

Effect of Phosphorus Ligands on the Hydroformylation of Olefins over Rhodium Catalysts under Atmospheric Pressure

Wanzhi Chen, Shijian Liao,* and Yun Xu

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, People's Republic of China

Received 9 July 1992

ABSTRACT

The hydroformylation of olefins over rhodium catalysts, with phosphorus ligands added *in situ*, has been studied under atmospheric pressure. In the case of the $Rh_4(CO)_{12}$ cluster, the phosphine-modified catalyst exhibits very high activity, but there is a decay of catalyst activity with time. The deactivation mechanism of this catalyst has been discussed. In the case of rhodium complexes, $Rh(LL')(CO)_2$, containing chelate ligands with oxygen and nitrogen as coordinate atoms, the phosphine-modified catalysts exhibit fairly active activity and very good stability. All these catalysts afford almost 100% chemoselectivity to aldehydes. The regioselectivity is strongly dependent on the nature of the substrate used. The choice of a suitable phosphorus ligand for the catalytic hydroformylation is dependent on the nature of the rhodium complex used. The effect of phosphorus ligands on the hydroformylation of olefins over rhodium catalysts under normal pressure displays some special features in comparison with that performed under a higher pressure.

INTRODUCTION

Rhodium catalysts have attracted much interest in the hydroformylation of olefins due to their high

reaction rate and selectivity. Usually, phosphine-modified systems are used because of their greater stability and selectivity to linear products, although the activity is somewhat reduced by the presence of an excess of phosphine ligand. Thus far, most of the hydroformylation reactions have been carried out under pressure, because the catalyst activities are usually not high enough to allow the reaction to be performed under atmospheric pressure at a moderate reaction rate. However, some articles have reported very active catalysts; for instance, rhodium cluster-phosphine systems have been reported to catalyze the hydroformylation under atmospheric pressure at very high reaction rates [1].

In this article, we report the effect of phosphorus ligands on the hydroformylation of olefins over rhodium complexes under atmospheric pressure. Various trivalent phosphorus ligands have been used, including monodentate and chelating groups. These ligands encompass a wide variation in steric and electronic properties. Styrene and 1-octene have been used as substrates.

RESULTS AND DISCUSSION

$Rh_4(CO)_{12}$ Cluster Modified with Phosphorus Ligands

Hydroformylation of 1-octene was carried out under atmospheric pressure and at 50°C with the $Rh_4(CO)_{12}$ cluster as the catalyst, modified with a variety of phosphorus ligands added *in situ*. A hydrogen:carbon monoxide ratio of 1:1 was used. The results are summarized in Table 1. Under normal pressure, the rate of hydroformylation is too low to be measured in the absence of a suitable ligand.

Dedicated to Prof. Yao-Zeng Huang on the occasion of his eightieth birthday.

*To whom correspondence should be addressed.

TABLE 1 Hydroformylation of 1-Octene Catalyzed by $\text{Rh}_4(\text{CO})_{12}$ in the Presence of Various Phosphorus Ligands

Phosphorus Ligand	P/Rh Ratio	Time (hours)	TOF ^a (min^{-1})	TO ^b	Conversion (%)
None	0	5	0	0	0
P(OEt) ₃	3	6	0.63	96	4.8
P(C ₆ H ₁₁) ₃	3	5	4.28	1230	61.7
PPh ₃	2	5	21.6	1670	83.0
DPPM ^c	3	5	0	0	0
DPPE ^c	3	11	2.85	710	35.7
DPPP ^c	3	11	5.35	1050	57.5

Reaction conditions: 0.1 MPa, 50°C, $\text{Rh}_4(\text{CO})_{12}$ 1.0×10^{-2} mmol, 1-octene 19.2 mmol, toluene 7 ml.

^aThe maximum turnover frequency.

^bCalculated turnover from (CO + H₂) uptake.

^cDPPM($\text{Ph}_2\text{PCH}_2\text{PPh}_2$); DPPE($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$);

DPPP($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$).

