

Rh(acac)(CO)₂–Diphosphine Catalyzed Hydroformylation of Vinylarene to Arylpropanals under Mild Conditions

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Hydroformylation of styrene and *p*-methylstyrene has been investigated using Rh(acac)(CO)₂ as catalyst precursor in the presence of various phosphines and phosphite. It has been demonstrated that the combination of P(OPh)₃ and Rh(acac)(CO)₂ showed very high catalytic activity but poor regioselectivity; diphosphines are a good cocatalyst, leading to 2-(*p*-methylphenyl)propanal in >90% regioselectivity. The catalytic activity strongly depends on the P/Rh ratio in the cases of P(OPh)₃ and diphosphines, but the regioselectivity is not markedly affected by the P/Rh ratio.

The hydroformylation of olefins catalyzed by transition metal complexes is of great importance in the synthesis of aldehydes, alcohols and other products indispensable to the chemical industry.^{1,2} Rh(acac)(CO)₂ is a convenient catalyst precursor which has been studied extensively in the literature,^{3–7} the effect of pressure, temperature and various additives including phosphites and aliphatic acids has been described detailed. Recently, the use of chelating diphosphine, diphosphite and P–N ligands has been received considerable attention.^{8–11} *In situ* high-pressure ¹H and ³¹P{¹H} NMR and FTIR studies have been conducted to elucidate the mechanism of hydroformylation reaction. Both spectroscopic^{8,9} and kinetic¹² data indicate that RhH(CO)₂L₂, formed *in situ* from Rh(acac)(CO)₂ and phosphorus ligands, is responsible for the high selectivity in the hydroformylation reaction.

In an attempt to search for new regioselective hydroformylation catalysts, we have found^{13–17} that rhodium complexes containing nitrogen and oxygen chelating ligands afford high regioselectivity for hydroformylation of vinylarenes in the presence of diphosphines. As a continuation, in this paper we report the hydroformylation of styrene and *p*-methylstyrene, the influence of phosphorus ligands on the reaction rate and selectivity under normal pressure.

Experimental

All reactions were carried out using standard Schlenk procedures under an atmosphere of argon. Solvents were

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purified and dried according to standard methods. Rh(acac)(CO)₂ was prepared¹⁸ by a published procedure.

The hydroformylation reactions were performed under normal pressure in 50 mL jacketed glass bottles at a constant pressure of 0.1 MPa. The reactor was evacuated, filled with CO and H₂ (CO/H₂ = 1), then the solution of catalyst and the appropriate phosphorus ligands in toluene were injected successively. The mixture was stirred for 20 min and the reaction was started by injection of olefins through a self-sealing silicon rubber cap into the reactor. The temperature was regulated with circulating water and a thermostat. The reaction rate was monitored by a constant-pressure gas burette connected to the reactor.

The hydroformylation products were analyzed by gas chromatography with a 2 m OV-101 column.

Results and discussion

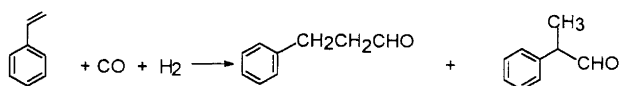
Hydroformylation of styrene. The hydroformylation of styrene was examined using Rh(acac)(CO)₂ as catalyst precursor in the presence of triphenylphosphite, triphenylphosphine and bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) under 0.1 MPa. The results are presented in Table 1. The complex alone and its combination with dppm were inactive for the hydroformylation of styrene even at elevated temperatures: GC showed that no aldehydes were produced. The combination of Rh(acac)(CO)₂ with the other four phosphorus ligands catalyzed styrene hydro-

Table 1. Hydroformylation of styrene catalyzed by Rh(acac)(CO)₂.^a

Ligand	P/Rh/mol mol ⁻¹	TOF ^b /min ⁻¹	TON ^c	Regioselectivity (%)	
				2-Phenylpropanal	3-Phenylpropanal
P(OPh) ₃	10	2.4	475	52.4	47.6
PPh ₃	10	0.46	82	86.7	14.3
dppm	10	0	0	0	0
dppe	10	0.75	190	92.7	7.3
dppp	10	0.57	125	95.5	4.5

^a 60 °C, CO/H₂ = 1, toluene 8 mL, styrene 2 mL, Rh(acac)(CO)₂ 2.0 × 10⁻⁵ mol. ^b Turnover frequency defined as mol of olefin converted per mol of Rh per min. ^c Turnover number defined as mol of olefin converted per mol of Rh within 5 h.

formylation smoothly at 0.1 MPa and 60 °C. Both 2-phenylpropanal and 3-phenylpropanal were produced, no hydrogenation products of the aldehydes and the starting olefins were detectable.



