oroacetic acid (DCA) (See Table 1). This is explained as follows: in DCA the entanglement juncture of PMLG (or PBLG) becomes loose, thus the peptide chain looses the elasticity and the helixity at the same time (*i.e.*, $c_2 = 0$ and $F_H = 0$).

We also found that $c_2 = 0$ for polyisobutylene, polystyrene, etc. (Table 2 and 3). This is due to the fact that the entanglement joints of the non-biopolymeric chains are not tight compared to that helix chains of polypeptides. [Note: it maybe noted that the 2-type non-Newtonian unit can work as a non-Newtonian unit even after attaining the state $c_2 = 0$, since this state signifys, only the state at which the entangled juncture becomes loose.]

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Catalytic Reactions of 3-Phenyl-2-propen-1-ol with Perchloratocarbonylbis (triphenylphosphine) rhodium (I)[†]

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Reaction of Rh (ClO$_4$) (CO) (PPh$_3$)$_2$ (1) with *trans*-C$_6$H$_5$CH$=$CHCH$_2$OH (2) produces a new cationic rhodium(I) complex, [Rh(*trans*-C$_6$H$_5$CH$=$CHCHO) (CO) (PPh$_3$)$_2$]ClO$_4$ (3) where 2 is coordinated throuth the oxygen atom but not through the olefinic group. At room temperature under nitrogen, complex 1 catalyzes dehydrogenation, hydrogenolysis, and isomerization of 2 to give *trans*-C$_6$H$_5$CH$=$CHCHO (4), *trans*-C$_6$H$_5$CH$=$CHCH$_3$ (5) and C$_6$H$_5$CH$_2$CH$_2$CHO (6), respectively, and oligomerization of 2 whereas under hydrogen, complex 1 catalyzes hydrogenation of 2 to give C$_6$H$_5$CH$_2$CH$_2$CH$_2$OH (7) and hydrogenolysis of 2 to 5 which is further hydrogenated to C$_6$H$_5$CH$_2$CH$_2$CH$_3$ (8). The dehydrogenation and hydrogenolysis of 2 with 1 suggest an interaction between the rhodium and the oxygen atom of 2, whereas the isomerization and hydrogenation of 2 with 1 indicate an interaction between the rhodium and the olefinic system of 2.

Introduction

Reactions of unsaturated aldehydes[1] and unsaturated

[†] Dedicated to professor Nung Min Yoon for this 60th birthday.

esters[2] with Rh(ClO$_4$)(CO)(PPh$_3$)$_2$ (1) produce cationic four-coordinated rhodium(I) complexes, [RhL(CO)(PPh$_3$)$_2$]ClO$_4$ (L = unsaturated aldehydes and unsaturated esters coordinated through oxygen atom but not through the olefinic

group of L) which show the catalytic activities for the hydrogenation of L to the corresponding saturated aldehydes and esters at room temperature. Attempts to prepare the related rhodium complexes of saturated aldehydes and esters have not been successful.[3] One could, therefore, expect an additional interaction between the π-system of the olefinic group of the unsaturated aldehydes and unsaturated esters with rhodium (such interaction was actually previously suggested[1] although no evidences have been obtained from the spectral data for [RhL(CO)(PPh₃)₂]ClO₄,[1,2] whereas such an interaction is simply not possible for saturated aldehydes and esters. In fact, the above-suggested interaction (rhodium-olefinic π-system) is the most plausible explanation for the catalytic hydrogenation of L with Rh(ClO₄)(CO)(PPh₃)₂.[1,2] Of oxygen bases, alcohols are known to be more basic for H⁺ than carbonyl comounds such as aldehydes and esters, whereas carbonyl compounds tend to interact (through the carbonyl oxygen) with transition metal complexes more readily than alcohols.

Accordingly, we decided to investigate the interaction of unsaturated alcohols with **1** and the catalytic activities of **1** for the reactions of unsaturated alcohols. In this paper, we wish to report a rhodium(I)-unsaturated aldehyde complex obtained in the reaction of **1** with an unsaturated alcohol, trans-3-phenyl-2-propen-1-ol (**2**) and the catalytic reactions of **2** with **1**.