$\text{Rh}_4(\text{CO})_{12}$ is a coordinatively saturated complex, and it has no vacant site for the coordination of an olefin. In the presence of phosphorus ligands, the rhodium cluster exhibits very high catalytic activity, which means that reaction occurs between phosphine (or phosphite) and the $\text{Rh}_4(\text{CO})_{12}$ cluster. The result is the dissociation of a carbonyl group and/or the cleavage of the Rh-Rh bond which, in turn, offers a vacant site for the coordination of olefins. However, $\text{Rh}_4(\text{CO})_{12}$ alone is an effective catalyst precursor for the hydroformylation under a higher pressure [2,3], and the structure of the $\text{Rh}_4(\text{CO})_{12}$ undergoes cleavage to form a catalytically active monomeric complex $\text{HRh}(\text{CO})_4$. This implies that the catalytically active species might be different for the reaction undertaken under normal pressure than that under high pressure. The weak electron donor, P(OEt)₃, listed in Table 1 does not give an active catalyst combination. P(C₆H₁₁)₃, the strongest electron donor in Table 1, forms a highly active species with the rhodium cluster, while PPh₃ gives the best catalyst combination. Bidentate phosphines form chelated clusters with $\text{Rh}_4(\text{CO})_{12}$ [4], but their activities are not very high, especially DPPM ($\text{Ph}_2\text{PCH}_2\text{PPh}_2$), which does not form a catalytically active species with $\text{Rh}_4(\text{CO})_{12}$. A similar result has been reported in the literature [5] for the hydroformylation of butadiene catalyzed by Rh(1,5-cyclooctadiene) OAc-diphosphine complexes under 1.2 MPa, where DPPM is not an active ligand for the reaction. The order of activities (turnovers) with respect to phosphines (or phosphite) is as follows: PPh₃ > P(C₆H₁₁)₃ > DPPP($\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$) > DPPE($\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$) > P(OEt)₃ > DPPM(= 0).

The variation of P/Rh ratios on the hydroformylation of styrene and 1-octene has been studied. The results are presented in Table 2. The catalytic activity increases with an increase of the P/Rh ratio, reaches a maximum, and then decreases at

TABLE 2 Hydroformylation of Styrene and 1-Octene Catalyzed by $\text{Rh}_4(\text{CO})_{12}$ -PPh₃ System

Substrate	P/Rh	TOF ^a (min^{-1})	TO	Conversion (%)	n/iso
Styrene	0.5	0.53	94	7.1	0.93
	1	2.77	1075	80.6	0.85
	1.25	10.5	1215	91.0	0.85
	2	12.5	1310	98.0	0.72
	3	18.5	1333	100	0.41
1-Octene	5 ^b	17.6	1938	96.7	0.26
	7.5 ^c	15.0	1357	67.8	0.001
	0.5	0.57	178	8.9	3.5
	1.25	7.3	939	47	6.0
	2	21.6	1670	83	7.4
5	18.4	1330	61	49.0	

Reaction conditions: 0.1 MPa, 50°C, CO/H₂ = 1, toluene 7 ml, $\text{Rh}_4(\text{CO})_{12}$ 1.5×10^{-2} mmol in styrene hydroformylation, 1.0×10^{-2} mmol in 1-octene hydroformylation, substrate, styrene 20 mmol or 1-octene 19.2 mmol, time 5 hours.

^aAverage turnover frequency in the initial 30 minutes.

^b $\text{Rh}_4(\text{CO})_{12}$: 1.0×10^{-2} mmol, time 4 hours.

^c $\text{Rh}_4(\text{CO})_{12}$: 1.0×10^{-2} mmol.

