Rhodium Complex Catalyzed Hydrogenation of α,β-Unsaturated Aldehydes to Unsaturated Alcohols

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Rhodium complexes were found to be effective in catalyzing selective hydrogenation of cinnamaldehyde to cinnamyl alcohol in the presence of strongly basic amine such as triethylamine or *N*-methylpyrrolidine under oxo reaction conditions. The selectivity of analogous hydrogenation of aliphatic unsaturated aldehyde was poorer than that of aromatic aldehyde. When a catalytic amount of triphenylphosphine was added, the selectivity was drastically changed to exclusive formation of hydrocinnamaldehyde. In order to elucidate the nature of rhodium-amine interaction, $Rh_2Cl_2(CO_4)$ was immobilized on a cross-linked chloromethylated polystyrene which was functionalized with pyrrolidine, the polymer amine acting as a tertiary amine. The polymer–rhodium complex was found to be stable and to effect the selective hydrogenation of cinnamaldehyde, while addition of triphenylphosphine seemed to liberate the rhodium complex from the polymer. It is concluded that a rhodium–amine–carbonyl complex is responsible for the selective hydrogenation of α,β-unsaturated aldehyde to the unsaturated alcohol.

Hindered unsaturated aldehydes having highly substituted carbon-carbon double bonds can be hydrogenated to the corresponding unsaturated alcoholes.[1] For unhindered α,β-unsaturated aldehydes such as cinnamaldehyde and crotonaldehyde, however, a very limited number of catalysts are known to be effective, *i.e.* platinum and palladium supported on carbon combined with zinc and iron(II) chlorides,[2] although no mechanistic study has been reported. On the other hand, a number of transition metal complexes have been reported to catalyze hydrogenation of olefin and aldehyde under mild reaction conditions.[3] No efficient homogeneous catalyst is known for preferential hydrogenation of these unsaturated aldehydes to the unsaturated alcohols using molecular hydrogen. In the presence of a tertiary amine, rhodium complex catalysts are much more active than cobalt carbonyls for oxo-alcohol syntheses without accompanying hydrogenation of olefin.[4,5] This suggested that rhodium complexes would be effective in the presence of carbon monoxide and tertiary amine for the selective hydrogenation of α,β-unsaturated aldehyde. Kogami *et al.* examined cobalt carbonyl catalyst in the presence of amine for hydrogenation of cinnamaldehyde and its derivatives under oxo reaction conditions, no preferential hydrogenation to the unsaturated alcohols being found.[6]

This work was undertaken to elucidate the necessary conditions for selective hydrogenation of cinnamaldehyde and croton aldehyde to the unsaturated alcohols with rhodium complex catalyst in the presence of tertiary amine under oxo reaction conditions, and to study the interaction of amine with rhodium atom in its coordination sphere by immobilizing $Rh_2Cl_2(CO)_4$ on an aminated polystyrene.

Experimental

Materials. Tetracarbonyldichlorodirhodium (I), $Rh_2Cl_2(CO)_4$, was prepared from $RhCl_3 \cdot 3H_2O$ and carbon monoxide[7] (Found: C, 11.2; Cl, 18.8%. Calcd for: C, 12.4; Cl, 18.2%). Commercial $RhCl_3 \cdot 3H_2O$, carbon monoxide (98%) and all the α,β-unsaturated aldehydes and amines (Tables 2 and 3) were used without purification. Benzene of extra pure grade guaranteed for UV spectrometry (Wako Pure Chemicals Industry Ltd.) was used as a solvent to avoid the effect of contaminants such as thiophene.

Aminated polystyrene was prepared by an appropriate modification of the method used for the amination of chloromethylated polymers.[8] A cross-linked chloromethylated polystyrene (divinylbenzene 3%. Mitsubishi Chemical Industry Ltd.) was washed with dioxane and water under nitrogen atmosphere, and dried at 50—60 °C in a vacuum (Found: H, 6.9; C, 75.2; Cl, 15.6%. Total 97.7%). The chloromethylated polystyrene (50 g) were aminated with pyrrolidine (100 g) in dioxane (150 ml) under nitrogen atmosphere at room temperature for 48 h. The resulting polymer was washed three times with a water–dioxane solution of hydrogen chloride to remove the excess pyrrolidine and then three times with an aqueous sodium carbonate solution to liberate the amine chemically linked to the polymer. Subsequently the aminated polystyrene was washed thoroughly with water and methanol and dried at 20 °C in a vacuum (Found: H, 9.1; C, 84.3; N, 5.4; Cl, 1.1%. Total 99.9%).