Results and Discussion

Formation of [Rh (trans-C₆H₅CH = CHCHO)(CO)(PPh₃)₂]ClO₄ from the reaction of Rh(ClO₄)(CO) (PPh₃)₂ with 3-phenyl-propen-1-ol. A new four-coordinated cationic rhodium(I) complex, [Rh(trans-C₆H₅CH = CHCHO)(CO)(PPh₃)₂]ClO₄ (**3**) has been obtained according to equation 1 where H₂ was not evolved from the reaction mixture but seems to be used quantitatively in the hydrogenolysis of **2** to give 3-phenyl-2-propene and H₂O (see text below and Experimental section).

$$\underset{\textbf{1}}{Rh(ClO_4)(CO)(PPh_3)_2} + \underset{\textbf{2}}{trans\text{-}C_6H_5CH = CHCH_2OH}$$

$$\xrightarrow[60°C,CHCl_3]{(-H_2)} \underset{\textbf{3}}{[Rh(trans\text{-}C_6H_5CH = CHCHO)(CO)(PPh_3)_2]ClO_4}$$

(1)
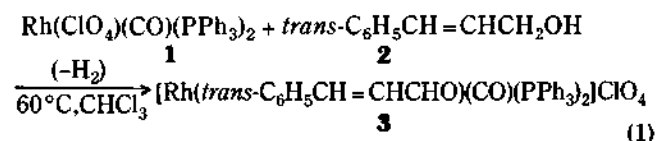
Attempts to prepare the related new rhodium-unsaturated aldehyde complexes from the reactions of **1** with other unsaturated alcohols (2-propen-1-ol, 2-buten-1-ol, 2-methyl-2-propen-1-ol, and 3-buten-2-ol, etc.) were all unsuccessful.

Complex **3** can be also prepared by the simple substitution of ClO₄ group in **1** with trans-C₆H₅CH = CHCHO (**4**) (equation 2). Complex **3** has been characterized by ¹H NMR, infrared and electronic absorption spectral data (Table 1) and elemental analyses and conductance measurements (see Experimental section).

$$\textbf{1} + trans\text{-}C_6H_5CH = CHCHO \xrightarrow{\hspace{2cm}} \textbf{3} \qquad (2)$$

4
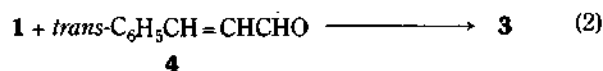
¹H NMR (ratios of signals) and infrared spectral data confirm the presence of both the carbonyl and olefinic aldehyde ligands. Infrared spectrum of **3** shows one broad and strong absorption band at ca. 1100 cm⁻¹ attributable to the anionic tetrahedral ClO₄ group,[4] which supports that **3** is 1:1 electrolyte as confirmed by the conductance measurements (see

Table 1. ¹H NMR (CDCl₃), Infrared (Nujol) and Electronic Absorption Spectra Data for trans-C₆H₅CH = CHCHO and [Rh(trans-C₆H₅CH = CHCHO)(CO)(PPh₃)₂]ClO₄ (3)

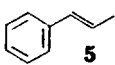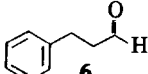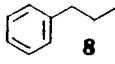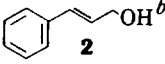| compound	¹H NMR, ppm[a]	
trans-C₆H₅CH = CHCHO	6.52 (dd, CHCHO), 7.30 (m, C₆H₅CH, C₆H₅CH) 9.67 (d, CHO)	
3	6.10 (dd, CHCHO, 1H), 7.53 (m, C₆H₅CH, C₆H₅CH, P(C₆H₅), 36H), 8.64 (d, CHO, 1H)	
	infrared absorption, cm⁻¹	
	$\nu_{C=O}$	$\nu_{C=O}$
trans-C₆H₅CH = CHCHO	1674, 1626	
3	1604, 1590	1996
	electronic absorption, nm (E)	
3	355 (3660)	

