-dimethylcyclopropane included *threo*- and *erythro*-1,3-dibromo-2-methylbutane (eq 1).[3] The absence of stereospecificity in the formation of these materials was interpreted in terms of open carbonium ion intermediates.[3] The reaction was carried out at low temperatures in the dark in order to minimize free-radical reactions. The conclusions reported previously would be unfounded if the products resulted either from a free-radical or an HBr-mediated pathway. The present paper is a report of the results of electrophilic catalysis (added ferric bromide), free-radical inhibition (molecular oxygen and isoamyl nitrite), and HBr inhibition (NBS) on the reaction of Br_2 with the dimethylcyclopropanes, in order to provide firm evidence for the electrophilic nature of the reaction and to determine which products arise from direct addition of Br_2 and which from the addition of Br_2 to alkenes that arose from initial attack of HBr. Absolute yields have been measured. We have been able to identify several more minor dibromide products, and the structures of two of the previously reported[3] minor dibromides are corrected. We have tentatively determined the structures of the major tribromide products. With the knowledge of the structures of essentially all dibromide and tribromide products and with the assurance that the reaction is indeed electrophilic in nature, we are able to construct a reasonable material balance of carbonium-ion pathways. The results of these experiments confirm the original conclusions regarding the mechanism of the addition of Br_2 to cyclopropanes.[3]



threo + erythro (1)

Results

The addition of bromine to *cis*- and *trans*-1,2-dimethylcyclopropane in chloroform was carried out at progressively higher temperatures beginning at −60°, always in the dark. The effect of temperature on the dibromide product distribution was found to be very small. Each dibromide product was collected by preparative gas chromatography and identified by comparison of its spectral and chromatographic properties with those of authentic materials. The tribromides were collected by gas chromatography and identified