Reaction Procedure. All the reactions were carried out with use of a stainless steel autoclave (100 ml) equipped with a magnetic stirrer. A benzene solution (20 ml) of a tertiary amine (2.5—40 mmol) and one of α,β-unsaturated aldehydes (20—23 mmol) and $RhCl_3 \cdot 3H_2O$ (0.13 mmol) or $Rh_2Cl_2(CO)_4$ (0.065 mmol) were placed in the autoclave under nitrogen atmosphere, followed by introduction of carbon monoxide and hydrogen at room temperature. The autoclave was then heated up to the desired temperature within 10—15 min, and the temperature was kept constant. After a given period of run, the autoclave was rapidly cooled with water to room temperature, and gaseous materials were purged out. The products were quantitatively analyzed by a gas chromatograph equipped with a 4 meter column of DC-550, polyethylene glycol, or ethylene glycol succinate polyester using an appropriate substance as internal standard. The hydrogenation products were isolated by a preparative gas chromatograph, and identified by NMR, IR, or mass spectroscopy, when necessary.

Results and Discussion

General Features of Reaction. The results for cinnamaldehyde using $RhCl_3 \cdot 3H_2O$ as a catalyst are shown in Table 1. In the absence of carbon monoxide

TABLE 1. HYDROGENATION OF CINNAMALDEHYDE CATALYZED BY RHODIUM COMPLEX

PhCH=CHCHO 20 mmol, C_6H_6 20 ml, P_{H_2} 40 kg/cm² at r.t., Temp 90 °C, React time 60 min.

Catalyst (mmol)	P_{CO} (kg/cm²)	NEt_3 (mmol)	Temp (°C)	Conv. (%)	Selectivity (%)		
					II$^{a)}$	III$^{a)}$	IV$^{a)}$
$RhCl_3 \cdot 3H_2O$ 0.13	40	0	90	35	≈0	≈0	≈0
	0	20	90	18	96	0	≈0
	40	20	90	93	7.9	63	22
	40	20 $+PPh_3$ 1.0	90	100	95	0	≈0
	40	20 $+AsPh_3$ 1.0	90	7.5	95	0	0.9
	40	20 $+NPh_3$ 1.0	90	86	10	51	22
$RhCl(PPh_3)_3$ 0.10	40	0	90	0	—	—	—
	0	20	90	44	81	0	3.1
	40	20	90	100	100	0	≈0
$RhCl_3 \cdot 3H_2O$ 0.13	40	20	70	10	—	—	—
	40	20	60$^{b)}$	72	5	61	8
$Rh_2Cl_2(CO)_4$ 0.065	40	20	60	94	2	85	11

a) II Hydrocinnamaldehyde, III Cinnamyl alcohol, IV Hydrocinnamyl alcohol.

b) Pretreatment with CO (40—50 kg/cm²) at 90 °C for 60 min.

or triethylamine, small amounts of hydrogenated products are obtained, no cinnamyl alcohol being detected. Addition of triethylamine, however, significantly increases not only the catalytic activity but the selectivity to cinnamyl alcohol under the oxo reaction conditions, giving no hydroformylation products. Addition of primary or secondary amine in place of tertiary amine was ineffective in giving hydrogenation products. This is presumably caused by the formation of highly stable Rh(III)–amine complexes.[9] On the other hand, the addition of a catalytic amount of triphenylphosphine strikingly increases the selectivity for the hydrogenation of the carbon-carbon double bond to give hydrocinnamaldehyde. Triphenylamine has little effect, while triphenylarsine decreases the catalytic activity. $RhCl(PPh_3)_3$ is a highly active catalyst for preferential hydrogenation of the carbon-carbon double bond under the same conditions. The results indicate that both carbon monoxide and tertiary amine play important roles for the selective hydrogenation to cinnamyl alcohol with rhodium complex catalyst.