higher P/Rh ratios. The P/Rh ratio also exhibits a pronounced effect on the n/iso ratio of the product aldehydes. For the hydroformylation of 1-octene, a straight chain aldehyde is always the predominant product and the n/iso ratio is increased with the increase of the P/Rh ratio. In the hydroformylation of styrene, the results are reversed. The product n/iso ratio decreases with an increase of the P/Rh ratio. When the P/Rh ratio is increased to 7.5, 2-phenylpropanal turns out to be the only product. The isoproduct is more important for the hydroformylation of styrene, since 2-phenylpropanal is a starting material for cosmetics, polymers and pharmaceuticals. This catalyst system exhibits very high chemoselectivity. No hydrogenation products of the substrates or side products other than the corresponding aldehydes were found in the reaction mixture by GC analysis. The effects of the phosphine on the hydroformylation under normal pressure and under high pressure are different. Under normal pressure, when the P/Rh ratio is increased from 0.57 to 1.25, the catalyst activity (turnover frequency) is increased from 0.57 min^{-1} to 7.3 min^{-1} ; the n/iso ratio is also increased remarkably in the hydroformylation of 1-octene, whereas it has been reported in the literature that the reaction rate and product regioselectivity almost remain constant with the variation of P/Rh ratios from 0 to 1 in the hydroformylation of 1-hexene under 3.2 MPa using the same catalyst [3].

In spite of the initial high activity of the phosphine-modified $\text{Rh}_4(\text{CO})_{12}$ catalyst under normal pressure, this catalyst suffers from a decay of activity during the hydroformylation process. In the literature, the phosphine-modified $\text{Rh}_4(\text{CO})_{12}$ cat-

alyst was reported to be stable under pressure. A slight decay of catalyst activity during the reaction process was ascribed to the oxidation of the phosphine to phosphine oxide, the breaking of C-P bond in the phosphine, etc. [6]. In our experiments, the syngas, substrates, and solvents used were strictly deoxygenated. Analysis of the reaction mixture by HPLC showed that no detectable amounts of Ph_3PO , benzene, biphenyl, or benzaldehyde were present in the reaction mixture. The amount of PPh_3 remained almost constant during the reaction process. The deactivation must be due to the instability of the catalytically active species itself. Experiments of aging the catalyst precursor, $\text{Rh}_4(\text{CO})_{12}\text{-PPh}_3$, confirmed this assumption. After the catalyst precursor had been aged for 180 minutes, the catalyst activity was reduced to a very low level. The color of the catalyst solution changed noticeably during the process of aging. After mixing the $\text{Rh}_4(\text{CO})_{12}$ and PPh_3 in toluene, the color of the solution changed immediately from orange red to dark red. This color faded and gradually turned yellow. After having been aged for more than 3 hours, the color of the solution gradually became red again. Aging under argon showed the same phenomena.

In order to obtain some further information on the structural change of the catalyst during aging, infrared spectra of the catalyst solution in the carbonyl stretching region were recorded. The absorption bands of the $\text{Rh}_4(\text{CO})_{12}$ cluster at 2076 cm^{-1} and 2040 cm^{-1} disappeared rapidly after mixing $\text{Rh}_4(\text{CO})_{12}$ with PPh_3 in toluene under the CO/H_2 atmosphere. A strong, broad absorption band appeared at 1985 cm^{-1} . This indicates that a part of the terminal carbonyl groups is replaced by triphenylphosphine (dark red solution). The color of the solution became yellow gradually and finally turned red. New absorption peaks at 2059 cm^{-1} and 2035 cm^{-1} appeared in the IR spectra which are different from those of the terminal carbonyl group in the $\text{Rh}_4(\text{CO})_{12}$ cluster. These peaks increased slowly in intensity with time (see Figure 1).

In the process of the hydroformylation reaction, the color change of the catalyst was the same as that in the process of catalyst aging. The reaction rate reached a maximum when the color of the reaction mixture became yellow. The reaction rate decreased in the course of reaction and became very low when the color of the solution turned red.

We have isolated a yellow complex from the reaction mixture of $\text{Rh}_4(\text{CO})_{12}$ with PPh_3 in heptane. The infrared spectrum of this yellow complex in the carbonyl stretching region is shown in Fig. 2. This isolated yellow complex is catalytically active in the hydroformylation of 1-octene. The spectrum of the dead catalyst solution after the hydroformylation reaction is shown in Fig. 3.