[a] Relative to TMS. At 25°C at 60MHz.
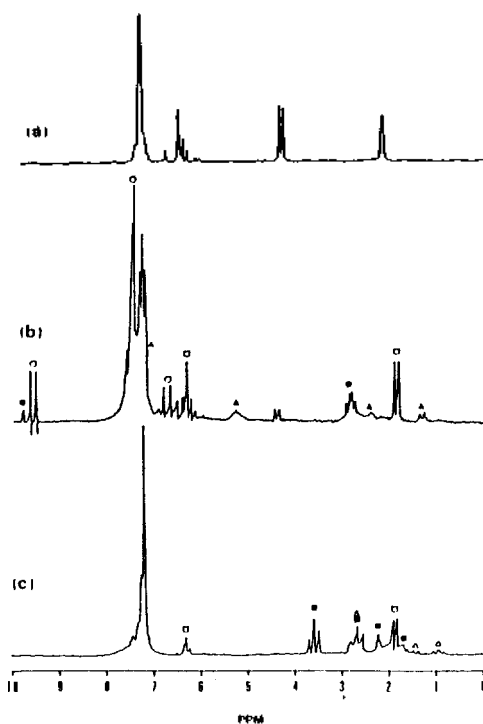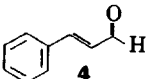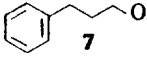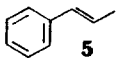
Figure 1. ¹H NMR spectra of the reaction mixture of Rh(ClO₄)(CO)(PPh₃)₂ (1) (0.15 g, 0.2 mmol) and 3-phenyl-2-propen-1-ol (2) (0.79 g, 6.0 mmol) in CDCl₃ (5.0 ml) at 30°C at 60MHz (a) Immediately after mixing **1** and **2**. (b) After 145 hours under nitrogen. (c) After 32 hours under hydrogen. Signals due to the products are marked with ○ (3-phenylpropenal, **4**), □ (3-phenyl-2-propene, **5**), ● (3-phenylpropanal, **6**), ■ (3-phenylpropan-1-ol, **7**), △ (3-phenylpropane, **8**) and ▲ (oligomers).

Experimental section). Electronic absorption spectral data suggest that **3** is a four coordinated rhodium (I) complex and **4** is coordinated to rhodium through the oxygen atom but not through the olefinic group. It is well-known that the four-coordinated rhodium(I) complexes, RhA(CO)(PPh₃)₂ (A = monodentate ligand) show an absorption band in the region of 350-400 nm(ε, 2600-4300) which shifts with respect to the ligating atom of A.[1,5-7] It is also known that the absorption band appears at 350-360 nm when A is the ligand that is coordinated through the oxygen atom such as OClO₃,

Table 2. Catalytic Reactions of *trans*-$C_6H_5CH=CHCH_2OH$ (6.0 mmol) with $Rh(ClO_4)(CO)(PPh_3)_2$ (0.2 mmol) in $CDCl_3$ (5.0 m*l*) at 30°C under N_2 and H_2 (P_{H_2} + vapor pressure of solution = 1 atm)

under N_2 after 145 hours		under H_2 after 32 hours	
[structure] 4	(34%)	[structure] 7	(69%)
[structure] 5	(20%)	[structure] 5	(24%)
[structure] 6	(9%)	[structure] 8	(7%)
Oligomer[a]	(23%)	H_2O	(1.8 mmol)
H_2O	(0.8 mmol)		
[structure] 2	(10%)[b]		

[a] See text. [b] Unreacted reactant.

OCO_2H, OH, $CH_2=CHCHO$ and CH_3CHCHO.[1,7] The chemical shifts of the olefinic protons of coordinated **4** in **3** are only slightly different from those of free **4** (see Table 1), which suggests that **4** in **3** is not coordinated to rhodium through the olefinic group. The absence of the spin coupling between ^{103}Rh and the olefinic protons of **4** in **3** also supports that the coordination of **4** in **3** does not occur through the olefinic group. It should rather be suggested that the olefin **4** is bound to rhodium through the carbonyl oxygen as judged from the decreased ν_{CO} value. It is well-established that the ν_{CO} of carbonyl compounds (aldehydes and ketones) decreases significantly upon coordination through the carbonyl oxygen atom.[1,8-10]