Although $RhCl_3 \cdot 3H_2O$ exhibits only a low activity at lower temperatures, it can be activated by treatment with carbon monoxide (30—50 kg/cm²) at 90 °C for 60 min before introduction of hydrogen, so that cinnamaldehyde can be hydrogenated even at 60 °C. When $Rh_2Cl_2(CO)_4$ is used as the catalyst, the selective hydrogenation takes place more readily without pretreatment, suggesting that $RhCl_3$ is reduced during the course of hydrogenation.

Effect of Tertiary Amine. The effect of tertiary amine in the hydrogenation of cinnamaldehyde is given in Table 2. Two features of amine effect are observed. Firstly, highly basic amines such as triethylamine (pK_b=3.3), *N*-methylpyrrolidine (pK_b=3.8) and *N*-methylpiperidine (pK_b=2.8) are effective not only for catalytic activity but also for preferential hydrogenation to cinnamyl alcohol. *N*,*N*-Dimethylbenzylamine (pK_b=5.1) is not effective, and less basic amines such as *N*,*N*-dimethylaniline (pK_b=8.9) and pyridine (pK_b=8.9) give no cinnamyl alcohol at all. Such a trend in the effectiveness of tertiary amines was also reported for oxo-alcohol synthesis from hexene or octene catalyzed by rhodium catalysts combined with tertiary amine and water.[4] Secondly, both catalytic activity and selectivity to cinnamyl alcohol substantially depend on the amount of amine, this being pronounced in the presence of large excess of triethylamine or *N*-methylpyrrolidine (amine/Rh=100—200 in mol). It is interesting to see the effect of diamines, since the interaction between rhodium atom and diamines could be strengthened by their chelate effect. The diamines (Table 2) are clearly effective for selective hydrogenation, but they are required in a large amount to increase the yield of cinnamyl alcohol, and no chelate effect is observed. *p*,*p*′-Bis(dimethylamino)diphenylmethane as well as *N*,*N*-dimethylaniline give no cinnamyl alcohol. The interaction between rhodium complex and amine will be discussed on the basis of the hydrogenation using $Rh_2Cl_2(CO)_4$ catalyst immobilized on an aminated polystyrene.

Effects of Carbon Monoxide and Hydrogen. Effects of carbon monoxide and hydrogen on the conversion of cinnamaldehyde and selectivity of hydrogenation are shown in Figs. 1 and 2. Under the conditions specified in Fig. 1, the highest conversion of cinnamaldehyde is obtained at 20 kg/cm² of carbon monoxide, where the selectivity to hydrocinnamyl alcohol is also the highest. The selectivity to cinnamyl alcohol increases with increase in the pressure of carbon monoxide, the formation of hydrocinnamaldehyde being significantly retarded by carbon monoxide. The increase in hydrogen pressure under a constant pressure of carbon monoxide (40 kg/cm²) increases the conversion of cinnamaldehyde,

Table 2. Effect of tertiary amine on hydrogenation of cinnamaldehyde
PhCH=CHCHO 20 mmol, C_6H_6 20 ml, $RhCl_3 \cdot 3H_2O$ 0.13 mmol,
Press. 80 kg/cm^2 ($CO/H_2=1$) at r.t., Temp 90 °C, Time 60 min.