Whyman [7] has investigated the reaction of

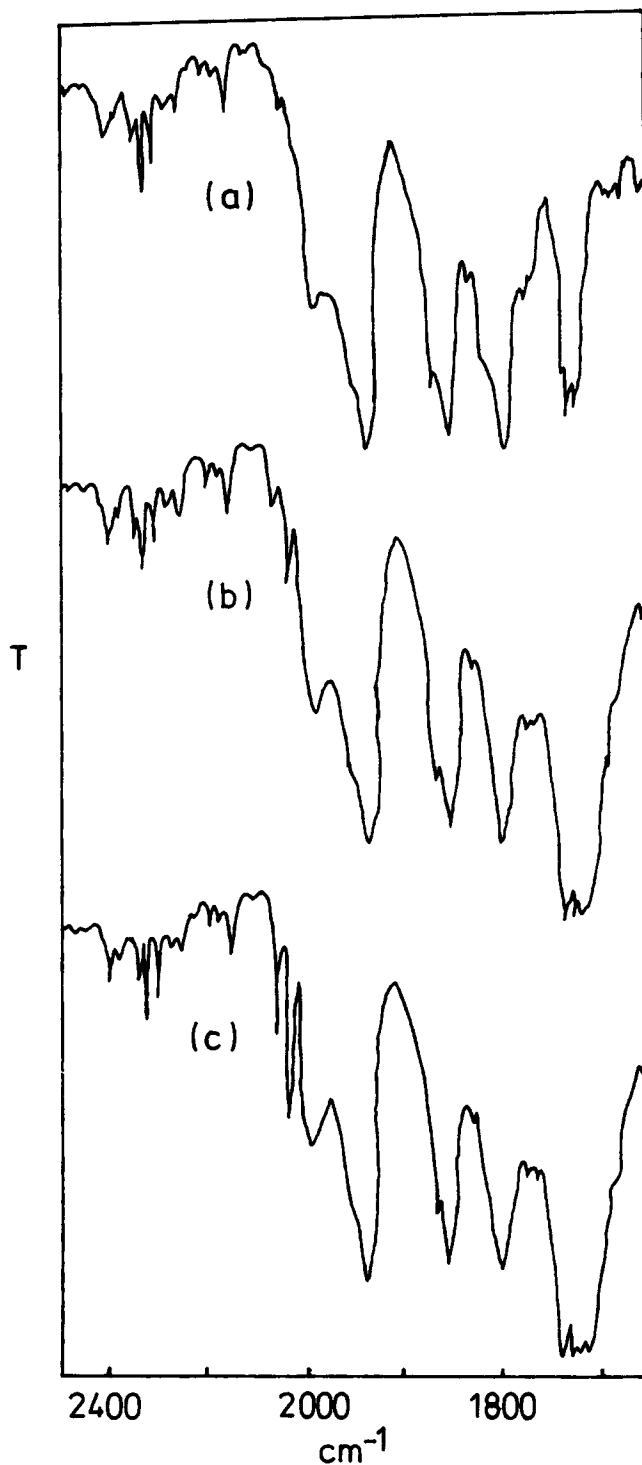


FIGURE 1 IR spectra of the reaction mixture of $\text{Rh}_4(\text{CO})_{12}$ and PPh_3 (1:5) in toluene under CO/H_2 . Aging time (min): (1) 60 (2) 120 (3) 280.