It can be seen from Table 1 that the highest catalytic activity (TOF = 2.4 min) was obtained with Rh(acac)(CO)₂-P(OPh)₃ system: 475 mol of styrene were converted into aldehydes within 5 h. The catalytic activity is much higher than that recently reported for [Rh(COD)]BPh₄ and [Rh(CO)₂Cl]₂-phospholes.^{19,20} The order of the reaction rate was P(OPh)₃ > dppe > dppp > PPh₃ > dppm (=0). These results differ from other rhodium catalyst systems in which PPh₃ was thought to be the best cocatalyst for styrene hydroformylation.²¹

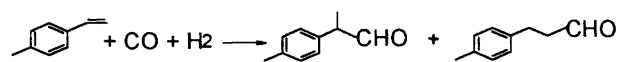
The regioselectivity of styrene hydroformylation strongly depend on the kind of phosphorus ligands. 2-Phenylpropanal is the prevailing product in the cases of diphosphine and triphenylphosphine; up to 95% of 2-phenylpropanal can be afforded. However, the reaction gives rise to very poor regioselectivity (*n*/*iso* being nearly one) in the case of the phosphite ligand. Clearly, the results show that regioselectivity is dominated by the electron-donating abilities of the ligands.

The strong donating ability of the two diphosphines increase the electron density on the central metal atom of the active species, which results in a decrease of the acidity of metal hydrides, LnRhH. Therefore, diphosphine ligands favor oxidative addition following the Markovnikov mode (Scheme 1). In another respect, P(OPh)₃ is a good π-electron acceptor which increases

the acidity of the active species; thus the possibility of following an anti-Markovnikov mode is increased.

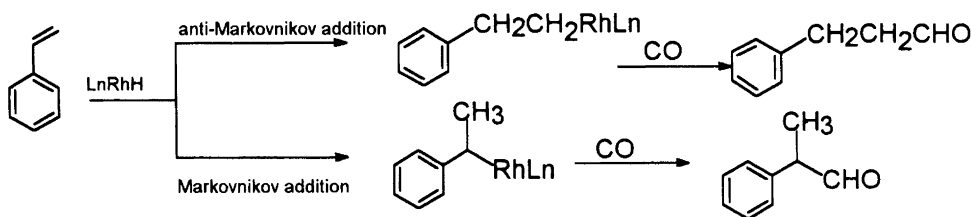
Both 2-phenylpropanal and 3-phenylpropanal are of significance in the perfume and pharmaceutical industries, which can be obtained selectively by hydroformylation of styrene under mild conditions.

Hydroformylation of *p*-methylstyrene. The hydroformylation of *p*-methylstyrene gives 2-(*p*-methylphenyl)propanal and 3-(*p*-methylphenyl)propanal, which are important intermediates for perfume and antiinflammation drugs.



Using Rh(acac)(CO)₂ as a catalyst precursor and P(OPh)₃ and dppe as coligand, the effect of the P/Rh ratio on the catalytic activity and regioselectivity was studied. The results are demonstrated in Figs. 1–4. For the Rh-P(OPh)₃ system, the highest reaction rate was found after a short induction time when P(OPh)₃/Rh = 2. However, catalyst deactivation occurred: it lost its activity almost completely after 4 h. Increasing the P/Rh ratio to 5 led to the best catalytic activity and stability; more than 400 mol of aldehyde were obtained per mol of Rh complexes (Fig. 1). 3-(*p*-Methylphenyl)propanal is the major product in the presence of P(OPh)₃, which allows the formation of 3-(*p*-methylphenyl)propanal in 72% selectivity. It should be noted that the regioselectivity was not affected remarkably by the P/Rh ratio (Fig. 2). This behavior is just the same as that of the Rh(sox)(COD) catalyst we previously reported.¹⁶

In the hydroformylation of *p*-methylstyrene, Rh(acac)(CO)₂-dppe behaves differently from the abovementioned Rh-P(OPh)₃ system. Figure 3 presents



Scheme 1.