Amine (mmol)	Conv. (%)	Selectivity (%)		
		II$^{b)}$	III$^{b)}$	IV$^{b)}$
NEt_3(10)	88	56	28	14
NEt_3(20)	93	7.9	63	22
N-Methylpyrrolidine(20)	100	≈0	83	10
N-Methylpyrrolidine(5)$^{a)}$	30	9.0	59	≈0
N-Methylpyrrolidine(10)$^{a)}$	67	3.7	83	11
N-Methylpyrrolidine(20)$^{a)}$	88	2.2	75	14
N-Methylpyrrolidine(30)$^{a)}$	99	0	69	11
N-Methylpiperidine(20)	100	0	83	13
$N(CH_3)_2CH_2Ph$(20)	55	28	39	16
$N(CH_3)_2Ph$(20)	7.7	0	0	0
NC_5H_5(20)	≈0	—	—	—
$(CH_3)_2N\text{-}(CH_2)_2\text{-}N(CH_3)_2$(2.5)	21	51	50	~0
$(CH_3)_2N\text{-}(CH_2)_2\text{-}N(CH_3)_2$(5)	53	21	52	12
$(CH_3)_2N\text{-}(CH_2)_2\text{-}N(CH_3)_2$(10)	96	6.5	58	35
$(CH_3)_2N\text{-}(CH_2)_2\text{-}N(CH_3)_2$(15)	99	1.3	65	34
$(CH_3)_2N\text{-}(CH_2)_2\text{-}N(CH_3)_2$(20)	63	12	77	9.1
$(CH_3)_2N\text{-}(CH_2)_3\text{-}N(CH_3)_2$(10)	77	14	73	17
$(CH_3)_2N\text{-}(CH_2)_6\text{-}N(CH_3)_2$(10)	72	14	59	17
$(CH_3)_2N\text{-}C_6H_4\text{-}CH_2\text{-}C_6H_4\text{-}N(CH_3)_2$(10)	13	—	—	—

a) Pretreatment with CO (30—40 kg/cm^2) at 90 °C for 60 min. b) II Hydrocinnamaldehyde, III Cinnamyl alcohol, IV Hydrocinnamyl alcohol.

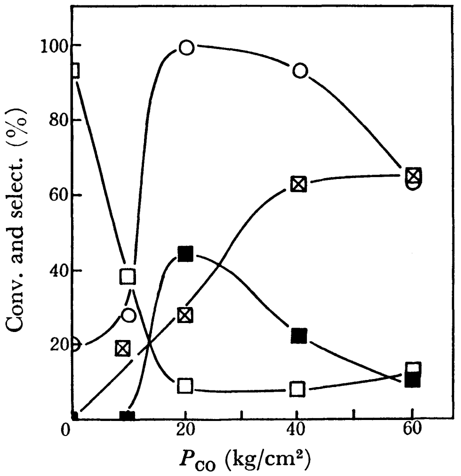


Fig. 1. Effect of the pressure of carbon monoxide on hydrogenation of cinnamaldehyde.
PhCH=CHCHO 20 mmol, NEt_3 20 mmol, C_6H_6 20 ml, $RhCl_3 \cdot 3H_2O$ 0.13 mmol, P_{H_2} 40 kg/cm^2 at r.t., Temp 90 °C, Time 60 min. ○ Conversion, □ hydrocinnamaldehyde, ⊠ cinnamyl alcohol, ■ hydrocinnamyl alcohol.

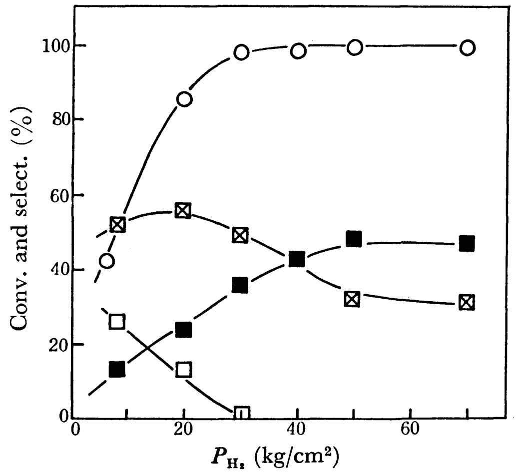


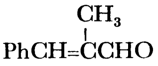
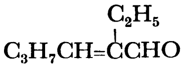
Fig. 2. Effect of the pressure of hydrogen on hydrogenation of cinnamaldehyde.$^{a)}$
PhCH=CHCHO 20 mmol, NEt_3 20 mmol, C_6H_6 20 ml, $RhCl_3 \cdot 3H_2O$ 0.13 mmol, P_{CO} 40 kg/cm^2 at r.t., Temp 90 °C, Time 60 min. ○ Conversion, □ hydrocinnamaldehyde, ⊠ cinnamyl alcohol, □ hydrocinnamyl alcohol.
a) Under low hydrogen pressure, it was supplied during the reaction to keep the pressure constant.