Catalytic Reactions of 3-Phenyl-2-propen-1-ol (2) with $Rh(ClO_4)(CO)(PPh_3)_2$ (1) Figure 1 shows ^1H NMR spectra of the products of the catalytic reactions of **2** with **1** and Table 2 summarizes the results. **Under N_2.** Dehydrogenation of **2** by **1** (equation 3) is expected since complex **3** was obtained by the reaction of **1** and **2** (equation 1). Dehydrogenation of an alcohol to give an aldehyde is well-known[11-14] (e. g., $RCH_2OH + MX \xrightarrow{-HX} RCH_2O-M \rightarrow RCHO-MH$ HX $RCHO + H_2 + MX$, $X = Cl$, $^{11}NO_3^{12}$). Dehydrogenation of **2** with **1** is most likely initiated by hydrogenabstraction from OH group of **2**. This hydrogen-abstraction could be obtained by the rhodium to form initially the oxidative-addition product, $C_6H_5CH=CHCH_2O-Rh(H)(ClO_4)(CO)(PPh_3)_2$ (A) and/or to give $[C_6H_5CH=CHCH_2O-Rh(CO)(PPh_3)_2]$ (B) by reductively eliminating $HClO_4$. The next step of the dehydrogenation may involve the β-hydrogen elimination of the $C_6H_5CH=CHCH_2-O-Rh$ moiety (A and/or B) in order to give **3** and H_2. Detailed mechanism for the dehydrogenation of **2** with **1** is yet to be known and currently under investigation in this laboratory.

$$\textit{trans-}C_6H_5CH=CHCH_2OH \xrightarrow[(-H_2)]{1} \textit{trans-}C_6H_5CH=CHCHO$$
$$\textbf{2} \qquad\qquad\qquad \textbf{4} \qquad (3)$$
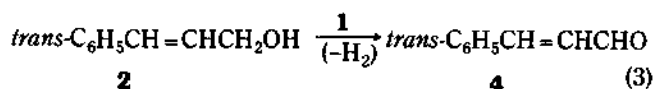
3-phenyl-2-propene (**5**) seems to be the product of the hydrogenolysis (equation 4) of **2** by the hydrogen abstracted by

equation 3 (see also the following section, **under H_2**). Disproportionation of an alcohol to give dehydrogenation product (aldehyde or ketone) and hydrogenolysis product (hydrocarbon) has been also well known.[15-17] Dehydrogenation (equation 3) and hydrogenolysis (equation 4) of **2** do

$$\textit{trans-}C_6H_5CH=CHCH_2OH \xrightarrow[(H_2)]{1}$$
$$\textbf{2}$$
$$\textit{trans-}C_6H_5CH=CHCH_3 + H_2O \qquad (4)$$
$$\textbf{5}$$
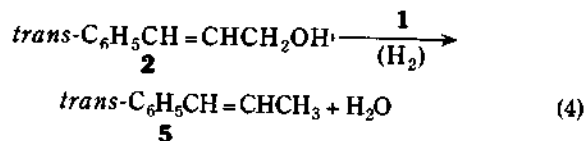
not seem to occur simultaneously since the yields of the products of the two reactions are not same (see Table 2). The combination of equation 3 and 4, therefore, may not exactly be a disproportionation of **2** (dehydrogenation seems to be followed by hydrogenolysis). The rest of the hydrogen obtained by the dehydrogenation of **2** might be used in the oligomerization of **2** (H_2 gas evolution was not observed in the reaction of **2** with **1**). The saturated alcohol ($C_6H_5CH_2CH_2CH_2OH$) has not been found in the reactions of **2** with **1** under N_2 while a disproportionation reaction of an unsaturated alcohol (2-propen-1-ol) to give an unsaturated aldehyde (2-propenal) and saturated alcohol (propan-1-ol) was reported to occur in the presence of an iridium (I) complex, $[Ir(COD)(PMePh_2)_2]PF_6$.[18]