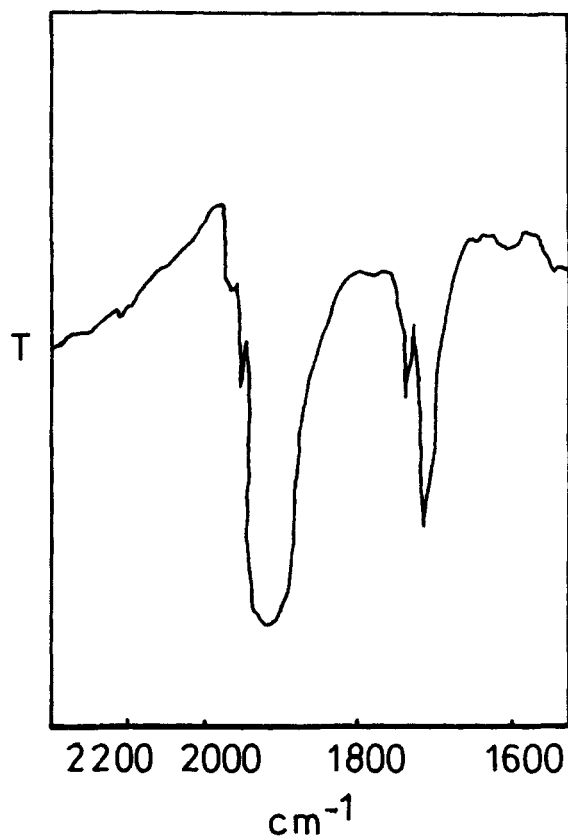


FIGURE 2 IR spectrum of the yellow complex from the reaction of $\text{Rh}_4(\text{CO})_{12}$ with PPh_3 in *n*-heptane.

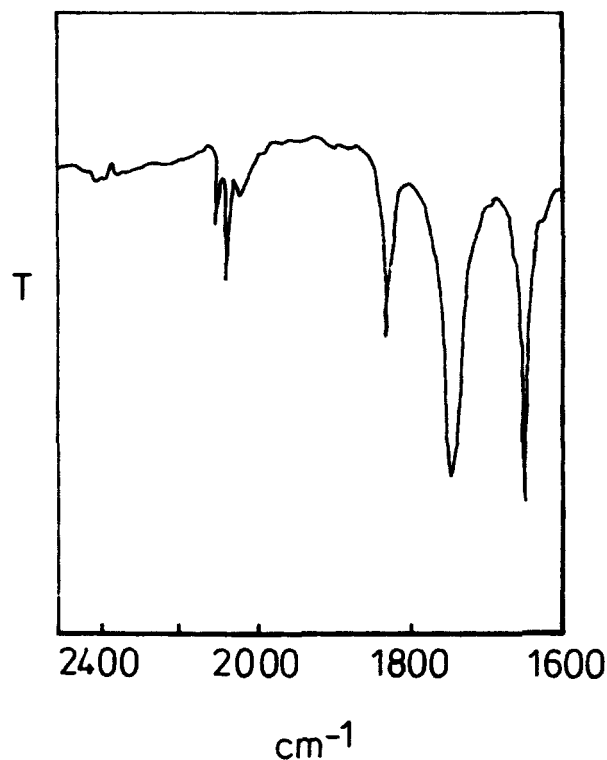


FIGURE 3 IR spectrum of the dead catalyst solution.

$\text{Rh}_4(\text{CO})_{12}$ with phosphine in hexane and isolated two dimeric rhodium species (yellow in color) which were referred to as $\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$ (I) and $\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$ (II). The accurate band maxima from Fig. 2 show that they are the sum of the IR spectra of species I and II (see Table 3), which indicates that dimeric rhodium complexes are the catalytically active species for the hydroformylation reaction performed under normal pressure. Obviously, this conclusion is different for the hydroformylation conducted under a high pressure. It has been reported in the literature that a monomeric rhodium complex is the catalytically active species in the hydroformylation of olefin over $\text{Rh}_4(\text{CO})_{12}\text{-PPh}_3$ catalyst under 6 MPa [8]. Moser et al. have shown that the dimeric rhodium complex dissociates into a monomeric complex at 70°C in the presence of syngas under pressure [9]; the difference between the IR spectra of the dimeric and the monomeric complex is that absorption bands attributable to bridging appear for the former. The difference in active species explains some of the different catalytic behaviors between hydrofor-

TABLE 3 Infrared Carbonyl Bands of Dimeric Rhodium Species

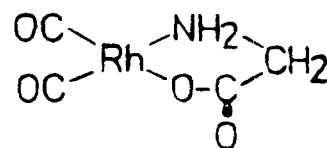
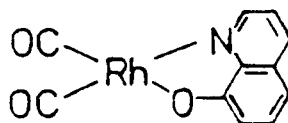
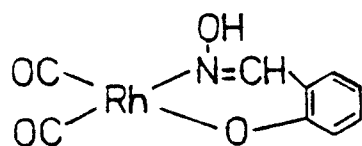
Dimeric Species	Reference Data (7)		IR Data of the Catalytically Active Species	
$\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$	2018s	1988vs	2016s	1985vs
	1791s	1766s	1794s	1764s
$\text{Rh}_2(\text{CO})_6(\text{PPh}_3)_2$	2065vw	2037w	2064w	2044w
	2014vw	2001vw	1980s	1958s
	1980m	1956vs		
	1912mw	1807vw		

mylation under normal pressure and high pressure.