while the consecutive hydrogenation of cinnamyl alcohol produced is much slower than that of cinnamaldehyde. (Fig. 2). Thus, in the presence of carbon monoxide, the hydrogenation of the CHO group can be preferentially enhanced. This was verified by separate runs of hydrogenation of hydrocinnamaldehyde and cinnamyl alcohol under the same conditions specified in Fig. 1. Under 30—50 kg/cm^2 of carbon monoxide, hydrocinnamaldehyde was almost quantitatively hydrogenated to hydrocinnamyl alcohol (90%), while the extent of hydrogenation of cinnamyl alcohol was less than 25% in the same period.

The highest conversion to hydrocinnamyl alcohol is obtained at 20 kg/cm^2 of carbon monoxide (Fig. 1), considerable amounts of hydrocinnamaldehyde being formed under lower pressures of hydrogen (10, 20 kg/cm^2) (Fig. 2). Strohmeier and Weigelt reported that 2-methyl-2-propanol is rapidly isomerized to

Table 3. Hydrogenation of other α,β-unsaturated aldehydes

C_6H_6 20 ml, P_{H_2} 40 kg/cm, Time 60 min.

Aldehyde (mmol)		$CH_3NC_4H_8$ (mmol)	P_{CO} kg/cm^2	Temp °C	Conv. (%)	Selectivity (%) II[e]	III[e]	IV[e]
 $PhCH{=}C(CH_3)CHO$	(20)[a]	20	40	60	99[d]	0	87[d]	13[d]
$PhCH{=}CHCHO$	(20)[a]	20	40	60	100	0	83	9.8
 $C_3H_7CH{=}C(C_2H_5)CHO$	(20)[a]	20	40	60	47	18	34	48
$C_3H_7CH{=}CHCHO$	(20)[a]	20	40	60	100	0	47	53
$CH_3CH{=}CHCHO$[c]	(23)[a]	30	40	40	99	4.6	41	53
$CH_3CH{=}CHCHO$[c]	(23)[b]	20	20	40	99	0	52	48
$CH_3CH{=}CHCHO$[c]	(23)[b]	10	20	40	74	14	50	33
$CH_3CH{=}CHCHO$[c]	(23)[b]	5	20	40	50	25	49	22
$CH_3CH{=}CHCHO$[c]	(23)[b]	5	0	40	99	99	0	1.3
$CH_3CH{=}CHCHO$[c]	(23)[c]	5	10	40	80	13	47	34

a) $RhCl_3 \cdot 3H_2O$ 0.13 mmol. Pretreatment with CO (40—50 kg/cm^2) at 60—90 °C for 60 min.
b) $Rh_2Cl_2(CO)_4$ 0.065 mmol. Without pretreatment. c) Water (12—14 wt%) was contained.
d) Calculated from peak areas on the gas chromatograph.
e) II Saturated aldehyde, III Unsaturated alcohol, IV Saturated alcohol.

isobutyraldehyde with $RhH(CO)(PPh_3)_3$ as a homogeneous catalyst in trifluoroethanol at 70 °C[10] ($CH_2{=}C(CH_3)CH_2OH \longrightarrow [(CH_3)_2C{=}CHOH] \longrightarrow (CH_3)_2CHCHO$). Thus, the isomerization of cinnamyl alcohol to hydrocinnamaldehyde should be taken into account for the formation of hydrocinnamyl alcohol. With the present catalyst system, it seems likely that carbon monoxide retards the isomerization of cinnamyl alcohol as well as hydrogenation of the carbon-carbon double bond, since the selectivity of hydrocinnamyl alcohol is considerablely low under higher pressures (40—60 kg/cm^2) of carbon monoxide (Fig. 1), gradually increasing even under high pressures of hydrogen (Fig. 2). However, we have no evidence for the course of formation of hydrocinnamyl alcohol.