It is well-established that a π-allylhydrido metal complex should be the intermediate for the catalytic hydrogenation of a simple olefin to the saturated hydrocarbon with a transition metal complex in the absence of H_2.[19] The isomerization of **2** to 3-phenyl-propanal (**6**) with **1** may occur via the π-allyl-Rh-H species (Scheme 1) but not through the dehydrogenation process (**2** $\xrightarrow{-H_2}$ **4** $\xrightarrow{H_2}$ **6**), since (1) it has been found in a separate experiment that **4** is not hydrogenated with **1** even under hydrogen and (2) it has been already known that an enol (2-methyl-1-propen-1-ol) was detected during the isomerization of an unsaturated alcohol (2-methyl-2-propen-1-ol) to the saturated aldehyde (2-methyl-propanal) with **1** under N_2 at room temperature.[20]

Oligomers formed in the reaction of **2** with **1** show signals spreaded in the region of 1.0-8.0 ppm (relative to TMS) (but no signals due to aldehyde gorup (-CHO)), several spots on a silica gel TLC plate even after treatment at 150°C, and will be investigated further.

Under H_2. Hydrogenation of **2** to 3-phenylpropan-1-ol (**7**) undoubtedly proceeds via the hydrido-alkyl-rhodium (Scheme 2) rather than through the hydrido-π-allyl-rhodium (Scheme 1) for the following reasons. (1) Saturated aldehyde, **6** was the most expected product in Scheme 1, but has never been found in the reaction under H_2 (see Table 2). (2)
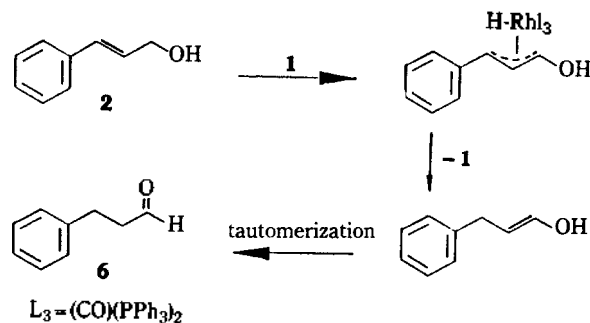
Scheme 1

Scheme 2
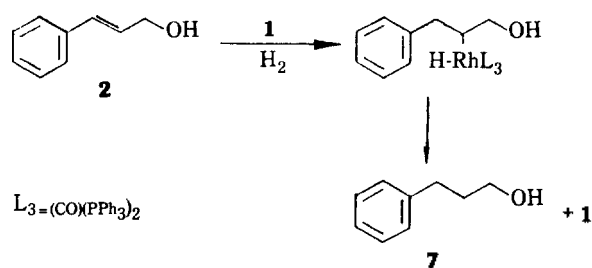
Hydrogenation of aldehydes (**4** and **6**) to **7** has never been observed, in separate experiments, in the presence of **1** under H_2 at room temperature.

The total number of moles of **5** and $C_6H_5CH_2CH_2CH_3$ (**8**) is practically equal to that of H_2O in the product mixture, and the formation of **5** (and **8**) is much faster under H_2 than under N_2 (see Table 2). The hydrogenation product, **7**, does not react with **1** to give **8** under H_2 at room temperature. It has been found that the amount of **8** increases at the expense of **5**. These observations clearly suggest that **5** and H_2O are the hydrogenolysis products, and **8** is the product of hydrogenation of **5** (*trans*-$C_6H_5CH = CHCH_2OH$ (**2**) $\xrightarrow[-H_2O]{H_2}$ *trans*-$C_6H_5CH = CHCH_3$ (**5**) $\xrightarrow{H_2}$ $C_6H_5CH_2CH_2CH_3$ (**8**)).

Interaction between $Rh(ClO_4)(CO)(PPh_3)_2$ (1) and *trans*-$C_6H_5CH = CHCH_2OH$ (2).

The isomerization and hydrogenation products, **6** and **7**, are the evidences for the interaction between **1** and the olefinic group of **2**. It is interesting to observe that the olefinic group of **2** is hydrogenated to give the saturated alcohol, **7**, while the olefinic group of **4** is not hydrogenated with **1** under the same experimental conditions. This difference certainly comes from the difference between the interactions of **1** with **2** and **4**. It is certain that the interaction of **1** with **2** is less effective to form a stable bond than that of **1** with **4**, since complex **3** is the only product in both reactions of **1** with **2** and **4**, and a related rhodium complex of **2** has not been isolated so far. Then it may be said that the bond between the rhodium and the oxygen atom of **4** in **3** is probably too stable and the one between the rhodium and the olefinic group of **4** is too insignificant to initiate the catalytic hydrogenation cycle of **4**.