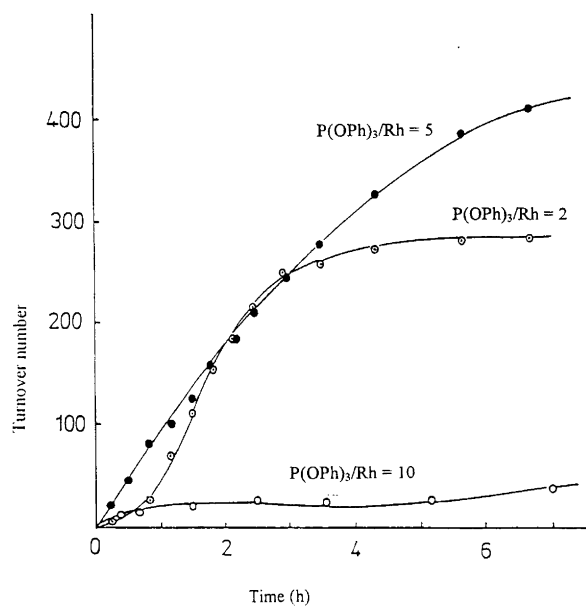


Fig. 1. Hydroformylation of *p*-methylstyrene catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2\text{-P}(\text{OPh})_3$. Reaction conditions: 1 atm $\text{CO}/\text{H}_2=1$, toluene 8 ml, *p*-methylstyrene 2 ml, $\text{Rh } 1.0 \times 10^{-5}$ mol.

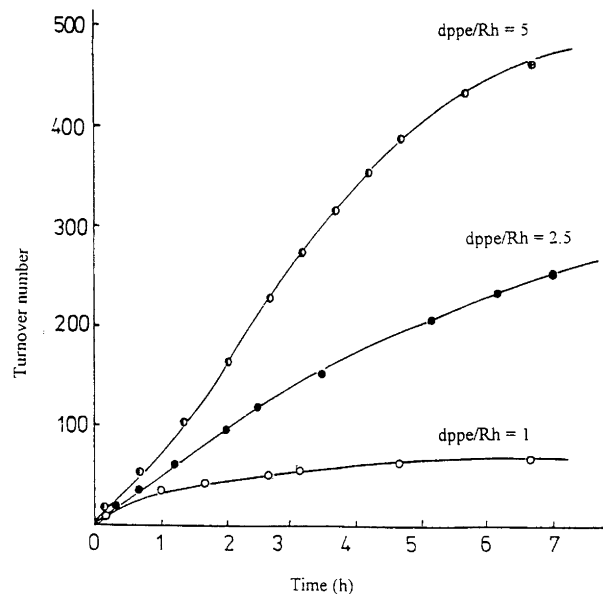


Fig. 3. Hydroformylation of *p*-methylstyrene catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2\text{-dppe}$. Reaction conditions: 1 atm $\text{CO}/\text{H}_2=1$, toluene 8 ml, *p*-methylstyrene 2 ml, $\text{Rh } 1.0 \times 10^{-5}$ mol.

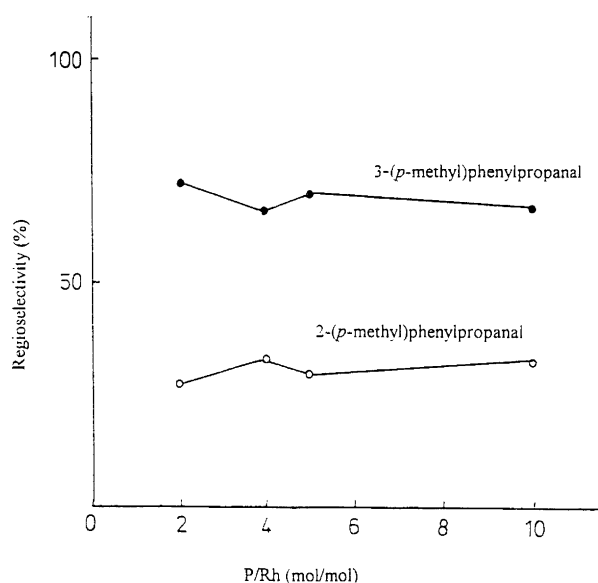


Fig. 2. Effect of P/Rh ratio on the regioselectivity in $\text{Rh-P}(\text{OPh})_3$ catalyzed hydroformylation reactions. Reaction conditions are the same as noted in Fig. 1.