Hydrogenation of Other α,β-Unsaturated Aldehydes. The results for other α,β-unsaturated aldehydes are given in Table 3. *N*-Methylpyrrolidine was used as the modifier, and the catalyst solutions were treated with carbon monoxide (40—50 kg/cm^2) at 90 °C for 60 min before the hydrogenation at 40—60 °C by introduction of hydrogen. α-Methyl cinnamaldehyde as well as cinnamaldehyde are hydrogenated to the unsaturated alcohol selectively, while in the case of aliphatic unsaturated aldehydes such as croton aldehyde, 2-hexenal, or 2-ethyl-2-hexenal, the unsaturated alcohols produced are further hydrogenated to the saturated alcohols. All attempts to increase the selectivity to *trans*-2-buten-1-ol by over 50% using $Rh_2Cl_2(CO)_4$ as the catalysts were unsuccessful. Acrylaldehyde, presumably oligomerized before hydrogenation, gave only a trace amount of propionaldehyde.

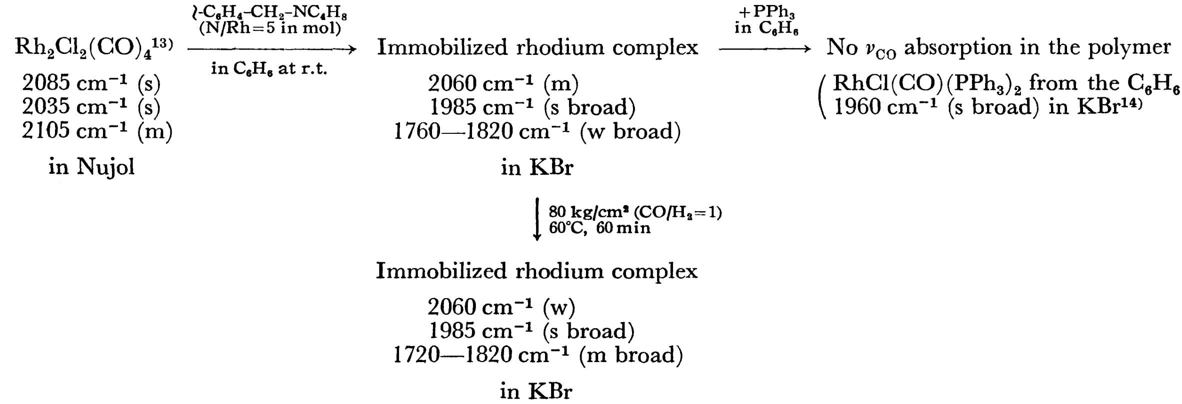
Immobilization of Rhodium Complex. Since a large amount of tertiary amine is required for the selective hydrogenation of cinnamaldehyde, and little evidence on the nature of interaction of amine with rhodium atom in its coordination sphere is available, attempts to isolate a rhodium–amine complex from the product solution being unsuccessful, we attempted to immobilize $Rh_2Cl_2(CO)_4$ on a cross-linked chloromethylated polystryrene functionarized with pyrrolidine, *i.e.* $\}$-C_6H_4-CH_2-NC_4H_8. When a deep red benzene solution of $Rh_2Cl_2(CO)_4$ is added to the pale yellow polymer swollen in benzene at room temperature under nitrogen atmosphere, the complex is rapidly adsorbed on the polymer, the deep red colour disappearing within a few minutes. A pale dark brown polymer was separated by filtration. The immobilized rhodium complex was used as a catalyst for the hydrogenation of cinnamaldehyde without addition of any other amine. The results are summarized in Table 4, the amounts of the polymer used for immobilizing $Rh_2Cl_2(CO)_4$ (0.065 mmol) being 0.65—5.2 g (2.5—20 mmol equivalents of N). After the runs, the immobilized rhodium complex suspended in a colourless product solution was washed twice with benzene and separated by filtration in the air before

Table 4. Hydrogenation of cinnamaldehyde with immobilized rhodium complex catalyst

$PhCH{=}CHCHO$ 20 mmol, C_6H_6 20 ml, $Rh_2Cl_2(CO)_4$ 0.065 mmol, Press. 80 kg/cm^2 ($CO/H_2 = 1$), Temp 60 °C, Time 60 min.