Rh(LL')(CO)₂ Complexes Modified with Phosphorus Ligands

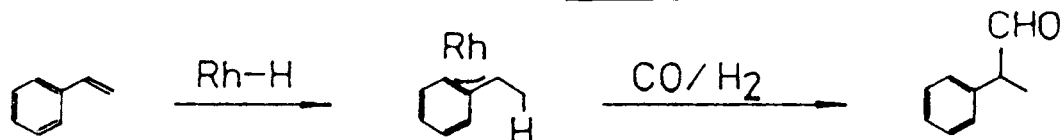
To our knowledge, hydroformylation of olefins using rhodium complexes $\text{Rh}(\text{LL}')(\text{CO})_2$ containing chelate ligands with oxygen and nitrogen as coordinate atoms has not been reported in the previous literature. Three such complexes were syn-

thesized and used in our experiments. Their structural formulas are as follows:



The experimental results are summarized in Tables 4-6.

In the absence of phosphorus ligands, none of the three rhodium complexes exhibit catalytic activity for the hydroformylation of styrene. The phosphorus-modified rhodium complexes are active catalysts in that they enable the hydroformylation to be performed under atmospheric pressure at a moderate reaction rate. Bidentate phosphines, except DPPM, combined with Rh give the most active catalysts. An increase in the P/Rh ratio from 2 to 10 usually decreases the rate of reaction (except for PPh_3 , for which the order is reversed). These catalysts exhibit very high chemoselectivity, the only product being the aldehyde. The regioselectivity is strongly dependent on the substrate used. The straight chain aldehyde is favored for the hydroformylation of 1-octene ($\text{Rh}(\text{oxine})(\text{CO})_2$ -DPPE catalyst). An *n*/*iso* ratio of 1.68 was obtained at P/Rh = 10. In the case of styrene as the substrate, the isoproduct, 2-phenylpropanal is usually the main product. Bidentate phosphines give the highest *iso*/*n* ratio, the order of regioselectivity for the formation of isoproduct being as follows: $\text{DPPP} \approx \text{DPPE} > \text{PPh}_3 > \text{P}(\text{OPh})_3$. This is in agreement with the order of the electron donating ability of the ligands. In the hydroformylation of straight chain olefins, the selectivity for normal chain aldehydes increases with an increase of electron donating ability of the ligands. The double bond in the styrene molecule is conjugated with the phenyl group. The distribution of electron density at the double bond of styrene is different from that of straight chain olefins. When Rh-H is added to the double bond of the styrene molecule, Markovnikoff addition predominates, giving the intermediate of the η^3 -allyl structure [10]:



Therefore, 2-phenyl-propanal is the main product. With the increase in the electron donating ability of ligands, the electron density around the rhodium center is strengthened, which favors the stabilization of the η^3 -allyl rhodium complex and enables the reaction to occur in accord with the

Markovnikoff direction. The regioselectivity using the bidentate ligand is much higher than that of

the monodentate phosphine, the reason for which may be connected to its chelating effect in addition to its electronic property. In contrast to the $\text{Rh}_4(\text{CO})_{12}$ cluster, the amount of phosphorus ligand used does not seriously affect the *n*/*iso* ratio of the product phenylpropanal for these three monomeric rhodium complexes. Also, it is interesting to note that the reaction pressure has a significant influence on the regioselectivity of hydroformylation. Reaction under a high pressure favors the formation of the isoproduct: e.g., hydroformylation of styrene under 1 MPa, using $\text{Rh}(\text{sox})(\text{CO})_2\text{-PPh}_3$ (or DPPE) at a P/Rh ratio of 2, gives almost pure 2-phenylpropanal.