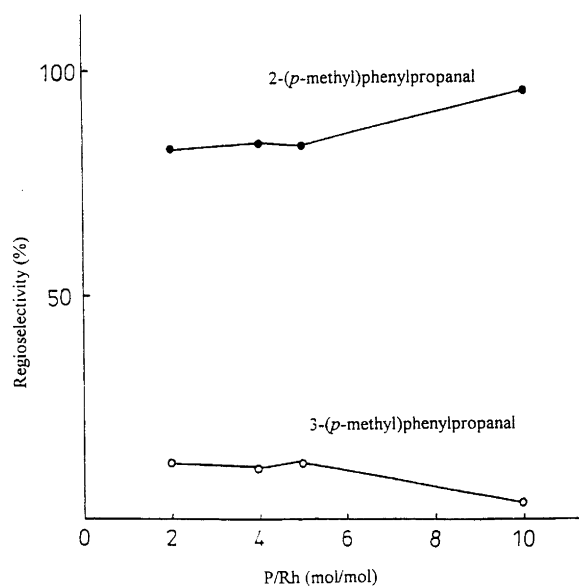


Fig. 4. Effect of P/Rh ratio on the regioselectivity in Rh-dppe catalyzed hydroformylation reactions. Reaction conditions are the same as noted in Fig. 3.

kinetic curves at different P/Rh ratios. The best catalytic activity and stability were found at a P/Rh ratio of 10; the results indicate that an excess of diphosphine ligands is needed to form the active species. In contrast to $\text{P}(\text{OPh})_3$, the branched aldehyde is the major product in the presence of dppe; a regioselectivity of over 95% can be obtained (Fig. 4). Furthermore, the regioselectivity has a tendency to increase as the P/Rh increases. Usually, a higher P/Rh ratio enhances the regioselectivity and

lowers the reaction rate. At present, it is not clear why an excess of dppe should produce a positive effect on the reaction rate.

It was found^{8,16} that $\text{Rh}(\text{sox})(\text{COD})$ (sox = salicylaldoximate) and other Rh complexes containing anionic chelate ligands having nitrogen- and oxygen-donating atoms are inactive for the hydrogenation of olefins. However, both $\text{Rh}(\text{acac})(\text{CO})_2$, which has the same square-planar structure as $\text{Rh}(\text{sox})(\text{CO})_2$, alone and its

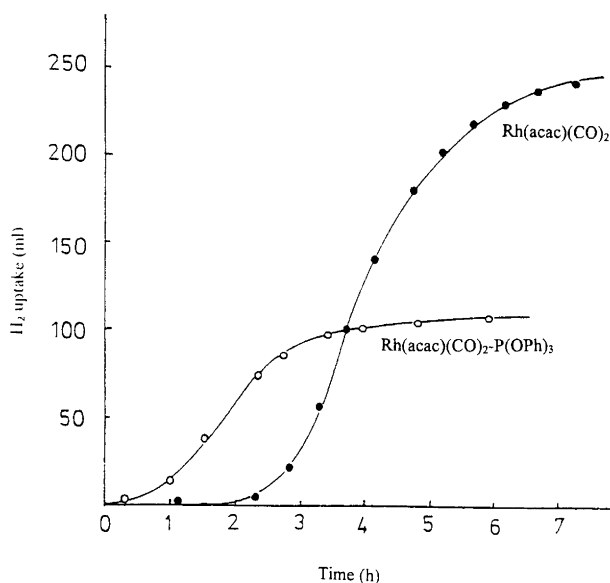


Fig. 5. Hydrogenation of styrene catalyzed by $\text{Rh}(\text{acac})(\text{CO})_2$. Reaction conditions: 1 atm H_2 , 50 °C, toluene 9 ml, styrene 1 ml.

combination with $\text{P}(\text{OPh})_3$ catalyze the hydrogenation of styrene. The kinetic curves are shown in Fig. 5. The presence of $\text{P}(\text{OPh})_3$ inhibits the hydrogenation reaction, thus the reaction rate is much lower than in the case of $\text{Rh}(\text{acac})(\text{CO})_2$ alone. Formation of rhodium black was observed in the absence of $\text{P}(\text{OPh})_3$, which indicates that the decomposition of $\text{Rh}(\text{acac})(\text{CO})_2$ occurred and the real active species is a rhodium precipitate.

Recent reports^{8,9} have shown that the reaction of $\text{Rh}(\text{acac})(\text{CO})_2$ and phosphorus ligands form $\text{RhH}(\text{CO})_2\text{L}_2$ species which are responsible for the catalytic reaction. $\text{P}(\text{OPh})_3$ is a poor δ -electron donor and a good π -electron acceptor, forming a more acidic RhLnH species. The species promotes oxidative addition of rhodium hydride to the olefinic bond; thus the hydroformylation reaction is enhanced. In contrast, strong δ -donating ligands such as dppe would result in a poorly acidic rhodium hydride; therefore, a low reaction rate was observed.

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