One may also expect an interaction between the rhodium of **1** and the OH group of **2**. There seems to be one for the following reasons although it may not be strong enough to give a stable bond between the rhodium and **2**. (1) The reaction of **1** and other unsaturated alcohols (L) give $[RhL(CO)(PPh_3)_2]ClO_4$ where L is *cis*-and *trans*-$CH_3CH = CHCH_2OH$ coordinated through the oxygen atom to rhodium.[21] (2) As shown above, complex **1** catalyzes both the dehydrogenation and hydrogenolysis of **2** which most likely involve the interaction between the rhodium and OH group of **2**. (3) Hydrogenation of **2** is faster than that of *trans*-3- phenyl-2-propene (**9**) with **1** (see Table 3). It remains still uncertain whether there are simultaneous interactions between rhodium and oxygen atom of **2**, and between rhodium and olefinic group of **2**, both of which are quite possible as shown below.
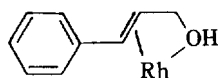

Table 3. Catalytic Hydrogenation of *trans*-$C_6H_5CH = CHCH_2OH$ (3.0 mmol) and *trans*-$C_6H_5CH = CHCH_3$ (3.0 mmol) with $Rh(ClO_4)(CO)(PPh_3)_2$ (0.2 mmol) in $CDCl_3$ (5.0 m*l*) under H_2 (P_{H_2} + vapor pressure of solution = 1 atm) at 30°C for 32 hours

product	yield
	(2.1 mmol, 35%)[a]
	(2.4 mmol, 40%)
	(1.5 mmol, 25%)[b]
H_2O	(0.9 mmol)[a]

[a] 0.9 mmol of *trans*-$C_6H_5CH = CHCH_2OH$ underwent the hydrogenolysis to give H_2O (quantitatively) and *trans*-$C_6H_5CH = CHCH_3$. [b] It most likely contains $C_6H_5CH_2CH_2CH_3$ obtained by the hydrogenation of *trans*-$C_6H_5CH = CHCH_3$ which was formed by the hydrogenolysis of *trans*-$C_6H_5CH = CHCH_2OH$.

Experimental

Methods. ^{1}H NMR, infrared and electronic absorption spectra were obtained on a Varian 60 MHz (EM-360A), Shimadzu IR-440 and Shimadzu UV-240 spectrometer, respectively. H_2O analyses were carried out by a 633 Karl Fischer Automat. Titrater (Metrohm, Swiss) at analytical lab. of Korea Advanced Institute of Science and Technology. Conductance measurements were carried out by a Yellow Springs Instrument Model 31 Contuctivity Bridge with Beckman Pt-Electrode Conductivity Cell. Elemental analyses were obtained by Spang Microanalytical Lab., Eagle Harbor, MI, U. S. A. A standard vacuum line and Schlenk-type glassware were used in handling metal complexes.

Materials. $Rh(ClO_4)(CO)(PPh_3)_2$ was prepared by the literature method.[4] *trans*-$C_6H_5CH = CHCH_2OH$, *trans*-$C_6H_5CH = CHCHO$ were purchased from Aldrich and used after distillation under nitrogen.