The catalyst activities of phosphine-modified $\text{Rh}(\text{LL}')(\text{CO})_2$ catalysts are usually stable under proper reaction conditions. Figure 4 shows an example using a $\text{Rh}(\text{sox})(\text{CO})_2$ -DPPE catalyst system. This catalyst is not stable at a P/Rh ratio of 2; however, it is stable at P/Rh ratios between 4 and 10. An excess of phosphine is necessary to maintain the stability of the catalyst.

EXPERIMENTAL

The rhodium complexes were prepared by a modified method in which $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was reacted directly with sodium salts of the corresponding nitrogen and oxygen anionic ligands. The method of synthesis will be published elsewhere. The analytical data of the complexes obtained are the same as those reported in the literature [11,12]. $\text{Rh}_4(\text{CO})_{12}$ was synthesized from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ according to a reported procedure [13]. Phosphines were obtained from Alfa Co. Other reagents and solvents were chemically pure. All of the ligands, reagents,

and solvents were crystallized or distilled before use.

The hydroformylation reactions were carried out in 100 mL three-necked, jacketed glass bottles closed with self-sealing silicon rubber caps, connected to a vacuum, argon, reaction gas lines and

TABLE 4 Hydroformylation of Styrene Catalyzed by Rh(sox)(CO)₂ in the Presence of Various Phosphorus Ligands

Phosphorus Ligand	P/Rh Ratio	TOF (min ⁻¹)	TO	Product Distribution (%)	
				2-Phenylpropanal	3-Phenylpropanal
P(OPh) ₃	2	0.64	107	32.9	67.1
	5	0.37	147	36.7	63.3
	10	0.21	56	37.9	62.1
	20	0.10	22	41.9	58.1
PPh ₃	2	0.07	26	70.2	29.8
	5	0.2	42	75.9	24.1
	10	0.51	193	72.8	27.2
DPPM	2	0	0	0	0
DPPE	2	1.50	260	92.8	7.2
	5	1.23	354	93.2	6.8
	10	0.64	163	94.4	5.6
DPPP	2	1.60	334	91.4	8.6
	4	1.17	457	94.7	5.3
	5	1.14	406	93.6	6.4
	10	0.92	333	92.2	7.8

Reaction conditions: 0.1 MPa, CO/H₂ = 1, 60°C, toluene 8 ml, styrene 17.4 mmol, Rh(sox)(CO)₂ 2.0 × 10⁻² mmol, time 400 minutes.

TABLE 5 Hydroformylation of Styrene Catalyzed by Rh(oxine)(CO)₂

Phosphorus Ligand	P/Rh Ratio	TOF (min ⁻¹)	TO	Product Distribution (%)	
				2-Phenylpropanal	3-Phenylpropanal
P(OPh) ₃	10	0.34	75	56.0	44.0
PPh ₃	10	0.10	19	72.0	28.0
DPPM	10	0	0	0	0
DPPE	10	0.61	161	92.1	7.9
DPPP	10	0.40	86	92.0	8.0

Reaction conditions: 0.1 MPa, CO/H₂ = 1, 50°C, Rh(oxine)(CO)₂ 1.0 × 10⁻² mmol, toluene 8 ml, styrene 17.4 mmol, time 5 hours.

TABLE 6 Hydroformylation of Styrene Catalyzed by Rh(gly)(CO)₂

Phosphorus Ligand	P/Rh Ratio	TOF (min ⁻¹)	TO	Product Distribution (%)	
				2-Phenylpropanal	3-Phenylpropanal
P(OPh) ₃	5	0.16	48	51.0	49.0
PPh ₃	5	0.53	150	87.8	12.2
DPPM	5	0	0	0	0
DPPE	5	0.54	160	92.7	7.3
DPPE	10	0.37	125	92.5	7.5
DPPP	5	1.1	268	95.3	4.7
DPPP	10	0.86	215	92.2	7.8