No.	Aminated polystyrene (N-mmol)	Conv. (%)	Selectivity (%) II	III	IV
1	2.5	69 (66)	11 (9.3)	73 (72)	13 (6.6)
2	5.0	84 (95)	7.1 (2.4)	76 (87)	16 (12)
3	10	77 (100)	8.6 (≈0)	62 (90)	14 (9.8)
4	20	65 (99)	13 (≈0)	58 (75)	13 (11)
5	Recycle (run 3)	77	9.2	60	14
6	Recycle (run 5)	67	12	65	11
7	Recycle (run 4)	69	13	63	14
8	5.0, $+PPh_3$ 0.13	79	78	0	4.6
9	Recycle (run 8)	63	16	54	10
10	5.0, $+PPh_3$ 0.195	92	78	0	1.3
11	Recycle (run 10)	13	—	—	—

Table 5. IR absorptions of rhodium carbonyl complexes



analysis of hydrogenation products of cinnamaldehyde, since some of them were adsorbed on the polymer. The results obtained from the corresponding homogeneous catalyst system using *N*-methylpyrrolidine under the same conditions are given in parentheses in Table 4. Selective hydrogenation is again observed in heterogeneous catalyst system, although its catalytic activity and selectivity are slightly lower than those in homogeneous one. The polymer catalysts recovered in the air from runs 3, 5, and 4 reproduce almost the same activity and selectivity (runs 5, 6, and 7 respectively), indicating that the rhodium complexes are fairly air-stable, retaining original linkage to the aminated polystyrene after the runs. Addition of catalytic amounts of triphenylphosphine ($PPh_3/Rh=2$—3), however, gave exclusively hydrocinnamaldehyde and no cinnamyl alcohol at all (comparison of run 1 with runs 8 and 10) as observed in homogeneous catalyst system (Table 1). Since the product solutions were pale yellow in the runs with triphenylphosphine, some part of the rhodium complex seem to have been eluted from the polymer. In fact, the polymer catalyst recovered from run 10 was almost inactive for hydrogenation, although the one recovered from run 8 had some activity for selective hydrogenation (comparison of run 9 with run 2).

The interaction of $Rh_2Cl_2(CO)_4$ with the polymer was investigated by IR. The immobilized complex ($N/Rh=5$)[11] showed three absorptions, 2060(m), 1985(s broad), and 1720—1820 (w broad) cm^{-1}, in carbonyl stretching region. The last broad absorption, which was not observed in the parent rhodium complex, $Rh_2Cl_2(CO)_4$ (2105(m), 2085(s), and 2035(s) cm^{-1}), could be assigned to bridged carbonyls, suggesting the formation of a polynuclear rhodium carbonyl.[12] After treatment of the immobilized rhodium complex with CO–H_2 mixture ($CO/H_2=1$) in benzene under 80 kg/cm^2 at 60 °C for 60 min, the first absorption became weaker and the last one (1720—1820 cm^{-1}) relatively increased. On the other hand, all these absorptions disappeared after the treatment with triphenylphosphine ($PPh_3/Rh=3$) in benzene either in the presence or absence of the CO–H_2 mixture. From the benzene solution, $RhCl(CO)(PPh_3)_2$ (Found: C, 63.0; H, 4.25%. Calcd for: C, 64.3; H, 4.38%. $\nu_{CO}=1960$ (s broad) cm^{-1}), was isolated and recrystalized from benzene–methanol, indicating that triphenylphosphine coordinates to rhodium atom much more strongly than the amine. The IR absorptions of carbonyls are summarized in Table 5.

From a comparison of these IR absorptions of immobilized complexes with the effects of amine and triphenylphosphine shown in Table 4, it is evident that under oxo reaction conditions the rhodium–amine–carbonyl complex catalyzes the selective hydrogenation of α,β-unsaturated aldehyde to the unsaturated alcohol, while $RhCl(CO)(PPh_3)_2$ is effective only for the preferential hydrogenation of the carbon-carbon double bond to give the saturated aldehyde.

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