Synthesis of $[Rh(trans$-$C_6H_5CH = CHCHO)(CO)(PPh_3)_2]ClO_4$ (3) from the reaction of $Rh(ClO_4)(CO)(PPh_3)_2$ (1) with *trans*-$C_6H_5CH = CHCH_2OH$ (2). The yellow solution of **1** (0.15 g, 0.2 mmol) and **2** (0.81 g, 6 mmol) in $CHCl_3$ (5 m*l*) was stirred at 25°C under nitrogen. No visual changes have been observed for two hours. (Addition of hexane (100 m*l*) to the reaction mixture solution resulted in precipitation of **1** quantitatively.) The reaction mixture (yellow solution) was refluxed under nitrogen for one hour and cooled to room temperature. After evaporating solvent by half, hexane (5 m*l*) was added to precipitate yellow microcrystals of **3** which were collected by filtration, washed with benzene (30 m*l*), and dried in vacuum. The yield was 0.13 g (75% based on **3**). Anal. Calcd for $RhC_{46}H_{38}O_6P_2Cl$: C, 62.28; H, 4.32; P, 6.98; Cl, 4.00. Found: C, 62.09; H, 4.39; P, 7.12; Cl, 4.10. $\Lambda_M = 33$ ohm^{-1}cm^{2}mol^{-1} ([Rh] = 4.4×10^{-4} M) in CH_2Cl_2 at 25°C. (Λ_M of a standard 1:1 electrolyte, (n-Bu)$_4$ $NClO_4$ was measured to be 34 ohm^{-1} cm^{2}mol^{-1} in CH_2Cl_2 at 25°C.)

Synthesis of $[Rh(trans$-$C_6H_5CH = CHCHO)(CO)(PPh_3)_2]ClO_4$ (3) from the reaction of $Rh(ClO_4)(CO)(PPh_3)_2$ (1) with *trans*-$C_6H_5CH = CHCHO$ (4). Two

drops of **4** (*ca.* 7 mmol) were added into the yellow solution of **1** (0.15 g, 0.2 mmol) in benzene (30 m*l*), and the resulting solution was stirred under N_2 at 25°C. Yellow microcrystals began to appear within 30 minutes, were collected by filtration after two hours, washed with benzene (15 m*l*), dried in vacuum, and identified as **3** by ^1H NMR, IR and electronic spectra. The yield was 0.13 g or 75% based on **3**.

Catalytic reactions of 3-phenyl-2-propen-1-ol (2). Under nitrogen. The reaction mixture of **1** (0.15 g, 0.2 mmol) and **2** (0.79 g, 6.0 mmol) in $CDCl_3$ (5.0 m*l*) was stirred at 30°C under nitrogen. A part (0.5 m*l*) of the reaction mixture was taken from the reactor and analyzed by ^1H NMR measurements at intervals. Identification of **4, 5, 7** and **8** was established by comparing ^1H NMR spectrum of the reaction mixture with those of authentic samples of **4, 5, 7** and **8** (each of authenic samples was added to the reaction mixture and it's ^1H NMR spectrum was compared with that of the reaction mixture only). Yields of the products were also determined by ^1H NMR measurements. The saturated aldehyde (**6**) was identified by the triplet due to -CHO at 9.72 ppm and the multiplet due to $C_6H_5CH_2CH_2$-CHO at 2.82 ppm[22] (see also Figure 1). In order to obtain more information on the unidentified signals in the ^1H NMR of the reaction mixture, the reaction mixture was distilled at 100°C under vacuum (1 mmHg) and the volatile materials (**2, 4, 5, 6** and H_2O) were collected on liquid nitrogen bath. The ^1H NMR spectrum of the nonvolatile materials (rhodium complex(es) and oligomers) shows the signals in the region of 1.0-8.0 ppm due to the oligomers. H_2O was analyzed by Karl Fischer reagent.

Under hydrogen. Reactions of **2** with **1** under hydrogen were followed until all of the starting material, **2**, disappeared in the reaction mixture in the same manner as described for the reactions of **2** under nitrogen above. Product analyses were carried out by the same methods described above.

Catalytic hydrogenation of a mixture of *trans*-$C_6H_5CH=CHCH_2OH$ (2) and *trans*-$C_6H_5CH=CHCH_3$(5). A mixture of **2** (3.0 mmol), **5** (3.0 mmol) and **1** (0.2 mmol) in $CDCl_3$ (5.0 m*l*) was stirred under H_2 (P_{H_2}+vapor pressure of the solution=1 atm) at 30°C until all of the starting material, **2**, disappeared in the reaction mixture. During the reaction, a part of the reaction mixture was taken at intervals to measure the amounts of the starting materials and products by ^1H NMR measurements. H_2O was analyzed by Karl Fischer reagent.

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