Reaction conditions: 0.1 MPa, CO/H₂ = 1, 50°C, Rh(gly)(CO)₂ 3.8 × 10⁻² mmol, toluene 8 ml, styrene 17.4 mmol, time 5 hours.

a constant pressure gas burette. The temperature of the circulating water passing through the jacket was maintained by use of a thermostat. Agitation was provided by means of magnetic stirring. In general, the reaction bottles were alternately evacuated and flushed with argon two times and evacuated

again, then filled with the reaction gas mixture (CO/H = 1/1). Toluene and the rhodium complex and phosphine (both dissolved in toluene previously) were injected into the reaction bottle successively. After 20 minutes of stirring, styrene was injected. Gas uptakes were followed by use of

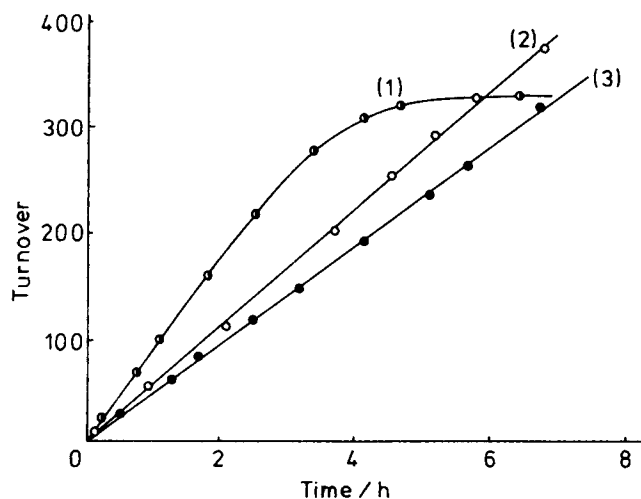


FIGURE 4 Effect of the P/Rh ratio on the catalyst stability.

a constant pressure gas burette immediately after adding the styrene. The products were analyzed by gas chromatography. The high pressure reactions were conducted in a 75 mL stainless steel autoclave which was immersed in an oil bath. The IR

spectra were recorded on a Perkin-Elmer 683 spectrometer.

REFERENCES

1. A. Ceriotti, L. Garlaschelli, L. Longoni, M. C. Malatesta, D. Strumolo, A. Fumagalli, S. Martinengo, *J. Mol. Catal.*, **24**, 1984, 309.
2. B. L. Booth, M. J. Else, R. Fields, R. N. Haszeldine, *J. Organometal. Chem.*, **27**, 1971, 119.
3. Li Xianjun, Chen Yueqiang, Xie Hui, Chen Yu, *Chin. J. Mol. Catal.*, **1**, 1987, 1.
4. D. F. Foster, J. Harrison, B. S. Nicholls, A. K. Smith, *J. Organomet. Chem.*, **248**, 1983, C29.
5. P. W. N. M. Van Leeuwen, C. F. Roobeek, *J. Mol. Catal.*, **31**, 1985, 345.
6. P. E. Garrou, *Chem. Rev.*, **85**, 1985, 171.
7. R. Whyman, *J. Chem. Soc., Dalton Trans.*, 1972, 1375.
8. W. J. Xie, F. Y. Jiao, S. K. Yang, Y. Q. Yin, D. G. Li, *Cuihua Xuebao (Chin. J. Catal.)* **6**, 1985, 172.
9. W. R. Moser, C. J. Papile, D. A. Brannon, R. A. Duwell, S. J. Weininger, *J. Mol. Catal.*, **41**, 1987, 271.
10. R. H. Crabtree, *Comments Inorg. Chem.*, **4**, 1985, 229.
11. R. Ugo, G. La Monica, S. Cenini, F. Bonati, *J. Organomet. Chem.*, **11**, 1986, 159.
12. Z. Nagy-Magos, P. Kvintovics, L. Marko, *Transition Met. Chem.*, **5**, 1980, 186.
13. S. Martinengo, G. Giordano, P. Chini, in D. H. Busch (ed), *Inorganic Synthesis*, Wiley, New York, vol. 20, p. 209 (1980).